Open Access Library Journal
2026, Volume 13, e15367
ISSN Online: 2333-9721
ISSN Print: 2333-9705

The Extractive Spectrophotometric Determination of Cu(II) Ions in Environmental and Industrial Samples

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How to cite this paper: Jamoliddin, T., Gulzoda, T., Nurmukhammat, T., Shahinabonu, K., Rano, K. and Bekhruz, T. (2026) The Extractive Spectrophotometric Determination of Cu(II) Ions in Environmental and Industrial Samples. *Open Access Library Journal*, **13**: e15367.
https://doi.org/10.4236/oalib.1115367

Received: April 17, 2026
Accepted: May 19, 2026
Published: May 22, 2026

Abstract

This review article summarizes and analyzes modern approaches to the extractive spectrophotometric determination of copper(II) ions in natural waters, ores, environmental, and industrial samples. The quantitative determination of Cu(II) ions is of great importance for scientific and medical research, as well as for environmental monitoring. In recent years, numerous methods have been developed to ensure high accuracy, rapid analysis, and high sensitivity in their determination. Particular attention has been devoted to the development and application of organic analytical reagents capable of forming intensely colored, stable, and selectively extractable complexes with Cu(II) ions. The paper discusses the physicochemical properties, environmental behavior, and toxicological significance of Cu(II) ions, emphasizing the necessity of their sensitive and selective monitoring in natural waters, wastewater, soils, food products, and pharmaceutical samples. In addition, the historical development of organic reagents in inorganic analysis and the role of coordination chemistry in advancing spectrophotometric methods are also highlighted. A wide range of chromogenic reagents-including hydrazones, thiosemicarbazones, azo compounds, triazoles, and Schiff bases-is reviewed. For each system, key analytical characteristics such as optimal pH, complex stoichiometry, extraction conditions, absorption maxima (λ_{max}), molar absorptivity (ε), linear dynamic ranges, limits of detection, limits of quantification, stability constants, and interference effects are comparatively analyzed. The advantages of extractive spectrophotometry-high sensitivity, simplicity, cost-effectiveness, and applicability to trace-level determination-are highlighted in comparison with instrumental techniques such as atomic absorption spectrometry. Overall, spectrophotomet-

ric techniques stand out among analytical methods due to their high precision, rapid operation, and low reagent consumption, making them effective tools in environmental and biomedical research.

Subject Areas

Analytical Chemistry, Environmental Chemistry, Green Chemistry

Keywords

Extractive Spectrophotometry, Copper(II), Organic Analytical Reagents, Chromogenic Ligands, Complex Formation, Liquid-Liquid Extraction, Trace Metal Analysis, Environmental Monitoring, Green Chemistry

1. Introduction

Heavy metal ions such as Cu(II) play dual roles in biological systems: while copper and zinc are essential trace elements involved in enzymatic and metabolic processes, their excessive accumulation causes oxidative stress and cellular toxicity. At present, the rapid development of technologies has led to an increase in the concentration of heavy and toxic metal ions in environmental objects, which progressively enhances their adverse impact on human health. This issue has acquired a global character and necessitates regular monitoring of heavy and toxic metal ions in environmental matrices [1]. In addressing these challenges, the development of economically cost-effective, highly sensitive, and selective methods for the detection of heavy and toxic metal ions is of primary importance [2]. In particular, the development of spectrophotometric methods for the determination and control of heavy and toxic metal ions based on organic reagents containing functional-analytical and analytically active groups is of significant practical relevance [3]. Specifically, the development of quantitative determination methods for Cu(II) ions in natural waters, ores, industrial wastes, and other complex matrices is of great practical importance [4] [5].

Spectrophotometric determination of transition metals using chromogenic reagents has long been recognized as a reliable and fundamental analytical method. Its main advantages include high sensitivity, selectivity, and high economy [6] [7]. In analytical chemistry, continuous efforts are devoted to the search for new methods and the improvement of existing techniques for the determination of metal ions in various objects. Among them, spectrophotometric methods occupy a special place because they combine simplicity with accuracy and therefore remain highly relevant today. On the other hand, organic reagents constitute the basis for the determination of chemical elements and are currently the most widely used tools among quantitative analytical methods in chemical, pharmaceutical, industrial, forensic, environmental, and clinical studies worldwide [8].

Robert Boyle was the first to report the use of organic analytical reagents in

inorganic analysis of systems such as plant materials [6]. Initially, these were mainly plant extracts, for example, litmus. A spot test for iron on papyrus impregnated with oak gall extract was described by Pliny in the first century AD. However, systematic investigation of the interaction between organic reagents and transition metal ions was stimulated by the emergence of Werner's coordination theory. Advances in coordination chemistry led to significant growth in quantitative methods for the determination of transition metal ions. Consequently, a large number of new analytical reagents have been introduced as spectrophotometric reagents. Specificity and selectivity are two major challenges in the application of any analytical organic reagent. The field of synthesis and application of metal complexes has significantly simplified this approach. Reaction conditions for metal complex formation-such as pH, solubility, stability, and the influence of other components or ions-determine the suitability of a reagent for a particular metal ion and facilitate method optimization.

The pioneering work of Robert Boyle, the discovery of 1-nitroso-2-naphthol as a precipitating reagent for cobalt ions by Ilinsky in 1884, the introduction of dimethylglyoxime as a specific reagent for Ni(II) ions by Chugaev in 1905, and the development of coordination theory by Alfred Werner in the 1890s were milestones that laid the scientific foundation for organic analytical reagents [6]. The contributions of these pioneering scientists established this field as one of the major applied sciences.

2. Properties of Cu(II) Ions and Their Impact on Environmental Objects

In recent years, the concept of heavy and toxic metal ions has gained considerable attention, as they rank second in terms of hazard after nuclear power plant waste and solid municipal waste. These metals are characterized by high toxicity, and many of them possess the ability to bioaccumulate in living organisms [8]. Cu^{2+}, Cd^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and Hg^{2+} are among the most significant ions in the study of environmental pollution, as they are widely distributed globally, exhibit toxic properties, and can accumulate in biological systems. It is well known that a number of metals, such as Fe, Co, Zn, Cu, Ca, and Mg, are essential elements for plants and the human body. Many biochemical processes occur in living organisms with their participation [9]. Numerous biologically active substances isolated from plants are not effectively activated without metal ions, and most proteins and enzymes exhibit activity only in combination with specific metal ions. Therefore, it is critically important to determine their concentrations in a timely manner in environmental objects, pharmaceutical preparations, soils, natural waters, and wastewater. Numerous analytical methods have been developed for the determination of heavy and toxic metal ions, including Cu^{2+}. However, in recent years, intensive research has been focused on the development of methods and tools for on-site environmental analysis.

Copper: is one of the most essential trace elements. Its physiological activity is

primarily associated with its participation in the active centers of redox enzymes. Insufficient copper content in soils negatively affects the synthesis of proteins, fats, and vitamins, and can lead to infertility in plants. Copper also plays a role in photosynthesis and influences nitrogen assimilation in plants. Copper is among the most widely used metals in the world. Due to its high heat, electrical conductivity, and flexibility, it is used in many industrial purposes [10]. At the same time, excessive copper concentrations exert toxic effects on both plant and animal organisms [11]. The copper content in natural freshwater ranges from 2.0 to 30.0 μg/l, while in seawater it ranges from 0.5 to 3.5 μg/l. Elevated copper concentrations are characteristic of acidic mine waters. The maximum permissible concentration (MPC) of Cu in water for domestic use is 0.1 mg/l, and in aquaculture water, it is 0.001 mg/l [12] [13].

3. Ligand Classes and Coordination Features Governing Analytical Performance of Cu(II) ions.

One of the most important factors determining the analytical efficiency of spectrophotometric methods for transition metal ions is the structural nature of the chromogenic ligand. Numerous organic analytical reagents reported in the literature can be grouped into several structurally related ligand classes that exhibit consistently strong analytical performance toward Cu(II).

Azo dyes represent one of the most widely used ligand classes due to the presence of –N = N– chromophoric groups conjugated with aromatic rings. These ligands typically contain nitrogen and oxygen donor atoms capable of forming stable chelate complexes with transition metal ions. The extended π-conjugation in azo systems enhances molar absorptivity and produces intense visible absorption bands.

Hydrazones and thiosemicarbazones are another important class of chromogenic reagents. These ligands possess multiple donor atoms (N, O, and S), enabling the formation of stable five- or six-membered chelate rings with metal ions. Their strong coordinating ability and high complex stability constants often lead to improved sensitivity and lower detection limits.

Schiff bases derived from aldehydes and primary amines also demonstrate high complexation ability toward transition metals. The presence of azomethine (–C = N–) groups and additional donor atoms facilitates the formation of stable coordination compounds with high molar absorptivity.

Triazole and heterocyclic derivatives have also attracted considerable attention due to their rigid structures and strong electron-donating nitrogen atoms. These compounds often produce highly selective complexes, particularly with Cu(II).

The high analytical performance of these ligand classes can be attributed to several structural factors:

1) the presence of multiple donor atoms (N, O, S),

2) formation of stable chelate rings,

3) extended π-conjugation that enhances absorbance intensity, and

4) favorable extraction behavior in organic solvents.

4. Sample Preparation Strategies for Different Matrices

The reliability of spectrophotometric determination of metal ions strongly depends on appropriate sample preparation procedures. Environmental and biological samples often contain complex matrices that may affect both selectivity and recovery.

Water samples. For natural and drinking waters, sample preparation typically involves filtration through membrane filters (0.45 μm) to remove suspended particles. In some cases, acidification with nitric acid is applied to stabilize metal ions and prevent adsorption onto container walls.

Soil and ore samples. Solid matrices such as soils and ores require acid digestion, usually using mixtures of nitric acid, hydrochloric acid, or aqua regia. Microwave-assisted digestion is increasingly preferred because it ensures complete dissolution of metals while minimizing contamination and analyte loss.

Food and biological samples. Food matrices often contain proteins, fats, and carbohydrates that may interfere with metal determination. These samples are commonly treated using wet digestion with nitric acid or nitric–peroxide mixtures prior to analysis.

Pharmaceutical samples. Pharmaceutical formulations generally require dissolution in appropriate solvents followed by dilution and pH adjustment before spectrophotometric measurement.

In many cases, preconcentration techniques such as liquid–liquid extraction, solid-phase extraction, or cloud point extraction are employed to improve detection limits. Control of the oxidation state of metal ions is also essential, particularly for mercury species.

5. Interfering Ions and Selectivity Enhancement

The presence of foreign ions may significantly influence the spectrophotometric determination of metal ions by forming competing complexes or altering extraction equilibria [14].

For Cu(II) determination, common interfering ions include Fe(III), Co(II), Ni(II), and Hg(II), which can form colored complexes with similar ligands.

To enhance selectivity, several masking strategies are commonly applied:

- EDTA to mask Fe(III) and other transition metals
- Cyanide ions to selectively complex certain metal ions
- Tartrate or citrate ions to stabilize competing metal ions in solution

The choice of masking agent depends on the coordination chemistry of both the analyte and interfering ions [14].

6. Spectrophotometric and Other Methods for the Determination of Copper(II) Ions in Environmental Objects

The present study [2] aimed to develop a new spectrophotometric method for the

determination of zinc(II) and copper(II) using a new chromogenic reagent, [4-amino-5-hydroxy-6-[(5-methyl-2-pyridyl)azo]-3-sulfo-1-naphthyl]sulfonyloxysodium (HR). A new organic HR reagent has been synthesized. The complexation of Zn(II) and Cu(II) with HR was studied spectrophotometrically at absorption maxima of 565 nm ($\Delta\lambda$ = 55 nm) and 595 nm ($\Delta\lambda$ = 90 nm) for Zn-HR and Cu-HR, respectively. The HR reagent interacts with Zn(II) and Cu(II) instantaneously at pH 6.5 and pH 4.0, respectively, and the absorbance of the solution is stable for 70 and 1440 minutes, respectively. Using isomolar series, Asmus straight line, equilibrium shift and spectrophotometric titration methods, the stoichiometries of the complexes were found to be 1:2 metal-to-ligand ratios for Zn and Cu. To determine the charge of the complex, the solution was passed through columns containing the cations KU-2 and KRS-10 and the anions AB-16-GS and AN-2FN. In this case, one proton is released from the reagent molecule, and a chelate cycle is formed mainly through the atoms of the oxygen-OH group, the nitrogen of the pyridine ring and the N=N group. The dilute Babko method was used to estimate the stability constant (Kstab) values, which were found to be on the order of 1.44×10^{21} ($\lg\beta = 21.16$) and 2.97×10^{17} ($\lg\beta = 17.47$) for the Zn and Cu complexes, respectively. The proposed spectro-photometric methodology established that the concentrations of zinc(II) and copper(II) could be estimated to be 1.0 - 18.0 and 0.50 - 6.50 ppm, respectively, corresponding to molar absorptivities of 4.2×10^4 and 2.0×10^4 l/mol·cm, respectively. Likewise, the formed complexes were stable at different pH values, allowing the simultaneous estimation of the two metals. The suggested spectrophotometric method of definition was applied in the analysis of model mixtures, industrial alloys based on aluminum and natural water, and the obtained results were metrologically evaluated (Sr = 0.043).

A spectrophotometric method for assessing microconcentrations of Cu^{2+} in water using 4-amino-3-mercapto-6-[2-(2-thienyl)vinyl]-1,2,4-triazine-5(4H)-one (HR) has been developed [15]. The reaction between Cu^{2+} and HR was carried out at a temperature of 25˚C ± 2˚C and a pH range of 4.0 - 6.0. This interaction yielded the complex $[CuR(NO_3)(H_2O)_2]\cdot H_2O$ with a molar ratio of 1:1, maintaining a fixed HR concentration of $2.8\cdot10^{-4}$mol/l for all measurements. The resultant complex exhibits a sharp and well-defined absorption peak at λ_{max} = 434 nm with a molar absorptivity (ε) of 1.90×10^4 l/mol·cm ($\mathrm{tg}\alpha = 0.18$) and a minimum detection limit of 0.003 mkg/cm^2. The absorbance of $[CuR(NO_3)(H_2O)_2]\cdot H_2O$ follows Beer's law in the concentration range of 0.7 - 25 μg/ml (A = 0.18·C - 0.009; R^2 = 0.992; n = 10) with a standard deviation of 0.011 μg/ml. It was found that the presence of Mn^{2+} and Al^{3+} ions interferes with the determination of Cu^{2+}. The validity of the proposed method was confirmed through the determination of Cu^{2+} in certified standard samples and actual samples of seawater and drinking water.

The study demonstrates the application of 4,5-bis-(4-methoxyphenyl)-2-(m-tolylhydrazinyl)-1H-imidazole (HR) for express spectroscopy of Cu^{2+} in a binary aqueous solution [16]. The resulting color of the complex is violet in the presence of the ion, exhibiting the highest absorbance (ESP) at a wavelength of λ_{max} = 573

nm (pH = 8). It was found that HR maintains stability for over 24 hours when the pH is optimized in accordance with Beer-Lambert Law within the concentration range of 0.1 - 6.0 μg/ml (y = 0.174x, R^2 = 0.9989). The influence of various factors was evaluated, including the concentration of the reagent (V_{HR} = 0.7 - 0.8 ml), reaction time (90 minutes), cations and anions, masking agents, ionic strength, and temperature (20˚C, α = 0.1377, $K_{met} = 2.650 \times 10^{10}$, S_r < 0.4%). The complex was investigated across different molar ratios of Cu^{2+}-HR (1:2), specifically at concentrations of $C_{Cu}^{2+} = 3.988 \times 10^{-5}$ M and $C_{HR} = 1.994 \times 10^{-5}$ - 13.958×10^{-5} M. The molar absorptivity (ε), detection limit, and quantification limit were calculated as 1.11×10^4 l/mol·cm, 0.0114 μg/ml, and 0.0376 μg/ml.

A spectrophotometric method for the determination of Cu^{2+} ions has been developed using a 0.1% solution of 2-hydroxy-1-naphthaldehyde-phenylhydrazone (HR) [17]. HR (λ_{HR} = 410 nm) forms a colored complex that is quantitatively extracted into n-butanol at pH 9.2 (λ_{CuR} = 360 nm, $\Delta\lambda$ = 50 nm). The method adheres to Beer's Law within the concentration range of 1.0 to 10.0 μg/L, with a molar absorptivity (ε) and limit of detection of 0.97×10^4 l/mol·cm and 0.26 μg/cm^2. The composition of the complex was determined using the slope method and molar ratio method, yielding a stoichiometry of Cu^{2+}:HR = 1:2 after a reaction time of 72 hours. The method has been successfully applied to both synthetic and commercial samples.

A spectrophotometric method has been developed [18] for the determination of Cu^{2+} using 2-acetylpyridine-4-phenyl-3-thiosemicarbazone (HR) as the analytical reagent. In the pH range of 3.0 - 5.5, HR forms a reddish-brown complex with Cu^{2+}. This Cu^{2+}-HR complex exhibits maximum absorption at 440 nm, with a molar extinction coefficient (ε) of 2.16×10^4 l/mol·cm and a limit of detection of 2.94×10^{-3} μg/cm^2. The method adheres to the Beer-Lambert law within the concentration range of 0.2 - 5.0 mg/l. The regression coefficient (b) is 0.338, with an R^2 value of 0.96. The method's limit of detection is 0.0065 μg/ml. Cations typically associated with Cu^{2+}, such as Ca^{2+}, Mg^{2+}, Pb^{2+}, Mn^{2+}, and Bi^{3+}, do not interfere up to concentrations of 5000 μg/ml. However, interference was observed from Al^{3+}, Cr^{3+}, Ag^{+}, and Sb^{2+} at concentrations up to 2500 μg/ml, and from Mo^{6+} and W^{6+} up to 2000 μg/ml. Anions such as F^-, Br^-, I^-, Cl^-, NO_3^-, SO_4^{2-}, $S_2O_3^{2-}$, CH_3COO^-, $C_6H_5O_5^{3-}$, and $C_4H_4O_6^{2-}$ do not interfere at concentrations up to 5000 μg/ml. The developed method has been successfully applied to the analysis of leafy vegetables and pharmaceutical products.

A spectrophotometric method has been developed for the determination of Cu^{2+} using 2-(5-bromo-2-oxoindolin-3-ylidene)hydrazinecarbothioamide (HR) [19]. HR quantitatively extracts Cu^{2+} (99.92%) into n-amyl alcohol from an aqueous solution within a pH range of 4.0 to 6.0, in the presence of 3.0 mL of phosphate buffer (pH = 5.0), at a maximum wavelength λ_{max} = 510 nm. Beer's Law was observed in the concentration range of 1.0 to 8.0 μg/ml, with a limit of detection and molar absorptivity (ε) of 25.0 ng/cm^2 and 2538 l/mol·cm respectively. The composition of the complex was determined to be 1:2 using the method of continuous

variations. The following ions do not interfere with the spectrophotometric determination of 50 μg/ml Cu^{2+}: 10 mg of Li^{+}, Ca^{2+}, Mg^{2+}, Al^{3+}, Ba^{2+}, Sr^{2+}, Pb^{2+}, Sn^{2+}, Be^{2+}, W^{6+}, Mo^{6+}, V^{6+}; 5 mg of Zn^{2+}, Hg^{2+}, Ag^{+}, As^{3+}, Bi^{3+}, Sb^{3+}; 2 mg of Mn^{2+}, Cd^{2+}; 1 mg of Cr^{3+}, Ce^{4+}, Th^{4+}, Zr^{4+}; 0.5 mg of Fe^{2+}, Fe^{3+}, Ni^{2+}; 0.1 mg of Co^{2+}, Pt^{4+}, Ru^{3+}, Ir^{4+}, Os^{4+}, Pd^{2+}; and 20 mg of Cl^{-}, Br^{-}, F^{-}, SO_4^{2-}, $S_2O_8^{2-}$, NO_3^{-}, PO_4^{3-}, CH_3COO^{-}, $C_2O_4^{2-}$, $C_6H_5O_7^{3-}$, and $C_4H_4O_6^{2-}$.

A spectrophotometric method has been developed for the determination of Cu^{2+} using 4-(4'-nitrobenzylideneamino)-3-methyl-5-mercapto-1,2,4-triazole (HR) [20]. HR forms a stable orange-red complex with Cu^{2+} at room temperature and can be quantitatively extracted with chloroform at pH 6.2 (λ = 470 nm). Beer's Law was observed within the concentration range of 4.75 to 16.13 μg, and the optimal concentration range determined from the Ringbom plot was 5.0 to 17.5 μg. The molar absorptivity (ε) and Sandell's sensitivity (S) were found to be 2.825×10^3 l/(mol·cm) and 0.0224 μg/cm^2, respectively. The use of masking agents enhances the selectivity of the method. The composition of the extracted species was determined using Job's method, molar ratio method, and confirmed through logarithmic analysis (Cu^{2+}:HR = 1:2). The proposed method has been successfully applied for the determination of Cu^{2+} in synthetic mixtures, pharmaceutical samples, and alloys.

The compound 1-(2-methoxyphenylamino)-3-methoxypropan-2-ol (HR) is proposed as a colorimetric reagent for the spectrophotometric determination of Cu^{2+} ions [21]. HR forms a blue complex with Cu^{2+} within the pH range of 5.4 to 6.8. Beer's law is observed for concentration ranges up to 16 μg/ml. The yellowish Cu^{2+}-HR complex exhibits a maximum absorbance at 605 nm (with a path length of 0.5 cm), with a molar absorptivity ε of 43200 l/mol·cm and a limit of detection of 1.48 ng/cm^2. The stoichiometry of the Cu^{2+}:HR complex is determined to be 1:2. The influence of various cations and anions on the determination of Cu^{2+} has been investigated: interference is caused by cations such as alkali metals (AM) and alkaline earth metals (AEM), as well as anions including Cl^{-}, $C_6H_5O_7^{3-}$, and $C_4H_4O_6^{2-}$, along with compounds such as thiourea ($CS(NH_2)_2$), F^{-}, J^{-}, CN^{-}, Co^{2+}, Ni^{2+}, Fe^{2+}/Fe^{3+}, V^{4+}/V^{5+}, W^{6+}, Mo^{6+}, Ti^{4+}, and Mn^{2+}. The interfering effect of Fe^{3+} can be mitigated using $H_2C_2O_4$, Ti^{4+}-FeF_3, or NaF, while interference from Hg^{2+}, SO_3^{2-}, Nb^{5+}, and Ta^{5+} can be reduced with $H_2C_2O_2$ as well. Additionally, Mo^{6+} and W^{6+} interference can be prevented using NaF and $H_2C_2O_4$. Utilizing a 1% solution of ascorbic acid ($C_6H_8O_6$) does not interfere with the detection of Mn^{7+}, V^{4+}, Nb^{5+}, Cr^{6+}, Mo^{6+}, and Fe^{3+}. Furthermore, using a 0.01M solution of $H_2C_2O_4$ does not interfere with the detection of V^{4+}, Nb^{5+}, Ta^{5+}, Cr^{3+}, Mo^{6+}, W^{6+}, and Fe^{3+}. This method can be applied for the determination of trace amounts of Cu^{2+} in pharmaceutical, food, and botanical samples.

The Cu^{2+} ion forms a light green complex with thiosemicarbazone-2-hydroxy-3-methoxybenzaldehyde (HR) in an acidic buffer at pH 4.5 - 5.0. This complex exhibits an electronic absorption spectrum (EAS) maximum at 395 nm and remains stable for more than 48 hours. Beer's law is observed within the concentra-

tion range of 0.254 - 2.542 μg/ml, with the linear relationship described by the equation A390 = 0.6092C + 0.0006. The molar extinction coefficient (ε) and limit of detection are calculated to be 6000 l/mol·cm and 0.011 μg/cm^2, respectively, indicating a Cu^{2+} to HR molar ratio of 1:1. The stoichiometry of the complex was determined using the Job's method, resulting in a β value of 12.306×10^5. The selectivity of the method for various ions was investigated, and it has been successfully applied to the determination of Cu^{2+} in water and real samples [22].

The spectrophotometric method developed [20] utilizes 4-(4'-nitrobenzylideneamino)-3-methyl-5-mercapto-1,2,4-triazole (HR) as a reagent for the rapid formation of a stable orange-red complex with Cu2+ ions at room temperature and a pH of 6.2 (λ = 470 nm). The Beer-Lambert law was observed to be applicable within the concentration range of 4.75 to 16.13 μg, while the optimal concentration range, as determined by the Ringbom graphical method, was found to be between 5.0 and 17.5 μg. The molar absorptivity (ε) and limit of detection were calculated to be 2.825×10^3 l/mol·cm and 0.0224 μg/cm^2, respectively. Operational variables such as pH (6.2), the stoichiometry of the complex (Cu^{2+}:HR = 1:2), the concentration of the HR reagent, solvent nature, shaking time, and the presence of interfering ions were thoroughly investigated. The use of masking agents was shown to significantly enhance the selectivity of the method. The proposed method has been successfully applied for the determination of Cu^{2+} ions in synthetic mixtures, pharmaceutical samples, and alloys.

In the work [23], a sensitive spectrophotometric method for determining Cu^{2+} in analytical samples was developed using the chromogenic reagent 1-((4-(1-(2-hydroxyphenyl)imino)ethyl)-phenyl)-diazenyl-naphthalene-2-ol (HR), with a melting point of 178˚C - 180˚C. The resulting complex exhibited a brown color (melting point: 196˚C - 198˚C) with an absorption maximum at λ_{max} = 500 nm at a pH of 9.0 (λ_{HR} = 326 nm, $\Delta\lambda$ = 174 nm). Beer's law is obeyed in the concentration range of 1.7 - 5.4 μg/ml (y = 0.0043 + 0.2519x, R^2 = 0.9994). The calculated molar absorptivity (ε), limit of detection, limit of quantification, and relative standard deviation (RSD) values were 0.5038×10^4 l/mol·cm, 0.0039 μg/cm^2, 0.2217 μg/ml, and 0.7385 μg/ml, respectively ($K = 1.145 \times 10^{-10}$, $K_{stb} = 8.728 \times 10^9$, lgK = 9.956). The composition of the complex was studied using various analytical methods, revealing a Cu:HR stoichiometry of 1:2. The presence of interfering ions such as Co^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Pd^{2+}, and Fe^{3+} affected selectivity; therefore, suitable masking agents were employed. This method was applied successfully for the determination of Cu^{2+} ions in copper alloys.

In the study [24], a spectrophotometric method for the determination of Cu^{2+} using N,N'-bis(salicylidene)-2,3-diaminopyridine (HR) was developed. The absorbance was measured at a maximum wavelength (λ_{max}) of 414 nm. The optimal conditions (pH = 4.8; concentration of HR, [HR] = 5×10^{-5} M; volume of HR, V_{HR} = 1.0 ml; molar ratio of Cu^{2+} to HR = 1:1) were established, adhering to Beer's Law in the concentration range of 6.35 - 318 μg/l, with the relationship given by A = 0.002 + 0.010 [Cu^{2+}] (μg/l). The molar extinction coefficient (ε), limit of detection,

and limit of quantification were determined to be 1.46×10^5 l/mol·cm, 6.38 μg/l, and 21.27 μg/l, respectively. The standard deviation (Sr, n = 5) was calculated to be 0.62% for the standard solution containing 63.5 μg/l of Cu^{2+}. The determination of 63.5 μg/l Cu^{2+} was found to be unaffected by the presence of background ions such as Na^+, K^+, NH_4^+, Ca^{2+}, ClO_4^-, SO_4^{2-}, CO_3^{2-}, NO_3^-, in addition to a 10,000-fold excess of Cd^{2+}, Ba^{2+}, F^-, Br^-, and a 5,000-fold excess of Pb^{2+}, Mn^{2+}, as well as a 2000-fold excess of Zn^{2+} and Mg^{2+}, and a 1,000-fold excess of Cr^{3+}, Co^{2+}, and Ni^{2+}. The developed method was applied to the determination of Cu^{2+} in wastewater samples.

Spectrophotometric methods [25] have been developed for the determination of Cu^+ and Ni^{2+} ions in sugarcane alcohol utilizing chromogenic reagents (HR) including neocuproine, cuproine, and bathocuproine. Various operational parameters were optimized, such as the HR concentration (0.020%, 0.024%, and 0.15%), the concentration of the reducing agent, pH levels (2.0 - 7.0; 3.2 - 8.0; and 7.3 - 9.5), the composition of the buffer (acetate, acetate/phosphate), the order of reagent addition, the maximum absorption wavelength (λ = 454 nm; 476 nm; and 476 nm), the detection range (12.44 ± 0.70, 12.05 ± 0.57, and 11.42 ± 0.18 μg/ml), and the stability of the complexes (24 h, 12 h, and 6 h, respectively). The established working range was from 1.0 to 10.0 μg/ml with a correlation coefficient (R^2) greater than 0.999 for all three optimized methods (standard deviations ranging from 0.01% to 0.17%, n = 10). The method utilizing cuproine exhibited the highest molar absorptivity, followed by bathocuproine and neocuproine. These methods were applied to the determination of Cu^{2+} in sugarcane alcohol, and the results were compared with those obtained through a reference method of flame atomic absorption spectroscopy (FAAS).

The complex formation of Cu^{2+} with 1-phenyl-2-(2-hydroxy-4-nitrophenylhydrazone)-butadiene-1,3 was investigated [26] using a spectrophotometric method in the presence of cetylpyridinium chloride (Cl) at pH 2, cetylpyridinium bromide (Br) at pH 3, and cetyltrimethylammonium bromide (A) at pH 3. The stoichiometry of the complexes was determined, revealing a molar ratio of 1:2:2, with absorption wavelengths recorded at 467, 484, and 476 nm, respectively. The molar absorptivity (ε) values were calculated as 15,000, 21,500, and 17,500 $L \cdot mol^{-1} \cdot cm^{-1}$. The linear range for the detection was found to be between 0.13 - 5.12, 0.13 - 2.56, and 0.13 - 3.07 μg/ml. The stability constants of the complexes were determined as follows: $\lg\beta$ (CuR) = 4.90 ± 0.04; $\lg\beta$ (CuR-Cl) = 10.36 ± 0.03; $\lg\beta$ (CuR-Br) = 11.26 ± 0.05; $\lg\beta$ (CuR-A) = 10.52 ± 0.04. The influence of foreign ions on complex formation was studied, revealing that ions such as Ni^{2+}, Co^{2+}, Fe^{3+}, Ga^{3+}, In^{3+}, Bi^{3+}, Sn^{4+}, Ti^{4+}, Mo^{4+}, W^{6+}, as well as oxalate ($C_2O_4^{2-}$), fluoride (F^-), thiourea ($CS(NH_2)_2$), citric acid ($C_6H_8O_7$), tartaric acid ($C_4H_6O_6$), EDTA, and disodium hydrogen phosphate dodecahydrate ($Na_2HPO_4 \cdot 12H_2O$) at a concentration of 1:500 significantly interfere with the complexation process. This method was successfully applied for the photometric determination of Cu^{2+} concentrations in bananas ($(3.65 \pm 0.03) \times 10^{-4}$), mushrooms ($(2.15 \pm 0.02) \times 10^{-3}$), and peas ($(2.63 \pm 0.06) \times 10^{-3}$).

A method for the determination of Cu^{2+} and Ni^{2+} ions was developed [27] using 1-(2-pyridylazo)-2-naphthol at a pH of 6.0 through UV-visible spectrophotometry. The method demonstrated a linear response within the concentration range of 0.1 to 100.0 μg/l, with the equation Y = 0.003x + 0.03916 and an R^2 value of 0.9976. The limits of detection were established at 0.031 μg/l for Ni^{2+} (λ = 460 nm) and 0.033 μg/l for Cu^{2+} (λ = 580 nm). This methodology was then applied to analyze Ni^{2+} and Cu^{2+} concentrations in marine brown algae. The metal content in the algae from Chabahar Bay was determined to range from 12.80 to 39.46 μg/l.

A spectrophotometric method has been proposed for the determination of Cu^{2+} ions through the formation of a red-brown chelate at a pH of 3.5 using 2,3,4,6-tetrahydroxy-3-sulfoazobenzene. The molar absorption coefficient (ε) of the complex, with a Cu^{2+}:HR [28] ratio of 1:2, is 4.03×10^4 l/mol·cm at a wavelength of 485 nm, and the calculated conditional stability constant (lgK) is 7.98. The developed method adheres to Beer's law within the concentration range of 0.032 to 1.905 μg/ml. The presence of alkali metal ions, alkaline earth metal ions, rare earth elements, G (presumably referring to a specific element not explicitly defined), phosphate ions (PO_4^{3-}), ascorbic acid ($C_6H_8O_6$), and cations does not interfere with the determination of Cu^{2+} ions. The proposed method is rapid and can be readily applied to certified alloys and pharmaceutical preparations.

In the study [29], two new azo dyes were presented: 1-[(5-benzyl-1,3-thiazol-2-yl)-diazenyl]-naphthol-2 (L^1) and 1-[5-(4-sulfonamido-benzyl-4-methyl-1,3-thiazol-2-yl)-diazenyl]-naphthol-2 (L^2). These compounds were evaluated as potential reagents for the spectrophotometric determination of Cu^{2+} ions in samples of tap and river water through the formation of a chelate complex at a wavelength of λ = 592 nm, under conditions of pH = 5.0 and a path length (ℓ) of 2.0 cm. The main characteristics of the reagents, such as molar extinction coefficients (ε_{490} = 1.53×10^4 and ε_{505} = 3.53×10^3 l/·см) and protonation constants (for L^1, pKa_1 = 0.41 and pKa_2 = 9.59; for L^2, pKa_1 = 2.43 and pKa_2 = 8.44), were assessed spectrophotometrically. A spectrophotometric method was developed for the determination of Cu^{2+} in the presence of Triton X-100. The linear range of the measurements was found to be 0.063 - 1.270 mg/l for the CuL^1 complex, represented by the equation A = −0.0128 + 0.9232C, and for the CuL_2 complex, represented by A = −0.0055 + 0.4410C, with a limit of detection of 0.044 mg/l. In the operational range, the determination of Cu^{2+} ions at concentrations of 0.318 mg/l was shown to be affected by oxalate ions ($C_2O_4^{2-}$) and phenolate ions ($C_6H_5O_7^{3-}$) at a 1:1 ratio, while ions such as NH_4^+, Na^+, K^+, Mg^{2+}, Al^{3+}, Ca^{2+}, Mn^{2+}, Cr^{3+}, Cr^{6+}, Zn^{2+}, Cd^{2+}, Ba^{2+}, Pb^{2+}, Cl^-, Br^-, I^-, SO_4^{2-}, NO_3^-, HPO_4^{2-}, ClO_4^-, and HCO_3^- did not interfere (at a 1:100 ratio). Additionally, ions such as Fe^{3+}, Co^{2+}, Ni^{2+}, Ag^+, F^-, and $C_4H_4O_6^{2-}$ showed interference at a 1:10 ratio, while Fe^{2+} and Hg^{2+} also interfered at a 1:10 ratio.

A novel environmentally friendly method for determining Cu^{2+} ions using Atomic Absorption Spectrometry (AAS) has been proposed. Various factors were studied and optimized, including the wavelength (λ = 324.8 nm), the pH of the

sample solution (pH = 2.0), the concentration of the reagent (2.0×10^{-5} M, volume = 120 ml), and the extraction time (0 - 15 minutes). The calibration curve was linear over the range of 3.0 to 120 μg/ml, with the relationship described by the equation $\Delta A = 2.9003C + 1.8 \times 10^{-2}$. The determination of 50.0 μg/l of Cu^{2+} ions at a wavelength of 324.8 nm was not significantly affected by varying concentrations of foreign ions, including NO_3^-, BrO_3^-, ClO_4^-, $S_2O_8^{2-}$, Cl^-, Cr^{3+}, Cr^{6+}, Mn^{2+}, Li^+, Co^{2+}, K^+, Al^{3+}, Pd^{2+}, Ni^{2+}, Ag^+ (1:5000), as well as PO_4^{3-}, IO_4^-, F^-, SO_3^{2-}, $S_2O_3^{2-}$, SCN^-, CN^-, $HCOO^-$, CO_3^{2-}, $C_2O_4^{2-}$, Ba^{2+}, Zn^{2+}, Fe^{2+}, Fe^{3+} (1:1000), ClO_3^-, NO_2^-, Cd^{2+}(1:500), Hg^{2+} (1:100), Sn^{2+}, and Pb^{2+} (1:10). It was noted that Hg^{2+}, Sn^{2+}, and Pb^{2+} ions reacted with phosphate ions, resulting in precipitation. The relative standard deviation (RSD) for six replicate measurements of Cu^{2+} ions at concentrations of 5.0, 20.0, and 50.0 μg/l were found to be 4.1%, 1.5%, and 1.8%, respectively. The proposed method also demonstrated successful application for the extraction and determination of Cu^{2+} ions in various water and food samples [30].

A chelating organic analytical reagent (OAR) [31], was synthesized, specifically 2-(2-bromophenyl)-imino)-methyl)-4-(5,6-dimethylpyridin-2-yl)-diazenyl) phenol (R), which was utilized for the determination of Cu^{2+} ions. During the optimization process, enrichment factors of 105 were achieved. The Goodness of Fit (GoF) was linear within a concentration range of 10 - 100 μg/l, with a limit of detection of 2.79 μg/l and a standard deviation for seven "Repeated Measurements" at 20 μg/l Cu^{2+} of 1.75%. This method was applied to several samples of honey, demonstrating its effectiveness in trace metal analysis.

Based on acetylacetone, a new organic analytical reagent, bis-[3-(fluorophenylazo-pentadiene-2,4)] -ethylenediamine, has been synthesized [32]. Its crystalline structure has been examined, characterized by the following parameters: a = 18.9757 (10) Å, b = 10.7254 (6) Å, c = 22.2875 (12) Å, Z = 8; space group P2/n. Spectrophotometric methods were employed to investigate the complex formation between the synthesized compound and Cu^{2+} ions at a concentration of KFK-2, with a path length of ℓ = 1.0 cm. The principal optical characteristics of the Cu^{2+} complexes with the third component during the complexation process were identified as follows: for the complexes Cu-R, Cu-R-F, Cu-R-D, and Cu-R-E, the maximum absorbance wavelengths (λ_{max}) = 442, 444, 447, and 452 nm, respectively. The stoichiometry of the complexes was determined to be 1:1 for Cu-R and 1:1:1 for the others; the optimal pH values were assessed as 3, 2, 2, and 2; and the molar absorptivity ($\varepsilon_{max} \cdot 10^4$) values were calculated at 0.42, 0.48, 0.47, and 0.51 l/mol·cm, respectively. Under the Beer-Lambert law, the detection limits were established, yielding values of 1.8 - 25.6 μg/25 ml, 2.0 - 25.6 μg/25 ml, 8 - 25.6 μg/25 ml, and 2.0 - 24 μg/25 ml.It was demonstrated that interference from alkali metals (including alkaline earth metals), as well as transition metals such as Fe^{3+}, Co^{2+}, Cr^{3+}, Cd^{2+}, Th^{4+}, Zn^{2+}, Pb^{2+}, Bi^{3+}, Be^{2+}, Al^{3+}, U^{6+}, and Mn^{2+}, as well as halides, thiocyanate (SCN^-), sulfate (SO_4^{2-}), and both sulfosalicylic and ascorbic acids, does not hinder the detection of Cu^{2+}. The proposed method has been recommended for the de-

termination of trace amounts of Cu^{2+} in copper-containing samples, with a standard deviation (Sr) of 0.04, n = 5, and a confidence level of P = 0.95. In cases where larger quantities of Fe^{3+} (over 30 mg) are present, Cu^{2+} detection is achieved by masking it with 5 ml of 5% NH_4F solution.

In the works referenced [33], N-acetyl-N'-(propylsulfonyl)hydrazine (L^1) and N-acetyl-N'-(butylsulfonyl)hydrazine (L^2) were synthesized, along with their complexes with Cu^{2+}. The results of the elemental analysis for L^1 indicated the following theoretical values for the molecular formula $C_5H_{12}N_2O_3S$: C - 33.32%; H - 6.71%; N - 15.54%; O - 26.63%; S - 17.79%. The experimental values obtained were: C - 32.87%; H - 6.48%; N - 14.98%; O - 25.93%; S - 17.20%. The yield was 70% with a decomposition temperature of 114-116°C. For L^2, the theoretical composition for the molecular formula $C_6H_{14}N_2O_3S$ was determined as follows: C - 37.09%; H - 7.26%; N - 14.42%; O - 24.71%; S - 16.51%. The experimental analysis revealed: C - 35.87%; H - 7.18%; N - 13.98%; O - 23.53%; S - 16.00%. The yield for L^2 was also 70%, with a decomposition temperature ranging from 45˚C to 48˚C. Additionally, the complex of Cu^{2+} with L^2 presented the following theoretical composition based on the formula $C_{16}H_{34}N_4O_{10}S_2Cu$: C - 33.71%; H - 6.01%; N - 9.83%; O - 28.06%; S - 11.25%. The experimental results were: C - 32.87%; H - 5.70%; N - 8.98%; O - 25.66%; S - 11.20%. The yield for this complex was 70%, with a decomposition temperature of 230˚C. The research results indicate the formation of a complex with a stoichiometry of Cu^{2+}:$L^{1,2}$ = 1:2, with a general formula of [$CuL^{1,2}_2$ $(CH_3COO)_2$].

In the study [34], the mechanisms for the formation of Cu^{2+} and Ni^{2+} complexes with ethylenediamine (HR) were examined at pH values of 6.0 - 7.0 and 8.0 - 9.0. Experimental conditions and the molar ratios of metal to ligand (M:HR) were determined using spectrophotometric analytical methods, yielding ratios of 1:2 and 1:3 (KFK-3). Data analysis revealed stability constants ($\lg\beta$) of the complexes, with $\lg\beta$ (Cu^{2+}) ranging from 8.02 to 16.05 at pH values of 4.1 to 5.23, and $\lg\beta$ (Ni^{2+}) ranging from 14.29 to 18.40 at pH values of 4.5 to 7.5. These findings facilitated the identification of the most stable Cu^{2+} and Ni^{2+} complexes with HR in solution.

A methodology for the determination of Cu^{2+} ions has been developed, based on the interaction of Cu^{2+} with the reagent 2,4-dinitrophenol-(6-azo-2)-1-naphthol-3,8-disulfonic acid (HR, C_{HR} = 5.0 μg/ml) [35] and the measurement of the corresponding spectral signal using a portable combined LED mini-photometer. The conditions for the sorption of the Cu^{2+} complex with HR were studied, achieving these conditions in a 0.1 M hydrochloric acid (HCl) solution with a C^{2+}_{Cu} = 0.1 μg/ml and C_{HR} = 0.4 μg/ml. The effect of the acidity of the medium (pH = 1), the time of maintaining the complex in solution (up to 40 minutes), and the initial volume of the solution passed through the membrane (1×10^5) on the recorded signal was investigated. The analytical performance characteristics were determined, revealing a maximum signal at λ_{min} = 560 nm and a minimum signal at λ_{max} = 574 nm. Using model solutions of Cu^{2+}, a calibration graph was constructed (y = 0.0089 + 0.301x, with R^2 = 0.97). The developed methodology was validated

for the determination of Cu^{2+} in white wine, S_r = 8% It was found that in the wine brand "Vagrus" (Russia), the concentration of Cu^{2+} using the standard addition method amounted to 0.0016 μg/ml.

A spectrophotometric method for the determination of Cu^{2+} using indigo as a reagent has been developed, as referenced in [36]. Optimal conditions ($\Delta\lambda$ = 160 nm, ε = 41666, $K_{met} = 1.1 \times 10^{12}$) for the assay have been established, taking into account the nature and composition of buffer solutions (universal buffer), reaction time (up to 240 minutes), temperature, and the interfering effects of foreign ions. The following ions do not interfere with the determination at specified ratios: Na^+, K^+, and NH_4^+ (1:1000), Ba^{2+}, and Br^- (1:500), Si^{4+}, Zn^{2+}, Cl^-, $S_2O_3^{2-}$, SCN^-, $C_6H_5O_7^{3-}$ (1:100), Cd^{2+}, Al^{3+} (1:10). In contrast, Fe^{3+} (1:2), Pb^{2+}, Tl^{4+} (1:1), and Mn^{2+} (1:10) are shown to interfere with the measurement under the given ratios. The accuracy of the method was verified using the "added-found" approach, yielding a standard deviation of Sr = 0.014, with a recovery range from 0.5 to 75.0 μg in a 25 ml sample. The proposed spectrophotometric method for Cu^{2+} determination has been successfully applied to the analysis of natural and technological waters, demonstrating a standard deviation of $S_r = 9.0 \times 10^{-2}$.

The results of a study on the spectrophotometric determination of Cu^{2+} cations in copper plating electrolytes are presented [37]. The investigation was conducted in the presence of ammonia and EDTA, utilizing a wavelength range of 500-1000 nm and a path length of 1.0 cm. It was found that in a model solution containing Cu^{2+} and NH_4^+ ions in a 1:5 ratio, Cu^{2+} exists in the form of tetraammine complex. The lowest concentration of Cu^{2+} that can be reliably detected by the spectrophotometric method is 0.1 μg/l. In the model solution containing EDTA, the composition of the Cu^{2+} ion complex is pH-dependent, pH (1.08 - 12.86) Additionally, the lowest concentration of Cu^{2+} in alkaline etching solutions with EDTA is determined to be 0.02 g/l, ($lgK_{met.}$ = 18.8).

In the study [38], the potential for determining Cu^{2+} ions after adsorption onto polyacrylonitrile fibers supplemented with the cation exchanger KU-2, which is immobilized with 1-(2-pyridylazo)-2-naphtol (HR), was investigated. The dependence of the absorbance of the Cu^{2+} complex on HR concerning the adsorption conditions was analyzed. Optimal conditions were established for the determination of Cu^{2+} concentrations ranging from 0.05 to 0.40 μg/ml, utilizing the measurement of the spectral density coefficient (SDO) at 640 nm or visual assessment via a color scale following the adsorption of Cu^{2+} from a 20 ml solution of 0.01 M HCl. The presence of equal amounts of Co, Zn, Pb, as well as double the quantities of Ag^+, Fe^{3+}, Cd^{2+}, Mn^{2+}, Bi^{3+}, and Cr^{3+} did not interfere with the determination of 0.1 μg/ml Cu^{2+}. A method was developed for the quantification of Cu^{2+} in urine samples with a detection limit of 0.03 μg/ml, while the strontium level remained below 0.25. The analysis duration for five to six samples was completed in 30 - 35 minutes.

The results of a study on the photometric determination of Cu^{2+} using 4-(2-pyridylazo)-resorcinol during the formation of thiocyanate complexes [39] are

presented. The thermodynamic feasibility of the dissolution process of Cu^{2+} in the presence of the oxidizing agent-air oxygen-was investigated, particularly in solutions containing KSCN. The dependencies of light absorption at a wavelength of λ = 540 nm with a path length of ℓ = 2.0 cm, and the specific dissolution rate of Cu^{2+} (W = 3.85×10^{-10} mol/cm^2 s) on thiocyanate concentration (C = 0.5 mol/l), pH of the medium, temperature (T, K), disk rotation frequency (ω, s^{-1}), and the limit of detection between 0.1 - 0.5 μg/ml, were studied. The dissolution mechanism of copper(II) and the interaction regime were established, along with the optimal method for the determination of Cu^{2+} from solutions.

The article [40] presents the findings of a study on the feasibility of determining the ions Cd^{2+}, Pb^{2+}, and Cu^{2+} using potentiometric methods. For this purpose, calibration graphs (C_{Cu}^{2+} = 0.006 - 0.06 mg/l, C_{Cd}^{2+} = 0.0112 - 0.112 mg/l, and C_{Pd}^{2+} = 0.021 - 0.21 mg/l) were constructed utilizing an acetate buffer at a pH of 6.0.

A spectrophotometric method has been developed [41] for the determination of Cu^{2+} ions using N-(o-methoxybenzaldehyde)-2-aminophenol (referred to as HR). This method quantitatively extracts Cu^{2+} ions (99.78%) into chloroform from an aqueous solution at a pH range of 5.7 to 6.8. The resulting complex exhibits a strong absorption peak at a wavelength of λ_{max} = 440 nm. Beer's law is applicable within the concentration range of 0.1 to 4.0 μg/ml, with a limit of detection and molar absorptivity (ε) of 0.00246 μg/cm^2 and 25,739 l/mol·cm, respectively. The stoichiometry of the complex formed between Cu and HR is found to be 1:2. The method allows for the determination of 20 μg of Cu^{2+} in the presence of various interfering ions: 10 mg each of Li^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Sn^{2+}, Bi^{3+}, Mo^{6+}, W^{6+}, Ce^{4+}, Th^{4+}, and Zr^{4+} do not interfere. However, ions such as 1 mg of Pd^{2+}, Pt^{4+}, and Hg^{2+}, as well as 0.1 mg of Co^{3+}, do interfere, along with 20 mg each of Cl^-, F^-, Br^-, SO_4^{2-}, NO_3^-, SCN^-, PO_4^{3-}, CH_3COO^-, $C_4H_4O_6^{2-}$, and $CS(NH_2)_2$. The proposed method has been successfully applied for the determination of Cu^{2+} in alloys and pharmaceutical samples.

In the study [42], the experimental feasibility of using sugar beet pectin (SBP) for the binding of Cu^{2+} ions was substantiated through the determination of the composition and stability of the soluble interaction products (CuSBP) using spectrophotometry and potentiometry. The composition and stability of the Cu^{2+}:SBP complex were investigated using various methods, including molar ratios, restricted logarithmic Bent-French analysis, least squares fitting, and equilibrium shifting, revealing a molar ratio of Cu^{2+}:SBP of 1:2 and logarithmic stability constants (lgβ) ranging from 6.97 to 7.69.

A methodology [43] has been developed for the kinetic determination of Cu^{2+} based on its catalytic effect on the reduction reaction of Fe^{3+} by thiosulfate ions, followed by photometric detection of the decomposition of $Fe(SCN)_3$, as referenced in. Optimal reaction conditions have been established, including a pH range of 2.5 to 3.0, with a Beer's law concentration range from 0.06 to 3.50 mg/l, a relative standard deviation (RSD) of 4%, a limit of detection of 0.06 μg/ml, an accuracy of 0.074 μg/ml, and a repeatability of 0.195 μg/ml. Interfering ions including

Ca^{2+}, Mn^{2+}, Pb^{2+}, Zn^{2+}, Mg^{2+}, Al^{3+}, Ni^{2+}, Co^{2+}, Cr^{3+}, and Cr^{6+} were found to diminish the accuracy of the Cu^{2+} determination. This methodology was successfully applied to water samples from the Argazinskoye Reservoir (Chelyabinsk region; n = 6; p = 0.95).

In the study [44], a spectrophotometric method was developed. The formation of a complex between the disodium salt of 4-hydroxy-3-(4-sulfonato-1-naphthylazo)-1-naphthalenesulfonate and Cu^{2+} ions in aqueous solutions was investigated. The method's sensitivity for determining Cu^{2+} under optimal analytical conditions was found to be as follows: (pH = 5.95; ε_{CuR} = 48077 l/mol·см; $K_{met.}$ = 1.28×10^{-5}; $\Delta\lambda_{CuR}$ = 75 nm, C^{2+}_{Cu} = 5.0 - 50.0 μg/25ml). The proposed method was applied in the analysis of model mixtures, and the obtained results were evaluated metrologically, Sr = 0.0087.

The study [45] presents the results of research on the complexation processes of N-benzoyl-N'-(phenylsulfonyl)hydrazine (HR) with Cu^{2+} ions using spectrophotometric methods in an ammoniacal medium (pH = 11.50). Key parameters were established, including the maximum absorption wavelength (λ_{HR} = 218 nm, λ_{CuRn} = 300 nm), the development time for the color of the complex (τ = 30 minutes), the pH range (11.4 - 11.8), the volume of HR used (V_{HR} = 9.5 ml), the molar extinction coefficient (ε = 2759 l/mol·cm), and the molar ratios of $[Cu^{2+}]$:[HR] at 2:1 and 1:1. Additionally, a calibration curve was constructed within the concentration range of 0.32 - 1.90 mg/25 ml, with a path length (l) of 1.0 cm. The method also examined the interfering effects of concomitant Cu^{2+} ions, specifically Co^{2+} and Ni^{2+}. The procedure was validated through trial applications on the flotation concentrate of sulfide copper-nickel ore from the Murmansk deposit, with composition values of Cu-0.197%, Ni-0.535%, and Co-0.022% (S = 0.013, relative error = 1.41%).

A new spectrophotometric method utilizing flow injection analysis has been developed for the determination of Cu^{2+} ions in the analytical probe 1-(4-(1-(2-hydroxyphenylamino)ethyl)-phenyl)-diazenyl)-naphthalene-2-ol (HR). The solution in the presence of a buffer exhibits a pH of 9, resulting in the formation of a water-soluble, stable complex that displays a maximum absorption wavelength at λ = 500 nm. Beer's Law is validated within the concentration range of 0.5 to 10 μg/ml, with a correlation coefficient (R^2) of 0.2213, a limit of detection of 0.7377 μg/ml, and a relative standard deviation (RSD) of 0.65%. The molar absorptivity and the limit of quantification of the complex were found to be 50,380 l/mol·cm and 0.0039 μg/cm^2, respectively. The methodology has been successfully applied for the determination of Cu^{2+} ions in an analytical sample, demonstrating good accuracy and precision [46].

The spectrophotometric method was employed to study the complex formation of Cu^{2+} [47] with 4-(2,4-bis-((2-aminoethyl)-imino)-pentan-3-yl)-diazenyl-benzoic acid (HR) in the presence of 8-hydroxyquinoline (O), diphenylguanidine (D), and ethylenediamine (E) at pH 2 - 3. The optimal conditions for complex formation were determined, and the composition of the resulting complexes Cu-R,

CuR_2-O, CuR_2-D, and CuR_2-E was established; the maximum absorption wavelengths (λ_{max}) were measured at 553, 564, 568, and 576 nm; and the stoichiometry of the complexes was found to be 1:2, 1:2:1, 1:2:1, and 1:2:1, respectively. The optimal pH values for these complexes were determined to be 5, 3, 3, and 2. Upon interaction of Cu^{2+} with HR at pH levels ranging from 3 to 10, the maximum absorbance at pH 5.0 corresponded to λ_{max} = 553 nm. The molar extinction coefficients ($\varepsilon \cdot 10^{-4}$) were calculated as 0.730, 0.940, 0.970, and 1.22 l/mol·cm for the respective complexes. The stability constants (lgK) of the complexes were determined to be 6.24 ± 0.05 for Cu-R, 6.59 ± 0.06 for CuR_2-O, 6.64 ± 0.07 for CuR_2-D, and 6.98 ± 0.04 for CuR_2-E. The study also established the applicability of Beer's law for concentrations in the ranges of 2 - 24 μg/25ml for all complexes, except for CuR_2-E which showed a range of 0.25 - 5.12 μg/25ml. A comparison of the stability constants of the homogeneous complexes and the resulting complexes of Cu^{2+} indicates that CuR_2-E is more stable than the other complexes examined. Furthermore, the influence of foreign ions (which do not interfere include alkali metal ions, alkaline earth metal ions, Co^{2+}, Cr^{3+}, Cd^{2+}, Th^{4+}, Zn^{2+}, Pb^{2+}, Bi^{3+}, Al^{3+}, Mn^{2+}, $C_2O_4^{2-}$, and the masking agents EDTA, I^-, Cl^-, F^-, Br^-, SCN^-, $C_6H_8O_6$) on complex formation was also evaluated.

The spectrophotometric method [48] was used to investigate the complex formation of Cu^{2+} ions with 2,6-dithiol-4-tert-butylphenol (HR) and various amines (aniline (A), N-methylaniline (M), and N,N-dimethylaniline (D)) using a KFK-2 spectrophotometer with a path length of 0.5 cm. The ratio of the components in the reaction mixture corresponds to Cu^{2+}:HR:amine = 1:2:4. The reactions exhibit high contrast: the initial reagents are colorless, while the resulting complexes are brown in color. Analytical characteristics for the complexes $[Cu(HR)_2A_2](AN)_2$, $[Cu(HR)_2M_2](MN)_2$, and $[Cu(HR)_2D_2](DN)_2$ have been determined, with the following results: the equilibrium constant (K) is 6.69 ± 0.25, 6.82 ± 0.19, and 6.90 ± 0.28, respectively; the pH ranges are 4.6 - 5.9, 4.7 - 6.0, and 4.8 - 6.1; the maximum absorbance wavelengths (λ_{max}) are 538 nm ($\Delta\lambda$ = 258), 540 nm ($\Delta\lambda$ = 260), and 545 nm ($\Delta\lambda$ = 265); the molar absorptivity ($\varepsilon \cdot 10^{-4}$) values are 3.82, 3.93, and 4.25, respectively; and the logarithm of the stability constants (lgβ) is 11.80, 11.88, and 12.05. The limit of detection in μg/ml is 0.4 - 17.5, 0.3 - 19, and 0.3 - 20, while the limit of quantitation is reported in ng/ml as 9.50, 8.60, and 7.80, respectively. The acceptable concentration range (ACR) in ng/ml is 28.75, 26.08, and 23.64, and the corresponding surface concentration (S) in ng/cm^2 is 1.67, 1.63, and 1.51. The developed methodology has been successfully applied to the analysis of plant materials, natural waters, and various grades of steel.

The conditions for micellar-extraction concentration of Cu^{2+} [49] in the form of a complex with 6,7-dihydroxy-4-methyl-2-phenylbenzopyrylium chloride in the micellar phase of the non-ionic surfactant Triton X-100 have been studied and optimized. A methodology for the determination of Cu^{2+} using Atomic Absorption Spectroscopy following micellar-extraction concentration has been developed. The calibration curve is linear at a pH of 4.5 within the concentration range

of 5.0 - 213 μg/l, with the limits of detection (C_{min}) and quantification (C_{lim}) being 1.5 and 5.0 μg/l, respectively. The proposed methodology has been validated through the analysis of natural and drinking water samples, with the results showing that strontium (Sr) levels do not exceed 0.04.

The authors [50] have developed a methodology for analyzing the composition of the Cu-Sn alloy. This methodology is based on spectrophotometry, which allows for the accurate determination of the concentration of components in solution. An absorbance spectrum for Cu^{2+} in an ammonia complex solution was obtained. A linear relationship was established between the optical density (OD) of the solution and the concentration of Cu^{2+} ions at 630 nm using the KFK-3 photometer. A calibration curve was constructed within the concentration range of 0.0106 - 0.0848 g/l (calibration equation: D = 72.5·mCu, R^2 = 0.99). Additionally, the methodology includes derived formulas for calculating the percentage composition of Sn and Cu in the copper-tin alloy. The mass and percentage content of Cu^{2+} in the alloy were calculated using the formulas mCu = 72.5/D and ωCu = mCu·100%/m_alloy.

Microfertilizer based on Cu^{2+} chelate [51] is a concentrated solution characterized by its intense blue color, density ranging from 1200 to 1230 g/l, and a copper (Cu) concentration of 30 g/l. The pH of the solution is approximately 7, with Cu^{2+} bound in a stable mono-chelate complex with Trilon B ($\lg\beta$ = 18.80). Research conducted has demonstrated that the maximum absorption of the Cu^{2+} complex is observed in the wavelength range of 740 - 780 nm, with a peak at λ_{max} = 755 nm. The optimal environment for this microfertilizer is found to be within the pH range of 4.5 to 6.5. The linearity of the calibration curve follows a range of 0.1 - 1.0 g/l; therefore, it is advisable to dilute the original microfertilizer solution by a factor of 30 - 60. The equation for the calibration curve is given by y = 0.012 + 1.33x; (R^2 = 0.99). Based on the conducted research, a rapid and reliable spectrophotometric method has been developed for monitoring copper content in microfertilizers based on Cu^{2+} mono-chelate with Trilon B, demonstrating good convergence (Sr ≤ 0.03).

A sorption-photometric method for the determination of Cu^{2+} ions in aqueous solutions has been conducted [52]. The study focuses on the adsorption process of Cu^{2+} ions onto novel sorbents derived from natural mineral components (designated as SV-1-AL and SV-1-AL2). Key analytical parameters have been examined, including the optimal wavelength (λ = 540 nm) and the path length (ℓ = 0.5 cm), leading to the establishment of the calibration curve (y = 0.1464 + 0.82546x). Static adsorption isotherms for metal ions from aqueous solutions have been presented, and thermodynamic changes have been calculated, including enthalpy changes (ΔH = 1.66 ± 0.20; 2.49 ± 0.30), isobaric-isothermal potential (ΔG = 37.87 ± 3.70; 39.60 ± 4.00), and entropy changes (ΔS = 115.68 ± 11.00; 118.80 ± 10.00) for adsorption (n = 6; R = 0.95; t = 2.57). The results obtained indicate that these modified sorbents can be employed for the removal of Cu^{2+} ions from water, achieving a removal efficiency of up to 93%.

For the spectrophotometric determination of Cu^{2+} and Hg^{2+}, 2-amino-4-(4-nitrophenyl)diazenylpyridin-3-ol (HR) was used in the presence of a surfactant. HR reacts with both Cu^{2+} and Hg^{2+} ions in a universal buffer solution (pH = 8.0 and 8.5; V_{HR} = 1.0 ml; $C_{HR} = 2.0 \times 10^{-4}$ mol/l; T = 25˚C ± 5˚C; t = 2.0 min) containing sodium dodecyl sulfate, forming violet-colored complexes. The Cu^{2+} and Hg^{2+} complexes exhibit maximum absorption at λ = 565 nm and λ = 605 nm, respectively (λ_{HR} = 450 nm; $\Delta\lambda$ = 115 - 155 nm). The molar ratio is 1:2 (M:HR). The linear concentration ranges are 10 - 180 and 10 - 160 μg/ml, with Ringbom ranges of 20 - 120 and 20 - 100 μg/ml, respectively. The molar absorptivities (ε) are 1.1×10^4 and 0.6×10^4 l/mol·cm, and Sandell's sensitivities are 0.056 and 0.03 μg/cm^2. The limits of detection are 1.36 and 1.74 μg/ml, and the limits of quantification are 4.1 and 5.26 μg/ml. The correlation coefficients (R^2) are 0.994 and 0.995. The relative standard deviations (Sr) for six replicate measurements were 1.01% and 1.2%. The method was successfully applied to the determination of Cu^{2+} and Hg^{2+} ions in real samples, with recoveries ranging from 95.0% to 98.0% [53].

The study [54] investigated N-acyl-N'-(p-toluenesulfonyl)hydrazines (HR) as reagents for the concentration of Cu^{2+}, Co^{2+}, and Zn^{2+} ions through precipitation methods and spectrophotometry. Spectrophotometric measurements were conducted using the SF-2000 instrument at wavelengths of λ_{HR} = 230 nm, and λ_{MR} = 279, 286, and 305 nm, with a path length of ℓ = 5.0 cm. The reagent effectively precipitated Cu^{2+} ions (green color) within a pH range of 7.5 to 9.5, Co^{2+} ions (blue color) between pH 8.8 and 10.7, and Zn^{2+} ions (yellow color) in the range of pH 7.4 to 10.1. The precipitation efficiency was determined to be 99.66% for Cu^{2+} (concentration = 0.23 mg/l), 98.89% for Co^{2+} (concentration = 0.76 mg/l), and 99.45% for Zn^{2+} (concentration = 0.36 mg/l). In solution, the reagents form complex compounds with the metal ions in a stoichiometric ratio of $[Me^{2+}]$:[HR] = 1:2. The complexes of HR with Cu^{2+}, Co^{2+}, and Zn^{2+} ions were prepared, isolated, and identified. Quantitative characteristics of the equilibria of the complexation reactions were determined, revealing stability constants ($K_{stabl.}$) of 2.14×10^{13}, 3.48×10^{10}, and 2.82×10^6, precipitation constants (K_p) of 7.74×10^{-16}, 5.23×10^{-14}, and 1.91×10^{-11}, and reaction equilibrium constants (K_{equil}) of 2.76×10^2, 6.63×10^3, and 1.48×10^5 for the respective complexation reactions.

The processes of complex formation between N-tridecanoil-N'-(2-naphthylsulfonyl)hydrazine (HR) and Cu^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} ions in an ammoniacal medium were studied [55]. The absorption spectra of HR (λ_{HR} = 208 - 210 nm) in aqueous solutions were determined as a function of pH ranging from 3.97 to 13.38 ($C_{HR} = 1.5 \times 10^{-4}$ mol/l; KOH and HCl solutions were used). The obtained values of pK_a for the reagent were established as $pK_{a1} = 6.93 \pm 0.58$ and $pK_{a2} = 11.23 \pm 0.03$. Cu^{2+} ions precipitate (S = 99.99%) over a relatively broad pH range of 6.0 to 11.0. $Co^{2+}$and Ni^{2+} ions are quantitatively extracted within the pH range of 8.0 to 10.0, while Zn^{2+} ions are extracted in the range of pH 7.0 to 10.0 C_{lim} (Cu^{2+}) = 71.4 mg/l, C_{lim} (Co^{2+}) = 69.2 mg/l, C_{lim} (Ni^{2+}) = 66.0 mg/l, C(Zn^{2+}) = 70.3 mg/l. The composition of the complexes was elucidated using the methods of saturation,

equilibrium shifting, and Asmus analysis. In solution, HR forms complex compounds with metal ions in molar ratios of [Me]:[HR] = 1:1 and 1:2.

A spectrophotometric method for determining Zn^{2+} and Cu^{2+} ions using murexide (HR) has been developed [56]. The method employs absorption spectrophotometry at wavelengths of 450 nm and 470 nm, with equilibrium constants $K_{stab.}$ of 1.35×10^{16} and 2.30×10^{7} for the Zn-HR and Cu-HR complexes, respectively. The interaction of HR with Zn^{2+} and Cu^{2+} occurs instantaneously at pH 7 and pH 5.5 (with a stoichiometry of 1:2), and the absorbance of the resulting solutions remains stable for 220 minutes and 120 minutes, respectively. The proposed spectrophotometric methodology allows for the quantification of Zn^{2+} and Cu^{2+} within concentration ranges of 0.2 - 2.0 μg and 0.5 - 5.0 μg, respectively. The limits of detection are 1.95×10^{4} and 6.55×10^{3} l/mol·cm for Zn^{2+} and Cu^{2+}, respectively.

For the spectrophotometric determinations of the studied metals, some organic analytical reagents (OARs) were used, such as 1-(4-(((4,5-dimethyl-1H-imidazol-2-yl)diazenyl)methyl)phenyl)-N-(4-nitrobenzyl)ethan-1-imine [57], nitrilotris(methylene) phosphonic acid [58], 4-(2-chloroacetamido)salicylic acid and Triton X-114 [59], 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol [60], 2-hydroxy-2'-carboxy-5-sulphophenylformazylbenzene [61], N-(2-hydroxybenzoyl)-N'-(p-tosyl)hydrazine [62], 4-((furan-2-ylmethylene)amino)-5-methyl-4H-1,2,4-triazole-3-thiol [63], 1-[2-(allylamino)-1-methyl-ethyl] [64], N'',N'''-bis[(E)-(4-fluorophenyl)methylene]thiocarbongydrazide [65], and 4,5,6-trihydroxyhexan-1,2-diylidenebis(N-phenylhydrazincarbothioamide) [66].

In addition, numerous organic reagents have been used for the determination of copper(II) ions, and research studies have been carried out for their analysis [67]-[71].

7. Green Analytical Approaches in Extractive Spectrophotometry

Traditional extractive spectrophotometric methods often employ organic solvents such as chloroform, carbon tetrachloride, amyl alcohol, or butanol. Although these solvents provide high extraction efficiency, many of them are toxic and environmentally hazardous.

Recent studies therefore focus on the development of green analytical alternatives, including:

- micellar media
- ionic liquids
- supramolecular solvents
- cloud point extraction systems

These approaches significantly reduce solvent consumption while maintaining high sensitivity and selectivity.

The replacement of toxic solvents with environmentally benign extraction systems represents an important direction for future development of spectrophoto-

metric analytical methodologies.

8. Conclusion

This review highlights the growing biomedical and environmental importance of accurate determination of Cu(II) ions due to their dual biological roles and toxicological impact. While copper functions as an essential trace element involved in enzymatic catalysis, metabolic regulation, and antioxidant defense, its excessive accumulation leads to oxidative stress and cellular dysfunction. Mercury, even at trace concentrations, presents significant neurotoxic and systemic health risks. Extractive spectrophotometric methods based on chromogenic organic reagents-including hydrazones, thiosemicarbazones, azo compounds, Schiff bases, and triazoles-demonstrate high analytical sensitivity, selectivity, and cost-effectiveness. Reported molar absorptivity values frequently reach 10^4 - 10^5 $L \cdot mol^{-1} \cdot cm^{-1}$, with detection limits at $\mu g \cdot dm^{-3}$ and sub-trace levels. Optimized pH conditions, stable complex formation, and masking strategies significantly enhance method reliability and interference tolerance. Compared with instrumental techniques requiring sophisticated infrastructure, extractive spectrophotometry remains accessible for routine laboratory applications, particularly in regions where advanced instrumentation may be limited. Its applicability to biological fluids, pharmaceutical formulations, food matrices, natural waters, and industrial samples makes it a versatile analytical tool. Overall, extractive spectrophotometric systems represent a robust and sustainable strategy for biomedical screening, toxicological risk assessment, environmental surveillance, and public health protection. Continued integration of coordination chemistry principles with modern analytical optimization is expected to further expand the clinical and environmental applicability of these methods.

Conflicts of Interest

The authors declare no conflicts of interest.

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