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Determination of Cu (II) ions using sodium salt of 4-phenylsemicarbazone 1,2-naphthoquinone-4-sulfonic acid in natural and industrial environments

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Abstract

Introduction: The copper content in natural waters usually range from 0.2 to 30 $\mu\text{g/L}$. The higher concentrations are habitually found in industrial effluents and other contaminated waters.

Methods: This work develops the spectrophotometric method of determination of copper (II) microgram amounts with a new reagent - sodium salt of 4- phenylsemicarbazone 1,2-naphthoquinone-4-sulfonic acid (L), used as a ligand for a new coordination compound of copper (II). The complex formation is accompanied by color change, allowing use of this property for quantitative determination of copper (II) ions in various objects such as: alloys, superconducting ceramics and tap water. The determination of copper (II) ions has been carried out by voltammetric and spectrophotometric methods.

Results: The complex of composition CuL is stable within the pH range from 5.74 to 6.51. Its stability constant is $\log\beta = 4.53$. The molar absorption coefficient of the complex has been found. Both methods give the same concentration of about 0.0400 mg/L of copper (II) in tap water, ceramics, and alloys. The detection limit of the spectrophotometric determination of copper (II) ions in the presence of the main metal ions in tap water is 0.012 mg/mL.

Conclusions: The advantages of this method are the simplicity of the synthesis of reagent, its ease of recrystallization from water-ethanol solution, and stability in the crystalline state.

Introduction

The diversity of chemical industries, a large number of chemical products (initial, intermediate, and final) used and produced in manufacturing processes, cause the formation of wastewater contaminated with organic and inorganic substances of very different composition and volume (Qadir et al. 2015). Among heavy metals, despite its less-significant toxicity, copper has become a widely distributed pollutant in natural water as a result of the dumping of electronic trash and mining residues (Zhang et al. 2014).

Cu constitutes an essential micronutrient for plants (photosynthetic electron transport, metabolism of carbohydrates) and animals (pigmentation, nucleic acid, protein

metabolism, integrity of immune system) (Courchesne et al. 2006). Concomitantly, copper belongs to the trace elements necessary for human life. Cu (II) is the third most abundant transition-metal ion in the human body (after Fe (III) and Zn (II) and is essential for many biochemical and physiological functions (Chandrasekhar et al. 2012). Its excess and deficiency lead to serious consequences such as: malfunction of the liver, neurological disorders, deterioration of connective and bone tissues, and heart diseases (Yee and Goodwin 1974). At high concentrations, the essential trace metal Cu can become highly toxic to plants and microorganisms (e.g., Aoyama and Nagumo 1997, Hattori 1992, Kraal et al. 2006). The toxicity of Cu in soils depends on the mobility and thus (bio) availability of the metal. The high copper concentration can also cause acute disorder of the gastrointestinal tract, which is accompanied by nausea, vomiting, and diarrhea. The concentration of copper in lakes and rivers ranges from 0.5 to

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1.000 ppb with an average concentration of 10 ppb. The average copper concentration in groundwater (5 ppb) is similar to that in lakes and rivers; however, monitoring data indicate that some groundwater contains levels of copper (up to 2.783 ppb) that are well above the standard of 1.300 ppb for drinking water (ATSDR 2004). Supplementary data can be found in the papers (Pesavento et al. 2004, Shengbiao et al. 2003).

The sodium salt of 4-phenylsemicarbazone 1,2-naphthoquinone-4-sulfonic acid reactant is an original synthesized reagent, used as a ligand for obtaining new coordinative compounds, which is important for the life ions as copper (II). Complex formation is accompanied by a color change, allowing the use of this property for analytical purposes for quantitative determination of copper (II) ions in various objects such as: alloys, superconducting ceramics as well as tap water.

Currently, for the determination of copper (II) ions, a variety of reagents and techniques is used (Ulmanu et al. 2007; Dharmarajan et al. 2004). According to the literature (Ramanjaneyulu et al. 2008), the existing reagents for the photometric determination of copper permit detection of 0.025 to 30 $\mu\text{g/mL}$ Cu. For example, one of the most frequently used reagents for the determination of copper (II) ions is diethyldithiocarbamate, which the detection limit is 0.1 $\mu\text{g/L}$.

This paper deals with the application of a novel reagent, the sodium salt of 4-phenylsemicarbazone 1,2-naphthoquinone-4-sulfonic acid, for determination of copper (II) ions in tap water, copper containing alloys and superconducting ceramics. The aim of this work is the use of a new reagent for quantitative determination of copper (II) ions in water and industrial objects, establishing optimum conditions for complex formation of copper (II) ion with a synthesized ligand, as well as the elucidation of the detection limit of copper (II) ions in tap water, and superconducting ceramics. This new reagent has proved to be suitable for quantitative spectrophotometric determination of copper (II) ions in objects of natural and industrial environments.

Methods

Experimental part

The solution of the organic reagent, the sodium salt of 4-phenylsemicarbazone 1,2-naphthoquinone-4-sulfonic acid (L), was prepared by dissolving its necessary sample amount in a small volume of 96 % ethanol and then diluting it in distilled water; the concentration of the reagent in solution was $2 \cdot 10^{-3}$ mol/L. Solutions of copper (II) were prepared by dissolving samples of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ of analytical grade of purity in distilled water and subsequent dropwise adding a solution of nitric acid for suppression of hydrolysis ($\text{pH} \approx 1$). Working solutions were prepared from batches of superconducting

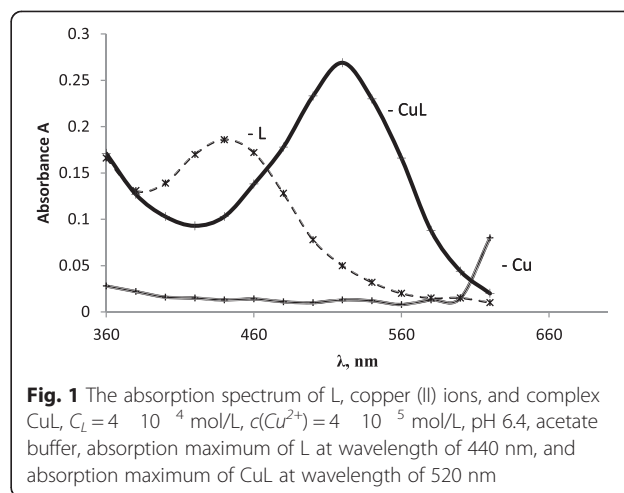
ceramics and bronze alloys, dissolving them in nitric acid and diluting with distilled water. The titers of solutions were adjusted by complexometric method in the presence of xylenol orange and iodometric method. The acetate buffer was prepared from CH_3COOH and CH_3COONa ($\text{pH} \approx 5.5$). The optical density was measured with the use of spectrophotometer SF-46 (LOMO, Russia); the pH of solutions was measured by the potentiometer—121 with a glass electrode.

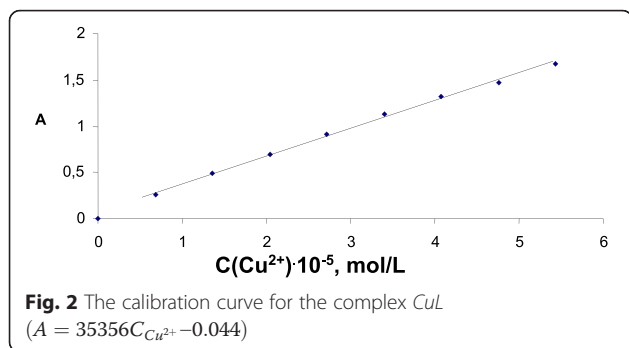
It has been found that the copper complex with the sodium salt of 4-phenylsemicarbazone-1,2-naphthoquinone-4-sulfonic acid absorbs at the wavelength of 500 nm, while the reagent has an absorption maximum at 430 nm (Fig. 1).

For the selection of the pH range, in which the absorbance value was maximal, different pH buffers were tested (bi-phthalate, acetate, oxalate, and borate). The maximum yield of the complex matched the use of acetate buffer solution with pH from 5.74 to 6.51. In strongly acidic solutions, the complexes do not reach their maximum output, since the value of the absorption decreases.

To select the optimal concentration of the complex, the calibration curves of the dependence of absorbance on the concentration for individual solutions of complex compounds were constructed. The linear relationship between absorbance and concentration is kept within the concentration range $(0.35\text{--}4.68) \cdot 10^{-5}$ mol/L (Fig. 2). These data are given in Table 1.

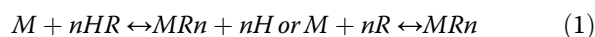
One way to establish the composition of complex compounds with organic ligands is the method of isomolar series (Bulatov and Kalinkin 1986). Its essence lies in finding the ratio of stoichiometric coefficients in the formula M_nL_k according the dependence, constructed in coordinates “absorbance – concentration ratio of one component to the sum of the concentrations of the two components” $(A - c(M^{2+}) / (c(M^{2+}) + c(L))$ or $(A - c(L) / (c(M^{2+}) + c(L)))$. For this purpose, a series of solutions is





prepared, in which the concentration of components varies in antibate ratios, e.g., 1:9; 2:8; 3:7; 8:2, 9:1, but wherein the total concentration of both components remains constant. The absorbance is plotted according to the ratio $c(M^{2+}) / (c(M^{2+}) + c(L))$. Through each group of points, straight lines are drawn, which intersect at some point. This point of intersection is the index ratio $n / (n + k)$ or $k / (n + k)$ in the formula M_nL_k . The stoichiometry is established by the isomolar series whose graph is shown in Fig. 3.

By the *Komar* method, the logarithm of the stability constant of complex was calculated. This is a versatile method for the accurate determination of the molar attenuation coefficients of light absorption and the equilibrium constants of complex formation reactions, based on the solution of an equation with two unknowns for two or more experiments. The method assumes knowledge of the type of reaction or complex composition set in an independent way. It is used to study reactions of the type:



Analytical version of the method

A number of solutions with a constant concentration of hydrogen ions C_H and stoichiometric ratio of reactant components $C_{HR}/C_M = n$ is prepared. Then the optical densities of the solutions at the chosen wavelength Λ are measured. Applying the law of mass action to the above

Table 1 Calculation of error for the calibration curve ($P = 0.95$, $t = 3.18$)

| $C \cdot 10^{-5}$, mol/L | Mass m_i , g | Confidence interval d_i | Standard error (SE) of arithmetic mean S | Mean square error Δ | $m_m \pm \delta$ |
|---------------------------|----------------|---------------------------|--|----------------------------|------------------|
| 1.41 | 0.0028 | 0.0001 | 0.0001 | 0.0002 | 0.0027 |
| 2.02 | 0.0027 | 0 | | | ± 0.0002 |
| 2.64 | 0.0026 | 0.0001 | | | |
| 3.29 | 0.0026 | 0.0001 | | | |

The arithmetic mean value of the mass is 0.0027 g

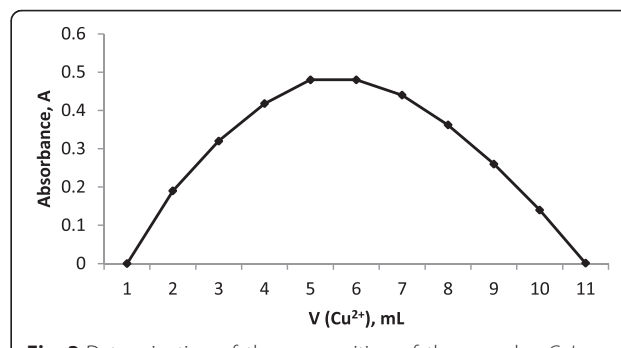


Fig. 3 Determination of the composition of the complex CuL , $c(Cu^{2+})/(c(Cu^{2+}) + c(L))$, where $c(Cu^{2+})$ is the concentration of copper (II), while $(c(Cu^{2+}) + c(L))$ denotes the sum of concentrations of copper (II) ions and ligand

complex formation reactions, the equilibrium constant K_p is expressed by the formula:

$$K_p = \frac{C_H^n C_K}{(C_M - C_K)^{n+k} i^n} \quad (2)$$

The optical density of solution, when at the selected wavelength Λ , the complex, and one of the reactants, for example, if a reagent HR is absorbed only, is expressed by the equation:

$$D = n(C_M - C_K) \epsilon_R l + \epsilon_K C_K l \quad (3)$$

Substituting the value of C_k from this equation for the i -th and j -th concentration values of M and dividing the resulting expressions on each other, we get the ratio:

$$\frac{C_i l \epsilon_K - D_i}{C_j l \epsilon_K - D_j} = \left(\frac{D_i - n \epsilon_R l C_i}{D_j - n \epsilon_R l C_j} \right)^{\frac{1}{n+1}} \quad (4)$$

Considering that $\frac{C_i}{C_j} = b$ and $\left(\frac{D_i - n \epsilon_R l C_i}{D_j - n \epsilon_R l C_j} \right)^{\frac{1}{n+1}} = B$, we obtain the formula for the calculation of the molar attenuation coefficient of light absorption of the complex:

$$\epsilon_K = \frac{1}{j} \left(\frac{D_i}{D_j} + B \frac{D_i - b C_i}{C_j (b - B)} \right) \quad (5)$$

If it is possible to choose such Λ wavelength, that except the complex any of the reactants does not absorb, the expression for B is simplified and takes the form:

$$B = \left(\frac{D_i}{D_j} \right)^{\frac{1}{n+1}} \quad (6)$$

The measurement of optical densities for the i -th and j -th concentration values should be carried out in strictly identical conditions (pH of solution, the wavelength, layer thickness, temperature, and ionic strength). Thus, from data of any pair of this solution, ϵ_K and then K_p are

determined. The concentration of the complex C_K is computed from the calculated value ε_K :

$$C_K = \frac{D}{\varepsilon_K l} \quad (7)$$

However, when calculating the quantities ε_K and K_p , the “loss of precision by subtraction” can occur, especially in the case of very stable complexes. To prevent the “loss of accuracy”, these are used: different ratio $C_i/C_j = b$, diluted solution (within preservation of ε_K) or reduced complex output by *pH* lowering, when the reagent is a weak acid. If the characteristic’s low-strength complexes are determined, then it is possible immediately to obtain suitable results. The required data are presented in Table 2.

Results

Determination of amount of Cu^{2+} in superconducting ceramics

The solution of superconducting ceramic was prepared by accurately weighing and dissolving in a small volume of nitric acid and diluting with acetate buffer; a portion of solution (10.0 mL) was diluted in a 50.0-mL flask, then a 10-fold excess of ligand was added. The absorbance was measured relative to ligand solution in acetate buffer at a wavelength of 520 nm.

Determination of Cu^{2+} in bronze BrAZhMts (used standard on the chemical composition is GOST 18175–78)
Foreign analogs of bronze BrAZhMts10-3-1.5 (Maslyuk et al. 1992)

| Germany | European Union | Poland | Czech Republic | Austria | International |
|--------------------------------|----------------|--------------|----------------|--------------|---------------|
| DIN, WNr | EN | PN | CSN | ONORM | ISO |
| 2.0936CuAl10Fe3Mn3CuAl10Fe3Mn2 | CuAl10Fe3Mn2 | CuAl10Fe3Mn2 | 423046 | CuAl10Fe3Mn2 | CuAl10Fe3 |

Composition of bronze: 83–88 % Cu, 9–11 % Al, 2–4 % Fe, 1–2 % Mn.

The solution of bronze is prepared by the accurate mass measurement. For determination, a series of solutions with different contents of copper, and the same concentration of the ligand (a 10-fold excess) in acetate

Table 2 The Komar method for $\text{Cu}:L$ relative to L for acetate buffer

| V_{Cu} , mL | $C_{Cu} \times 10^{-5}$, mol/L | V_L , mL | $C_L \times 10^{-5}$, mol/L | Absorbance A | ε ($\text{L mol}^{-1}\text{cm}^{-1}$) $\times 10^5$ |
|---------------|---------------------------------|------------|------------------------------|----------------|---|
| 1.0 | 0.68 | 2 | 1.6 | 0.068 | 0.11 |
| 1.5 | 1.02 | 3 | 2.4 | 0.115 | 0.12 |
| 2.0 | 1.36 | 4 | 3.2 | 0.179 | 0.13 |

Molar attenuation coefficient $\varepsilon = 29170$; logarithm of the complex stability constants $\log\beta = 4.53$

buffer mixture was prepared. The absorbance was measured relative to ligand solution in acetate buffer at a wavelength of 520 nm.

Determination of amount of Cu^{2+} in tap water

To determine the copper (II) ions, 200 mL of tap water are poured by a volumetric flask in the beaker. Water is evaporated to a volume of 50 mL. Then, it is again transferred into a volumetric flask, and the determination is performed. To different volumes of water, the ligand solution is added, and the solution is brought up to the mark by acetate buffer mixture. The absorbance is measured relative to ligand solution in acetate buffer at a wavelength of 520 nm. The data are presented in Table 3.

Discussion

The content of copper (II) ions was determined by the spectrophotometric method. The maximum of absorption of the complex (1:1) is observed at a wavelength of 500 nm. The complex $\text{Cu}:R$ is stable in the pH range from 5.74 to 6.51. Using the Komar method, the logarithm of the stability constant, $\log\beta = 4.53$, was calculated. The molar attenuation coefficient is of $3 \cdot 10^4 \text{ L} \cdot \text{mol}^{-1} \text{ cm}^{-1}$. The Beer–Lambert–Bouguer law complied within the concentration range of $0.3 \cdot 10^{-6}$ to $4.0 \cdot 10^{-5}$ mol/L ($A = 30094.2 \text{ Ci} + 0.07$). The data are presented in Table 3.

The spectrophotometric determination of the copper content using the sodium salt of 4-phenylsemicarbazone 1,2-naphthoquinone-4-sulfonic gives 0.0396 mg/L. In

this case, the detection limit is 0.012 mg/mL. The obtained results allow recommending this reagent for the spectrophotometric determination of copper (II) ions in tap water. The ions of iron, magnesium, calcium, sodium, and potassium (at concentrations not exceeding $1.0 \cdot 10^{-2}$ mol/L) do not interfere with these measurements. The ions lead, bismuth, and mercury (II) at

Table 3 Content of copper in objects ($P = 0.95$)

| Sample | Contained | Found |
|----------|-------------|--------------------------|
| Ceramics | 0.2745 g | 0.2720 ± 0.0041 g |
| Bronze | 0.1090 g | 0.1037 ± 0.0053 g |
| Water | 0.0400 mg/L | 0.0396 ± 0.0004 mg/L |

concentrations of $1.0 \cdot 10^{-5}$ mol/L and above have been found to affect measurements.

Conclusions

In conclusion, we have reported a spectrophotometric method of the determination of copper (II) microgram amounts with a new compound, sodium salt of 4-phenylsemicarbazone 1,2-naphthoquinone-4-sulfonic acid (L), used as a ligand for an original coordination compound of copper (II). The stability constant of the complex of composition CuL has been determined. The molar absorption coefficient of the complex has been established.

Data obtained by the spectrophotometric measurement of copper (II) amounts have been compared with those obtained by voltammetric method. Both methods give the same concentration of about 0.0400 mg/L of copper (II) in tap water, ceramics, and alloys. The detection limit of the spectrophotometric determination of copper (II) ions in the presence of the main metal ions in tap water has been found to be 0.012 mg/L. The main advantages of the developed method are the simplicity of the synthesis of reagent, its ease of recrystallization from water-ethanol solution, and stability in the crystalline state.

In the next work, we are also going to examine if the synthesized reagent has no detrimental effect in biological systems, which would allow its potential use for in vivo applications.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

IP analyzed and interpreted the data and drafted the manuscript. OZ was involved in obtaining experimental data, participated in manuscript design, and helped to draft the manuscript. All authors, IP and OS, read and approved the final manuscript.

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