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RESEARCH ARTICLE

EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF COPPER (II) BY USING 2, 6-DITHIOL-4-ETHYLPHENOL AS AN ANALYTICAL REAGENT

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ABSTRACT

2, 6-dithiol-4-ethylphenol (DTEP) as a photometric reagent for the extractive spectrophotometric determination of Copper (II) is presented in this paper. The reagent DTEP in the presence hydrofobic amins gave instantaneous and stable blue colour with Copper (II) in the pH range 6.2 to 7.7. The Beer's law was applicable in the range of 0.05 - 4.0 µg/ml at 534-540 nm. The Limit of Detection (LOD) is found to be 8.5-8.7ng/mL. The stoichiometry of the complex is established as 1:1:1 (M: L: Am) by equilibrium shift method. The standard deviation and the coefficient of variance are presented. The results of the prescribed procedure applied for the determination of the micro amounts of Cu (II) in pharmaceutical, food and in plant samples are presented.

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INTRODUCTION

Copper is an essential trace nutrient to all high plants and animals. In animals including humans, it is found primarily in the blood stream, as a co factor in various enzymes, and in copper based pigments. Copper is absorbed, transported, distributed, stored and excreted in the body. Copper is required for normal metabolic processes. Copper combines with certain proteins to produce enzymes that act as catalysts to help a number of body functions. Copper helps provide energy required by biochemical reactions. Although copper is an essential micronutrient and is required by the body in very small amounts, excess copper in the human body can cause stomach and intestinal distress such vomiting, diarrhea, and stomach cramps. The lowest level at which these adverse effects occur has not been well defined. Copper is also a commonly occurring element in natural waters. Most copper contamination in drinking water happens in the water delivery system, as a result of corrosion of the copper pipes or fittings (Podchaynova *et al*., 1990). Copper is one of the essential elements in human body. Lack of copper in the body results in health problems such as anemia. Copper extensive use as an electrical conductor, heat conductor, building material, and a constituent of various metal alloys.

Hence, it is necessary to seek highly, accurate and selective analytical methods for quantitative determination of copper at trace levels. Various spectrophotometricmethods have been proposed for the determinationof copper contents of the various samples including naturalwaters and pharmaceutical samples (Turkoglu, 2005). Naphthazarin (5,8-dihydroxy-1,4-naphthoquinone) is proposed as a chromogenic reagent for the spectrophotometric determination of copper(II). The method was applied for copper determination in alloy samples with satisfactory results (Chaisuksant, 2000). 1-phenyl-1-hydrazonyl-2-oximino propane -1, 2-dione was synthesized and employed to develop an extractive spectrophotometric method for the determination of Cu (II). The method has been successfully applied for the determination of copper in synthetic mixtures, alloy samples, water sample and pharmaceutical samples (Tekale *et al*., 2011) 4-(*N,N*-(Dimethyl)amino) benzaldehydethiosemicarbazone is proposed as an analytical reagent for the extractive spectrophotometric determination of copper (II) (Karthikeyan *et al*., 2011). Thus the method can be employed for the determination of trace amount of copper (II) in water, alloys and other natural samples of significant importance. A simple, rapid and sensitive spectrophotometric method has been developed for the determination of Cu (II) by using 2-(5-Bromo-2-Oxoindolin-3-ylidene) Hydrazine Carbothioamide as an analytical reagent. The proposed method is rapid, sensitive, reproducible and has been successfully applied for determination of Cu (II) in alloy and pharmaceutical

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samples (Madan and Barhate, 2016). A rapid extractive spectrophotometric method is developed for the determination of copper (II) using o-hydroxyacetophenoneisonicotinoylhydrazone as one of the sensitive analytical reagent. The optimized method has been successfully applied for the determination of copper (II) in the presence of diverse ions and also in biological, geological and pharmaceutical samples. It is also observed that the obtained results are in agreement with ICP-MS and AAS methods. The proposed method is selective, sensitive and reproducible (Reddy *et al*., 2015). A simple, selective and rapid extractive spectrophotometric method has been developed for the extraction and determination of Cu (II) with 4-(4'-nitrobenzylidene imino)-3-methyl-5-mercapto-1, 2, 4-triazole.The proposed method was successfully applied for the determination of Cu (II) in synthetic mixtures, pharmaceutical samples and alloys (Shaikh *et al*., 2016). 2-Hydroxy-3-methoxy Benzaldehyde Thiosemicarbazone as a photometric reagent for the extractive spectrophotometric determination of Copper (II) is presented in this paper. The results of the prescribed procedure applied for the determination of the micro amounts of Cu (II) in standard steel samples, alloys, pharmaceutical and synthetic samples are presented (Patil *et al*., 2016).

The reagent, 2-acetylthiophene thiosemicarbazone has been synthesized and characterized based on spectral data. The reagent gives intense yellowish green coloured complexwith copper(II) in sodium acetate-acetic acid buffer (pH 5-7) medium. The method has been used for the determination of copper(II) in alloys, edible oils and seeds (Rao *et al*., 2006). Oxyphenolate and dithiophenolate complexes of cobaltare insoluble in chloroform, while mixed-ligand complexes with hydrophobic amines and aminophenols easily dissolve invarious organic solvents (Kuliev *et al*., 2015; Kuliyev *et al*., 2016; Kuliyev *et al*., 2015; Zalov *et al*., 2011; Zalov *et al*., 2016). In this respect, a very promising reagent is dithiolphenols (DP), which contains one hydroxyl and two sulphohydrylgroups and is a sulfur-containing analogue of mononuclear poly-phenols with two oxygen atoms replaced with sulfur atoms. The real work is devoted to studying of reaction of a complex formation of Copper (II) with 2, 6-dithiol-4-ethylphenol (DTEP) in the presence of hydrophobic amines (Am). As hydrophobic amine phenantroline (Phen), batophenantrotline (BPhen) and dipiridile (Dip) were used.

MATERIALS AND METHODS

Reagents and Apparatus

The stock solution (1mg / ml) of Copper(II) was prepared by dissolving weighed amount of Copper Sulphate ($CuSO_4$) in doubly distilled deionized water (Korostelev, 1964). More dilute standard solutions were prepared from this stock solution as and when required.

Solutions of DTEP and Am in chloroform (0.01M) were used. DTEP were synthesized according to the procedure (Kuliev *et al*., 1976) Their purity was verified by melting point determination and paper chromatography. To create the optimal acidity, 0.1M solutions of KOH and HCl or ammonium acetate buffers were applied. Acetate buffer solution, prepared by mixing of 2 mol x L^{-1} aqueous solutions of CH_3COOH and NH_4OH.

The extractant was purified chloroform. The absorbance of the extracts was measured using a Shimadzu UV1240 spectrophotometer and KFK 2 photocolorimeter (USSR). Glass cells with optical path of 5 or 10 mm were used. pH of aqueous phase was measured using an I-120.2 potentiometer with a glass electrode. Muffle furnace was used for dissolution of the samples. The process of thermolysis of the compounds was studied using derivatograph system «ShimadzuTGA-50H». IR spectra were recorded on a spectrophotometer "Bruker" (Germany).

General procedure

General procedure for the determination of Copper

Portions of stock solutions of Copper (II) varying from 0.1 to 1.0 mL with a 0.1-mL step, a 2.0 mL portion of a 0.01 M solution of DTEP, and a 2.5 mL portion of a 0.01M solution of Am were placed in to calibrated test tubes with ground-glass stoppers (the volume of the organic phase was 5 mL). The required value of pH was adjusted by adding 0.1M NaOH. The volume of the aqueous phase was increased to 20 mL using distilled water. In 10 minnute after the complete separation of the phases, the organic phase was separated from the aqueous phase and the absorbance of the extracts was measured on KFK-2 at room temperature and 590 nm (l=0.5cm).

Procedure for Determination of Cu (II) in Pharmaceuticals samples

Boiling with 10 ml of aqua regia dissolved 0.5gm of Pharmaceuticals samples. The solution was evaporated to dryness and the residue was dissolved in 10 ml of 1M HCl filter, if required and resulting solution was diluted to 100 ml with doubly distilled water. The working solution was prepared by appropriate dilution of stock solution. From an aliquot of this solution 1 ml was analysed for Cu(II) by the procedure as described earlier.

Determination of copper in the beans

A portion of beans (10 g) was crushed and dried in a porcelain dish at 105°C. The dry residue is heated in a muffle furnace at 500°C. The ash was dissolved in diluted (1: 1) HNO_3 and evaporate to moist salts, which are then dissolved in water, filtered into a volumetric flask of 100 ml. The copper content is determined with DTEP and Am.

Determination of copper in the gelatin

5 grams of gelatin in a porcelain dish soak 50 ml of distilled water for 2-3 hours. By the swollen gelatin was added 25 mL (1: 1) HNO_3 and heated in a boiling water bath for 2 hours. The solution was filtered and neutralized with NH_4OH (1: 1) was transferred into a volumetric flask of 50 ml. In solution, the copper content is determined DTEP and Am as well as dietilditiokarbaminatom.

Determination of copper in wheat bran

5 g sample of wheat bran was dried in an oven at a temperature porcelain cups 105°C. Then, the cup was set to asbestos plate contents burned on an open fire. Charred residue with a cup was transferred into a muffle furnace and calcined at a temperature 800°C. Mineralized residue was dissolved in 0,1 N

HNO_3 and filtered through a medium density filter in a 100 ml flask. The copper content was determined DTEP and BPen, and with dietilditiokarbaminat.

RESULTS AND DISCUSSION

Cu(II) reacts with DTEP and gives a yellow colored complexes. These complexes are insoluble in non-polar solvents. Experiments on electromigration in a U-shaped tube and on sorption on EDE-10P (EDE-ethylenediamine, epichlorohydrin; 10- serial number of the brand: P-means that the matrix has a macroporous structure) anion exchangers have demonstrated the anionic nature of single-ligand complexes, in the electromigration study of the complexes, it was found that the yellow dithiophenolate complexes of Copper(II) moved to the cathode. When the sign of the charge of the single-ligand complexes was determined by ion chromatography, the EDE-10P anion exchanger completely absorbed the colored component of the solution. When hidrophob amins (Am) were introduced into the system, the extraction of these compounds into the organic phase as a mixed-ligand complex (MLC) was observed.

Extraction as a function of pH

Change in pH affected the complexation of Cu (II)–DTEP-Am. Therefore, the absorbance of complex was studied between pH1 to 10 by using dilute HCl and NaOH solutions. The absorbance values of extracted complex were measured. The maximum absorbance was obtained in the pH range 6.2 to 7.7. Beyond this pH range, the observed absorbance values were lower. Thus further extraction and determination carried out at 7.

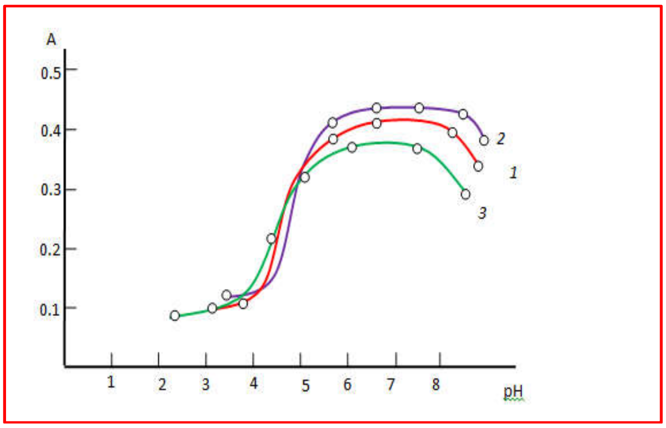

Figure 1. Absorbance of mixed-ligand complexes as a function of the pH of the aqueous phase

1.Cu – DTEP –Phen, 2.Cu – DTEP-BPen, 3.Cu – DTEP - Dip

C_{Cu} = 1,875 •10^{-5}M; C_{DTEP}=0,8•10^{-3}M,$C_{Aм}$= 1,0•10^{-3}M, КФК-2, λ=590nm, l=0.5 см.

The choice of the extract ant

The extraction of the complex has been tried with several solvents: chloroform, 1, 2-dichloroethane, tetrachloromethane, dichloromethane, benzene, chlorobenzene, toluene, xylol, isobutanol, isoamyl alcohol, cyclohexane, ethyl acetate, 1-butanol, isoamyl acetate and their mixes. Extractibility of complexes was estimated in coefficient of distribution and extent of extraction. Thus basicity of amines has no noticeable impact on conditions and extraction of complexes. Fast division of layers and the maximum value of molar coefficient of absorption were received at extraction of complexes by chloroform. After a single extraction with chloroform, 97.8-98.5% of copper was extracted as an ion associate (in a case the dichloroethane and carbontetrachloride was removed 95.6-96.6% of Copper). Further researches were conducted with chloroform. The concentration of Molybdenum in the organic phase was determined with rubeanic asid (1) by photometric measurements afterback extraction, while in the aqueous phase it was determined by the difference.

Absorption spectrum

The absorption spectrum of Cu (II): DTEP in chloroform shows the maximum absorption at 475nm. Maximum absorbance of MLC is observed at 634-640 nm. The absorption due to reagent at this wavelength is nearly negligible. Hence the absorption measurements were carried out at 590nm (Fig. 1) Contrast of reactions was high: initial reagents - are colourless, and complexes – are intensively painted. Molar coefficients of absorption make (3.61-4.82) x 10^4 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$.

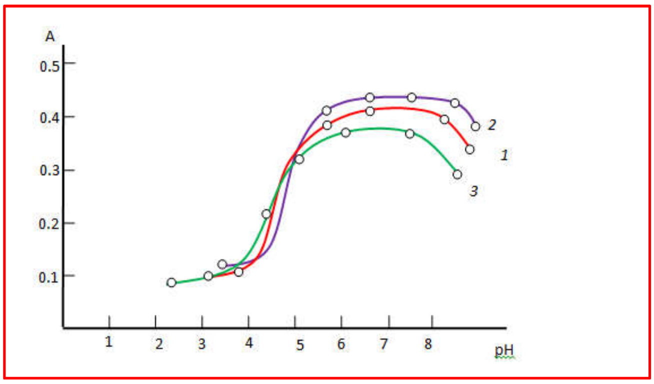

Figure 2. Absorption of mixed-ligand complexes

Cu-DTEP-Am.

1.Cu-DTEP-Phen, 2.Cu - DTEP-BPen, 3.Cu – DTEP - Dip

C_{Cu} = 1,875 •10^{-5}M; C_{DTEP}=0,8•10^{-3}M,$C_{Aм}$= 1,0•10^{-3}M, Shimadzu UV3100, l=1см.

Influence of Reagent Concentration and Incubation Time

For the formation and extraction of MLC, a 10-15-fold excess of complexing reagents is required; for example, theoptimal conditions for formation and extraction of these compounds are provided by 0.8x10^{-3} M DTEP and 1.0 x10^{-3} M Am. A large excess of hydrophob amin interferers with the determination. However it was found that the presence of excess of the reagent solution does not alter the absorbance of the color reaction. The equilibration time of 1.0 minute is sufficient for the quantitative extraction of Copper. The stability of colour of the Cu (II): DTEP complex with respect to time shows that the absorbance due to extracted species is stable up to 36 hours, after which slight decrease in absorbance is observed.

Stoichiometry of the complexes and the mechanism of complexation

Starik-Barbanel relative yield method, equilibrium shift method, crossed lines method and Asmus' methods were

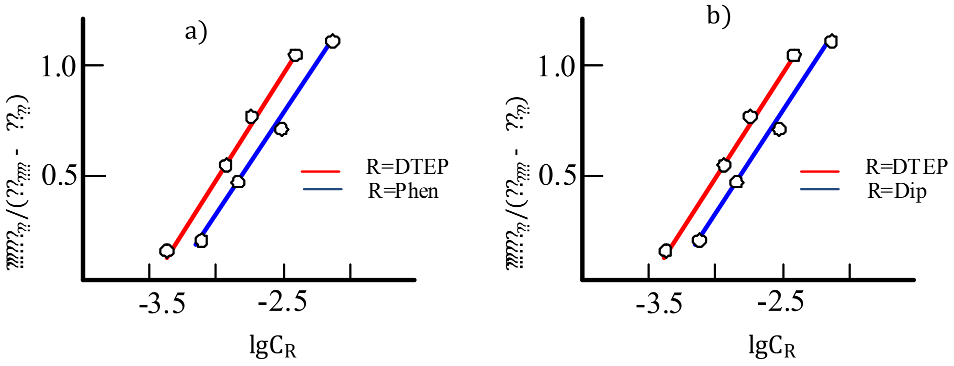

Figure 3. Determination of the ratio of components by equilibrium shift methodfor Cu -DTEP-PHen (a) и Cu -DTEP-Dip(b)

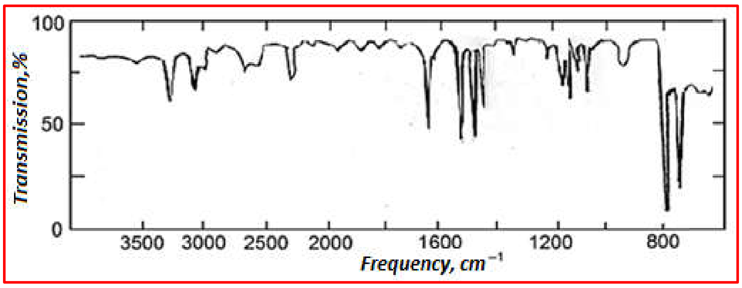

Figure 4. IR spectrum of the complex Cu(II)-DTEP-Phen

employed to elucidate the composition of the complex (19). It shows that the composition of Cu (II): DP: Am complex is 1:1:1(Fig 3) C_{Cu}= 1.875 $\times10^{-5}$M; C_{DTEP}=0/8$\times10^{-3}$M, C_{Am}= 1.0$\times10^{-3}$M, pH=7,λ=590 nm, KFK-2. ℓ=1.sm. The disappearance of the pronounced absorption bands in the 3200-3600 cm^{-1} with a maximum at 3460 sm^{-1}observed in the spectrum of DTEP, says that the -OH group is involved in the formation of the complex (Fig.4). The observed decrease in the intensity, absorption bands in the area 2580 sm^{-1}shows that one of the -SH groups involved in the formation of coordination bond in the ionized state. Detection of the absorption bands at 1360 cm^{-1} indicates the presence of a coordinated phenantroline (20, 21). It was found using the Nazarenko method that Cu(II) in the complexes was present in the form of $Cu^{2+.}$ The number of protons replaced by cobalt in one DTEP molecule appeared to be one (Nazarenko and Biriuk, 1967; Nazarenko *et al.*, 1969). The calculations were carried out based on the hydrolysis of copper ions (K_{h1}= 1$\times10^{-8}$, K_{h2}=1.9$\times10^{-7}$), dissociation constant of DP (K_0 = 1.5$\times$ 10^{-7}, K_1 = 1.7$\times$ 10-) and protonation constants Phen (K_{pr} = 3$\times$ 10^{-5}).

Interaction of copper with DTEP and Am can be represented as follows:

$$Cu^{2+} + qH_2R^{-} + pAm \rightarrow (Cu(H_{2-n}R)_q)(Am)_p + qnH^{+} \qquad (1)$$

Calculations were carried out according to the equation:

$$-\lg B = qnpH + \lg\frac{K_{н}}{(K_0 \ldots K_n)^q} \qquad (2)$$

где

$$B = \frac{[Cu](C_R - qC_k)^q (C_{Am} - pC_k)^p}{C_k\left(1+\frac{[H^+]}{K_0}+\frac{K_1}{[H^+]}\right)^q \left(\frac{K_{пр}}{[H^+]}\right)^p} \qquad (3)$$

The equilibrium concentration of the complex (C_c) found spectrophotometrically by the following relationship:

$$C_{к} = C_{Cu}\frac{A_x}{A_{пр}} \qquad (4)$$

Where C_{Cu}- the total concentration of Cu(II), mol/l, A_x- optical density at a specific pH, A_{max} optical density at full binding copper (II) a colored complex.

Unbound concentration of copper (II) in the colored complex is expressed:

$$C_{Cu} - C_{k} = [Cu^{2+}] + [CuOH^{+}] \qquad (5)$$

Hence the equilibrium concentrations of ions and hydroxocomplexes are:

$$[Cu^{2+}] = \frac{C_{Cu(II)} - C_k}{1+\frac{K_г}{[H^+]}}; \qquad [CuOH^{+}] = \frac{C_{Cu(II)} - C_k}{1+\frac{[H^+]}{K_г}} \qquad (6)$$

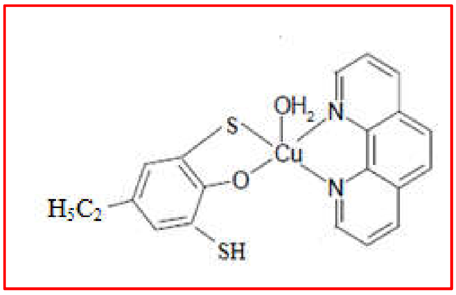

Figure 5. Structure of complex Co(DTEP)(H_2O)Phen

Thermogravimetric study of the complex Cu-DTEP-Phen shown that thermal decomposition of the complex takes place in three stages: at 60-120°C water evaporates (weight loss - 4.035%), at425-490°C-decomposed Phen (weight loss - 40.36%), and at 495-520°C- DTEP (weight loss -41.25%). The final product of the termolysis of the complex is CuO. Structure extractable complexes can be represented as in Figure 5. Influence of a number of cations and anions on the accuracy of determination of Cu (II) was studied. Experiments were performed according to the recipe, by which established calibration curves, with the only difference that a solution other than Cu (II) injected a certain amount of the corresponding ions. The stability constant of Cu(II)-DTEP-Am complexes wascalculated and found to be lgβ = 10.52-10.96 at room temperature. The sizes of equilibrium constant K ecalculated on a formula lgK_e= lg D - lg (Am) were presented in Table 1. Calculation of extent of polymerization of complexes was carried out on the equation (24). The made calculations showed that MLC in an organic phase won't be polymerized and are in a monomeric form (γ = 1.04 - 1.09). In conclusion the analytical parameters pertaining to the proposed method are given in Table 1.

Influence of foreign ions

To find selectivity of proposed method, the study was carried out for the determination of Cu (II) in presence of higher concentration of foreign ion. The tolerance limit of the ions shows minimum deviation (±2 %) in absorbance. The interference of various cations was removed by using suitable masking agents. The ions which show interference in the spectrophotometric determination of Copper were overcome by using appropriate masking agents. The effect of various ions and reagents on the extraction-spectrophotometric determination of 30 mg copper(II) is summarised in Table 2. It can be assumed that large amounts of alkaline ions, alkaline-earth ions, chloride, sulphate, nitrite, nitrate and oxalate not interfere determination of Cu(II). Tartrate, citrate, F^- , J^-,CN^-, thiourea interfere determination of Cu(II). Co(II). Ni(II), Fe(II,III), V(IV,V), W(VI), Mo(VI), Ti(IV) and Mn(II) interfere determination of Cu(II). However, the interfering effect of some of these ions can be reduced by masking with oxalate, citrate or EDTA. Interference of Fe(III) eliminated oxalic acid; Ti(IV) - tiron or sodium fluoride; Hg (II) ion -sulfit; Nb (V)

Table 1. Optical characteristics, precision and accuracy of the spectrophotometric determination of Cu(II) with DTEP and Am

Compound	pH	λ, нм	Δλ, нм	$\varepsilon \bullet 10^{-4}$	lgβ	lgK_p	$lgK_{эк}$
Cu-DTEP-Phen	6,3-7,5	535	259	3.70	10.82	6.71	12.33
Cu-DTEP-BPhen	6,4-7,7	540	264	4.82	10.96	6.81	12.47
Cu -DTEP-Dip	6,2-7,4	534	260	3.61	10.52	6.73	12.29

Table 2. Influence of interfering ions on the determination of copper(II) as MLC with DTEP and Phen (30,0 μg Cu added)

Ion	Molar excess of the ion	Masking agent	Found Cu, μg	S_r
Co(II)	50		30,5	0,05
Ni(II)	50	Sodium cyanide	29,8	0,02
Fe(II)	45		29,8	0,04
Cd(II)	200		29,6	0,05
Al(III)	180		29.7	0,02
Fe(III)	50	Sodium Fluoride	30,2	0,05
Zr(IV)	50		29,8	0,03
W(VI)	25		29,6	0,05
Hg(II)	38	$Na_2S_2O_3$	30,2	0,05
Ti(IV)	30	Sodium Fluoride	29,6	0,03
V(IV)	20		29,8	0,06
Mo(VI)	10	Citrate	30,4	0,04
Cr(III)	120		29,8	0,04
Nb(V)	50	Sodium Fluoride	30,3	0,05
Ta(V)	50	Sodium Fluoride	30,2	0,05
Pb (II)	25		30,3	0,04
Pd (II)	5		29,2	0,05
Pt(II)	8		30,3	0,05
Ag (I)	10	Potassium iodide	30,2	0,05
UO_2^{2+}	50		29,2	0,04
Bi(III)	40		30.5	0.05
Ag(I)		Potassium iodide	30,3	0,05
Acetate	100		30,2	0,05
Tartarate	120		30,3	0,05
Sulphate	125		29,8	0,02
Thiourea	24		29,8	0,04
Fluoride	100		30,2	0,05
Thiosulphate	40		30,4	0,04

Table 3. Comparative characteristics of the procedures for determining of copper

Reagent	pH (solvent)	λ, nm	$\varepsilon \times 10^{-4}$
Dyétyldytyokarbamat (Umland *et al*., 1975; Marczenko and Baltsejak, 2007)	4-11(carbontetrachloride)	436	1.40
Cuproin (Umland *et al*., 1975; Marczenko and Baltsejak, 2007)	4-7(isoamylalcohol)	546	0.64
Neokuproin (Umland *et al*., 1975; Marczenko and Baltsejak, 2007)	3-10(isoamylalcohol)	454	0.79
DTEP+Phen	6.3-7.5 (Chloroform)	635	3.72
DTEP +BPhen	6.4-7.7 (Chloroform)	640	4.82
DTEP +Dip	6.2-7.4 (Chloroform)	634	3.61

and Ta (V) - oxalic acid, and Mo (VI) and W(VI) - sodium fluoride and oxalic acid. When using a 1% solution of ascorbic acid does not interfere with determination Mn(VII), V(IV), Nb(V), Cr(VI), Mo(VI) и Fe(III). When using 0.01M oxalic acid definition not interfereV(IV), Nb(V),Ta(V),Cr(III), Mo(VI) , W(VI) и Fe(III). The proposed method compares favourably with the existing ones (Table 3) and offers the advantages of better simplicity, rapidity, sensitivity and selectivity.

Effect of Copper (II) concentration

The adherence to Beer's law was studied by measuring the absorbance value of the series of solutions containing different concentrations of the metal ion. A linear calibration graph drawn between absorbance and the metal ion concentration indicates that Cu(II) may be determined in the range 0.05-3.8μg/ml (27). Table 4 summarizes the calibration characteristics obta-ined with DTEP+ Phen, DTEP+ Bphen and DTEP+ Dip. The pertaining calibration graph is shown in the Fig. 6. C_{DTEP} =0.8 ×10^{-3}M; C_{Am}= 1.0×10^{-3}M; pH = 3; λ = 590 nm, l=1.0 cm. The proposed method compares favourably with the existing ones (Table 3) and offers the advantages of better simplicity, rapidity, sensitivity and selectivity (28). Table 4. Analytical characteristics of some ternary complexes of Cu with 2, 6-Dithiol-4-ethilphenol and Hydrophobic Amine

Application

The proposed method was successfully applied for the determination of copper from various pharmaceutical, food and in plant sample.. The results found to be in good agreement with those obtained by the standard known method (Table 5 and Table 6).

Conclusion

1. The results obtained show that the newly developed method in which the reagent DTEP was used, can be effectively used for quantitative extraction and estimation of Cu (II) from aqueous media.
2. Mixed-ligand complexes of Copper (II) with 2, 6-dithiol-4-ethylphenol (DTEP) in the presence of hydrophobic amines have been investigated by spectrophotometric method.
3. Extraction of mixed ligand complexes is maximal at pH 2.8-5.3. The proposed method is quick and requires less volume of organic solvent.
4. The optimal conditions for the formation and extraction of mixed-ligand compounds have been found and the ratios of components I the complexes have been determined.
5. The Beer's law was applicable in the range of 0.04-3.6μg/ml.
6. A simple, rapid and sensitive methods proposed for the determination of trace amounts of Copper.The method is very precise, faster and simpler than other methods. The developed method is compared with result obtained with the

REFERENCES

Akhmedly, M. K., Kly'gin, A.E., Ivanova, L.I., Bashirov, E.A. 2007. On the chemistry of interaction of gallium ions with a number of sulphophtaleins. *Zhurnal Neorganicheskoi Khimii*., 1974; 19(8) -2012.

Bellami, L. 1991. Infrakrasnie spectra slojnikh molecule (The infrared spectra of complex molecules). Moscov: Mir, 592.

Bulatov, M.I. and Kalinkin, I.P. 1972. Prakticheskoe rukovodstvo po fotokolorimetricheskim I spektrofotometricheskim metodam analiza (Practical Guide on Photocolorimetric and Spectrophotometric Methods of Analysis), Moscow: Khimiya. 1972.

Chaisuksant, R., Palkawong-na-ayuthaya, W. and Grudpan, K. 2000. Spectrophotometric determination of copper in alloys using naphthazarin. *Talanta*, V. 53, № 3, 4, P.579–585.

Dorokhova E.N. and Prokhorova, G.V. 1991. Analytical chemistry (physical-chemical methods of analysis). M.: Higher School, 1991. 250 pp.

Karthikeyan, J., Naik, P. P. and Shetty, A. N. 2011. A rapid extractive spectrophotometric determination of copper(II) in environmental samples, alloys, complexes and pharmaceutical samples using 4-*N*,*N*(dimethyl)amino) benzaldehydethiosemicarbazone. *Environmental Monitoring and Assessment*, V.176, №1, pp 419–426.

Korostelev, P.P. 1964. Preparation of solutions for chemical analysis works. M. Publishing house of Academy of Sciences of the USSR, 401.

Kuliev, A. M., Aliev, S. R., Mamedov, F. N. and Movsumzade, M. 1976. Synthesis of aminomethyl derivatives of 2-hydroxy-5-tert-alkylthiophenols and their cleavage by thiols. Zhurnal Organicheskoi Khimii, V. 12, No 2, pp. 426-431.

Kuliev, K. A., Verdizadeh, N. A., Gadjieva, A. B. 2015. Liquid-Liquid Extraction and Spectrophotometric Determination of Molybdenum with 2, 6-Dithiolphenol and its Derivatives in the Presence of Hydrophobic Amines // *Chemistry Journal*, V. 05, № 3, pp. 45-53.

Kuliyev, K. A. and Verdizade, N. 2015. A. Spectroscopic Investiqation Complex Forma-tion of Vanadium Using 2,6-Dithiolphenol and Hydrofob Amins //*American Journal of Chemistry*, V. 5, №1, pp. 10-18.

Kuliyev, K. A., Verdizadeh, N. A., Gadjieva, A. B., Mamedova, S. 2016. A. Spectroscopic investigation complex formation of molybdenum with 2, 6-dithiolphenol and its derivatives in the presence of hydrophobic amines. *International Journal of Chemical Studies,* 4(3): pp. 42-48.

Kuliyev, K. A., Verdizadeh, N. A., Suleymanova, G.S. 2016. Spectrophotometric Determination of Cobalt (II) with 2, 6-Dithiolphenol and Its Derivatives in the Presence of Hydrophobic Amines //*American Journal of Chemistry*, V. 6, №4, p. 95-103

Madan, P. U. and Barhate, V. 2016. D.Extractive spectrophotometric determination of copper (II) using 2-(5-bromo-2- oxoindolin-3-ylidene) hydrazine carbothioamide as an analytical reagent, *European Journal of Biomedical and Pharmaceutical sciences*, V. 3, № 4, pp. 392-396.

Marczenko, Z., Baltsejak, M. K. Metodı Spectrophotometrii v UF I vidimoy oblastyax (Spectrophotometrically in the UV and visible regions in inorganic analysis). M. Binom. Laboratoriya znaniy. 2007. P. 711 p.

Nakamoto, K. 1991. IK-spectr KR neorqaniceskikh I koordinatsionnikh soedineniy (Infrared and Raman Spectra of Inorganic and Coordination Compounds). Moscov: Mir. 536.

Nazarenko V.A., Biriuk E.A. Issledovanie khimizma reaktsii ionov mnogovalentnykh elementov sorganicheskimi reagentami [Research of chemism of reactions of ions of multivalent elements with organicreagents]. Zhurn. analit. khimii. 1967. Vol. 22, N 1. pp.57. (In Russian)

Nazarenko V. A. Vzaimodeistvie ionov mnogovalentnykh elementov s organicheskimi reagentami [Interactionof ions of multivalent elements with organic reagents]. Trudy komis. Po analit. khimii AN SSSR [Proc. of the Commission on analytical chemistry of Academy of Sciences of the USSR]. Moscow, Nauka, 1969. Vol. 17. pp.22. (In Russian)

Patil, Y. K., Lokhande, R. S., Rana, P. K. *et al*. 2016. Extractive spectrophotometric determination of copper(II) by using 2-hydroxy-3-methoxy benzaldehydethiosemicarbazone as an analytical reagent. World *Journal of Pharmacy and Pharmaceutical Sciences*, V. 5, № 2, 965-970).

Podchaynova, V.N., Simonova, L.N. 1990. Analiticheskay akhimiya Medi. M.: Nauka, 280 p. (In Russian)

Rao, M. Sayaji Prasad, N.B.L. Reddy, K. Hussain Spectrophotometric determination of copper(II) in alloys and edible oils using 2-acetylthiophene thiosemicarbazone. *Indian Journal of Chemistry-Section A (IJC-A)IJC-A*, Vol.45A(07) (July 2006) >1659-1662).

Reddy, G. T., Kumar Reddy, P. N., Gangi Reddy, N. C. *et al*. 2015. A rapid extractive spectrophotometric determination of Cu(II) in biological, geological and pharmaceutical samples using o-hydroxyacetophenoneisonicotinoylhydrazone. Scholars Research Library Der Pharmacia Lettre, V. 7 № 3, pp. 274-286 (http://scholarsresearch library.com/archive.html)

Shaikh, B., Barache, U. B., Anuse, M. A. and Gaikwad, S. H. 2016. 4-(4'-Nitrobenzylideneimino)-3-methyl-5-mercapto-1, 2, 4-triazole, A New Chromogenic Reagent for Extractive Spectrophotometric Determination of Copper (II) in Pharmaceutical and Alloy Samples *S. Afr. J. Chem*., V. 69, pp. 157–165, .

Tekale, P., Tekale, S., Lingayat, S., Pabrekar, P. N. 2011. Extractive Spectrophotometric Determination of Copper (II) using 1-phenyl-1- hydrazonyl-2-oximino propane –1, 2 –dione. *Science Research Reporter*, V.1, № 2: p.83 - 87.

Turkoglu, O., Soylak, M. 2005. Spectrophotometric Determination of Copper in Natural Waters and Pharmaceutical Samples with Chloro(phenyl) glyoxime. *Journal of the Chinese Chemical Society,* 52, 575-579

Umland, F. *et al*. 1975. Kompleksnye soedineniya v analiticheskoi khimii: teoriya i praktika primeneniya (Complex compounds in analytical chemistry: theory and practice of application). M., Mir,. 531 p.

Zalov, A. Z., Amanullayeva, G. I. 2016. Spectrophotometric determination of cobalt (II) in a liquid-liquid extraction system containing 2-hydroxy-5-iodothiophenol and diphenylguanidine. *IJRDO-Journal of Applied Science*, V.2 | №-7 | July, | P.2 17-25.

Zalov, A. Z., Verdizade, N. A 2011. Jamalova R.I. Extraction-photometric determination of niobium (V) with 2-hydroxy-5-bromthiophenol and hydrophob amines. *Az. Chim. Journ*., № 1. P. 97-102.

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