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Review Article

Spectrophotometric Methods for Determination of Cu(II), Zn(II) and Ni(II) ions

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Abstract *- In this study, the practical aspects of determining Cu(II), Zn(II), and Ni(II) ions using various analytical techniques are investigated. The quantification of these metal ions is crucial for scientific and medical research, as well as for environmental monitoring. In recent years, numerous methods have been developed that ensure high accuracy, speed, and sensitivity in their determination. The paper reviews different analytical methods for determining Cu(II), Zn(II), and Ni(II) ions, emphasizing spectrophotometric and associated physicochemical techniques. The spectrophotometric technique stands out among other analytical methods due to its high precision, rapid operation, and low reagent consumption, making it an effective tool in environmental and biomedical research. Special spectrophotometric reagents, their application conditions, measurement procedures, and possible sources of error are examined in detail. Apart from spectrophotometric analysis, other instrumental techniques like atomic absorption spectroscopy, potentiometric titration, ion-selective electrode measurements, and X-ray fluorescence spectroscopy are systematically reviewed regarding their advantages and drawbacks. These methods enable the detection of trace concentrations of Cu(II), Zn(II), and Ni(II) ions, allowing for a deeper understanding of their biological activity and physiological effects. Overall, the study focuses on the practical applications of analytical chemistry and highlights its significance in medicine, environmental science, and biological research.*

Keywords *- Determination of Cu(II), Zn(II), and Ni(II) ions, Spectrophotometric Method, Ion-Selective Electrodes, Potentiometric Titration.*

1. Introduction

In the world, the pollution of science, technology, medicine, the environment, food, and industrial products with various industrial wastes, as well as ions of heavy and toxic metals, causes serious environmental problems of socio-economic importance; therefore, their prevention is one of the main tasks. Extensive work is being carried out on the rational use of heavy and toxic metal ions in industry, as well as the development and control of new, inexpensive, and selective methods for determining their microquantities. In particular, the development of methods for the quantitative determination of Cu (II), Zn, Ni (II) ions in natural waters, ores, industrial waste, and other complex mixtures is of great practical importance [1].

Analytical control of environmental object composition is of great importance for protecting the natural environment and preserving human health. This process aims to determine the level, composition, and quality of pollution in the atmosphere, water, soil, and other environmental components. Analytical control methods must operate with high precision. This allows for accurate and reliable measurement of pollutant or chemical element quantities. Analysis results should yield the same outcomes when repeated several times under identical conditions. This ensures the reliability of the results. Environmental monitoring often requires promptness, as some dangerous types of pollution can spread quickly. Therefore, analysis methods should be carried out swiftly [2]. It should have high efficiency, allowing the collection of more information from a small sample. Also, the processes should be conducted with minimal time and resource consumption. Analysis methods should be able to detect tiny amounts of pollutants in the environment. This level of sensitivity helps to identify harmful substances promptly. The measurement method should be able to determine the minimum level of pollution, which helps to identify environmental risks at an early stage. Analysis methods themselves should not harm the environment. Chemical reagents and equipment must be environmentally safe. Substances and methods used in the analysis process must be safe for analysts, and measures must be taken to protect against harmful effects [3].

2. The Role and Impact of Cu (II), Zn, and Ni (II) Ions in the Human Body

Copper (Cu) is considered a microelement that plays a crucial role in the biochemical processes of living organisms

[4]. It participates in numerous enzymatic processes and metabolic activities. Copper is a component of many enzymes, particularly those involved in redox reactions, such as cytochrome oxidase and superoxide dismutase [5]. These enzymes are essential for cellular energy production and antioxidant defense. Copper is necessary for the proper absorption of iron in the body and the synthesis of hemoglobin [6]. This element supports blood formation and plays a significant role in combating anemia. Copper participates in the synthesis of neurotransmitters, which are necessary for the proper functioning of the nervous system. It is essential in the formation of the myelin sheath, in the insulation and transmission of nerve impulses [7].

Copper also participates in the synthesis of proteins such as collagen and elastin. These proteins ensure the elasticity and strength of tissues, skin, bones, and blood vessels. Copper-containing enzymes help neutralize free radicals in the body, preventing cell damage [8]. This process is important as a defense against aging, cancer, and cardiovascular diseases. Copper ions play a crucial role in the process of mitochondrial respiration, which is necessary for cellular energy. They ensure the Production Of Energy (ATP) in cells through the respiratory chain. Although copper is necessary for living organisms as a microelement, excess amounts can be toxic and may cause health problems. Therefore, it is important to maintain copper balance in the body [9].

Zinc (Zn) is one of the essential microelements for living organisms and is a component of many metal-containing enzymes [10]. Zinc participates in numerous biochemical processes and is necessary for the proper functioning of the body. Zinc is a component of many enzymes, including carbonic anhydrase, alcohol dehydrogenase, and superoxide dismutase [11]. These enzymes play important roles in many biological processes, such as cellular metabolism and antioxidant protection. Zinc participates in the synthesis of DNA and RNA and is necessary for cell division and growth [12]. Therefore, zinc plays a crucial role in cell renewal and proper functioning. Zinc is essential for the effective functioning of the immune system. It plays an important role in the formation and activity of lymphocytes and other immune cells [13].

Zinc deficiency reduces immunity and increases susceptibility to infections. Zinc-containing enzymes help neutralize free radicals and protect cells from oxidative damage. The enzyme superoxide dismutase plays a vital role in this process. Zinc has a positive effect on skin and hair health [14]. It ensures rapid wound healing and also helps protect against skin diseases. Additionally, zinc is used to treat acne and other skin problems. Zinc regulates the activity of certain hormones, particularly insulin and growth hormones. Specifically, it improves insulin activity and helps regulate blood sugar levels [15]. Zinc is also important for the reproductive systems of both men and women. In males, it supports spermatogenesis and ensures healthy formation of sperm [16]. In women, it plays an important role in regulating ovulation and during pregnancy [17]. Although zinc is an essential micronutrient for the body, its deficiency or excess can lead to various health problems. Therefore, it is important to obtain sufficient zinc from food to maintain balance. Zinc is mainly found in meat, nuts, grains, and seafood [18].

Nickel (Ni) is one of the essential trace elements for the body and is a component of many metal-containing enzymes [19]. Although nickel occurs in tiny quantities in the human body, it participates in several important biochemical processes. Nickel plays a crucial role in the activity of some enzymes, especially urease. The enzyme urease regulates nitrogen metabolism by breaking down urea accumulated in urine [20]. Nickel acts as a catalyst in this process. Nickel may be present in enzymes involved in the proper synthesis of DNA and RNA, the genetic material in cells [21]. This supports cell division and growth processes. Nickel plays an important role in nitrogen metabolism, being especially necessary for bacteria involved in nitrogen fixation. This process is a biological mechanism that plays a crucial role in nitrogen assimilation by plants [22].

Nickel can also help maintain water and electrolyte balance inside and outside cells. It contributes to the organism's overall homeostasis. There is no strictly defined recommended intake of nickel for humans, but some studies indicate that it is necessary as a micronutrient. Deficiency in animal experiments has shown that it can lead to growth retardation and metabolic disorders. High levels of nickel accumulation can be toxic [23]. Excessive exposure to nickel (e.g., in industrial settings) can cause skin allergies, lung damage, or other health problems. Therefore, nickel should be present in a balanced amount in the body. Natural sources of nickel include plants, nuts, and grains. Although the body requires tiny amounts of nickel as a micronutrient, its role in biological processes is important [24].

3. Detection of Cu (II) ion by Spectrophotometric and other Physicochemical Methods

In this article, a simple, fast, and inexpensive spectrophotometric method was developed to simultaneously determine the concentrations of copper (II) and nickel (II) ions in a combined solution from 0.5 to 3 g/L and from 0.1 to 1.7 g/L, respectively [25].

In this research work proposed by the authors, a spectrophotometric method is presented for the simultaneous quantitative determination of iron (III) with a concentration of about 10^{-4} mol/L and copper (II) with a concentration of about 10^{-2} mol/L. Based on the photometric reaction of copper (II) and iron (III) ions with sulfosalicylic acid, the spectral data were then processed using the Vierordt method at wavelengths of 350 and 414 nm. When using the Vierordt method, the studied ions were determined with a smaller error compared to other methods of mathematical processing of spectral data [26].

From the research work in this article, it can be seen that the maximum absorption of copper (II) complexonate was observed in the wavelength range of 740-780 nm, with λ_{max}=755 nm. The optimal pH is 4.5-6.5. The calibration curve was linear over the concentration range of 0.1-1 g/dm^3. The linear equation of the calibration curve has the form y=0.012+1.33x (R^2=0.99). In this case, the relative standard deviation does not exceed Sr ≤ 3 % [27].

In this article, as a result of studying the complex formation of copper salt with the potassium salt of quinazolone-4 in a methanol solution, it was found that the 1:1 complex is poorly soluble in methanol. In contrast, the 1:2 and 1:3 complexes are soluble. This method was developed with maximum light absorption at 360 and 580 nm. A copper complex with a composition of 1:2 ($\varepsilon=2\cdot10^3$ L/mol·cm) is more sensitive than a complex with a composition of 1:3 ($\varepsilon=2.5\cdot10^2$ L/mol·cm) [28].

In the article, the optimal conditions for spectrophotometric determination of Cu (II) ion with N-benzoyl-N'- (phenylsulfonyl) -hydrazine (BPSH) were studied: λ= 300 nm, 30 minutes, pH = 11.5, BPSH = 9.5 mL. A calibration curve was constructed under the optimal conditions studied. The range of compliance with the Beer-Lambert law was determined to be 0.32 mg to 1.90 mg in 25.0 mL of solution. It was established that the molar absorption coefficient ε=2759 L/mol·cm. Using the "added-found" method, the accuracy and reproducibility of the spectrophotometric method for determining copper (II) ions with BPSH were determined. The relative error of determination was 1.41 %. The influence of interfering Ni (II) and Co (II) ions on copper (II) determination was investigated using the standard addition method [29]. The authors synthesized a new reagent based on salicylaldehyde: 3- ((E) -2-hydroxybenzylidene) hydrazono) indolin-2 (HBHI). The interaction of copper (II) with HBHI in the presence of 4-aminoantipyrine was studied. It was established that the ethanol solution of HBHI has a maximum absorption region (λ= 275 nm) at pH 4. Optimal conditions for the formation of Cu (II) -HBHI and Cu (II) -HBHI-4-aminoantipyrine complexes were established: λ=326 nm, pH=4, ε=13000 L/mol·cm and λ=357 nm, pH=3, ε=28500 L/mol·cm, respectively. The molar composition ratio of the components was determined by the methods of isomolar series, Job's method of continuous variations, and equilibrium shift. All methods showed that the ratio of Cu (II) -HBHI components in binary complexes is 1:1, and in mixed-ligand Cu(II) -HBHI-4-aminoantipyrine complex is 1:2:1 [30].

The article presents a spectrophotometric method for determining copper (II) using an indigo reagent obtained from a local plant. Optimal conditions were found: λ=750 nm, pH=2.20, 240 minutes, and 2 mL of 0.1 % added reagent. It was established that the Beer-Lambert law is obeyed in the range of 0.5-70 μg/25 ml. The equilibrium constant of complex formation, $K_{eq}=1.1\cdot10^{12}$, ε=41666 L/mol·cm, and the molar ratio of R: M were calculated using various methods. The proposed spectrophotometric method for determining copper(II) ions was assessed as metrologically selective, with a relative standard deviation not exceeding 1.4 %. The accuracy and reproducibility of the developed method were mathematically processed using the "added-found" method. Interfering ions were studied: K^+, NH_4^+, I^-, Na^+, F^- (1:1000), Br^-, Ba^{2+} (1:500), Zn, $S_2O_3^{2-}$, Si^{4+}, Cl^-, SCN^-, citrate (1:100), Al^{3+}, Cd^{2+} (1:10) did not interfere at these ratios. Pb^{2+}, Fe^{3+} (1:2), Tl^{4+} (1:1), Mn^{2+} (1:10) interfered. The developed method is a simple, fast, and convenient spectrophotometric method used in the analysis of natural and process waters [31].

In this study conducted by the authors, the chemical and analytical properties of copper (II) complexes with 1-phenyl-2[2-hydroxy-3-sulfo-5-nitrophenylazo] butadione-1,3 (FGSNFB) in the presence of three components are presented in Table 1 [32].

Table 1. Analytical parameters of Cu(II)–PHSNB complexes

Complex	pH	λ(nm)	ε·10^4 L/mol·cm	lgβ	Molar ratio of components	Calibration range (μg/mL)
Cu–FGSNFB	3	444	1,40	6,04±0,12	1:2	0,25-3,07
Cu–FGSNFB–ETD	2	461	2,2	10,16±0,14	1:2:2	0,12-2,56
Cu–FGSNFB–phenanthroline	3	468	1,85	9,12±0,09	1:2:2	0,18-2,56
Cu–FGSNFB–α,α′-dipyridine	3	471	1,72	9,44±0,13	1:2:2	0,18-2,56

In this research conducted by investigators, the interaction processes of cefotaxime with copper (II) ions in aqueous solution at λ=390 nm and pH=10 were studied spectrophotometrically. The molar ratios of the components were determined to be Cu (II): R=1:1 using the isomolar series method [33]. This article examines the conditions for Forming Copper Complexes With Hydroxyhalogen Thiopheno (GGTF) and Aminophenols (AP) derivatives, and optimal values were determined (pH=3.0-6.0; λ_{max} = 450-460 nm; Δλ = 275-285 nm; εmax = (3.5-4.3) 10^4 L/mol·cm;

$lgK_{stability}$=8.32-9.37). It was proven that mixed ligand compounds form at molar ratios of Cu(II):GGTF: AP=1:2:2 and 1:2:1 for AP2. Beer's law was observed in the range of 0.010-0.014 µg/ml for copper concentrations of 0.2-16 µg per 1 mL of extract. It was established that at P=0.95, the relative Standard Deviation (Sr) for Cu (II) detection did not exceed 1.5-4.5 % [34]. In this study, the complex formation reactions of Cu(II) with dithiolphenols (2,6-dithiolphenol, 2,6-dithiol-4-methylphenol, 2,6-dithiol-4-ethylphenol, and 2,6-dithiol-4-tert-butylphenol) in the presence of heterocyclic amines were investigated using the spectrophotometric method. The heterocyclic amines used were Phenanthroline (Phen), Bathophenanthroline (BPhen), and 2,2'-Dipyridyl (Dip). It was established that mixed-ligand complexes form in a weakly acidic medium (pH=6.0- 8.5). The maximum in the light absorption spectrum of the complexes was observed at λ=622-650 nm. The obtained analytical results are presented in Table 2 [35].

Table 2. Obtained analytical results

Kompleks	$\varepsilon \cdot 10^4$ L/mol·cm	lgβ	lgK_p	lgK_{ek}	Calibration range, µg/25 mL
Cu–DTF–Phen	3,15	8,20	6,52	10,15	0,5-16
Cu–DTF	4,26	8,40	6,55	10,28	0,5-18
Cu–DTF–BPhen	3,08	7,90	6,39	10,16	0,5-15
Cu–DTMP–Phen	3,45	11,62	6,70	10,25	0,5-16
Cu–DTMP–BPhen	4,37	11,94	6,79	10,32	0,5-19
Cu–DTMP–Dip	3,28	11,47	6,64	10,21	0,5-16
Cu–DEF–Phen	3,70	10,82	6,71	10,33	0,5-17
Cu–DEF–BPhen	4,28	10,96	6,81	10,47	0,5-19
Cu–DEF–Dip	3,61	10,52	6,73	10,29	0,5-17
Cu–DTBP–BPhen	3,91	11,95	6,75	11,04	0,4-18
Cu–DTBP–Phen	4,92	12,26	6,84	11,18	0,4-20

This article examines the optimal conditions established for the Cu-R complex (sodium salt of 2,7-bis (azo-2-hydroxy-3-sulfo-5-nitrobenzene) -1,8-dihydroxynaphthalene-3,6-disulfonic acid) as follows (Table 3):

Table 3. Characteristics of Cu(II) Complexes

Complex	pH	λ(nm)	$\varepsilon \cdot 10^4$ L/mol·cm	lgβ	Molar ratio of components	Calibration range, µg/mL
Cu-R	3	538	1,04	8,75±0,05	1:2	0,12-2,32
Cu-R-Triton X-114	1	512	1,50	9,59±0,05	1:2:2	0,07-2,32
Cu- R-DPG	2	491	1,55	9,85±0,05	1:2:2	0,07-2,32
Cu- R- TPG	2	572	1,60	9,92±0,04	1:2:2	0,07-2,32
Cu-NNDSK	10,5	490	1,47	-	1:1	0,63-6,39

In this work, carried out by researchers, alkali, alkaline earth, and some intermediate elements: Ca, Ba, Mn(II), Cr(III), Sn(IV), Ga(III), In(III), Zr(IV), practically do not interfere with the determination of copper (II). It is noted that the proposed express method exhibits high sensitivity and selectivity. It is noted that the developed method was used to determine copper (II) in food products [36].

In this work, the complexation of copper with 2,6-dimercaptophenol (DMF) and its Derivatives (2,6-mercapto-4-methyl-phenol (DMMF) and 2,6-dimercapto-4-tert-butyl-phenol (DMBF)) in the presence of Aminophenols (AP) was studied by the spectrophotometric method. 2- (N, N-dimethylaminomethyl) -4-methylphenol (AF1), 2- (N, N-dimethylaminomethyl) -4-chlorophenol (AF2), 2- (N, N-dimethylaminomethyl) -4-bromophenol (AF3), 2,6-bis (N, N-dimethylaminomethyl) -4-methylphenol (AF4), 2,6-bis (N, N-dimethylaminomethyl) -4-chlorophenol (AF5), and 2,6-bis (N, N-dimethylaminomethyl) -4-bromophenol (AF6) were used as aminophenols The analytical values of the obtained complex compounds are presented in Table 4 [37].

In this article, copper (II) is proposed as an analytical reagent for spectrophotometric determination with 1- (2-methoxyphenylamine) -3-methoxypropanethiol-2 (MFAMPT). MPAMPT forms a blue complex with copper(II) in the pH range of 5.4-6.8. Beer's law was observed over a concentration range of up to 16 µg/mL. The yellowish Cu (II) -MFAMPT complex showed maximum light absorption at 605 nm, the molar damping coefficient was 43200 L/mol·cm, and the Sandel sensitivity was 1.48 µg·cm^{-2}. It was established that the composition of the Cu (II) -MFAMPT complex is 1:2 (M:O). The influence of various cations and anions was studied in the method: non-interfering ions Co(II), Fe(II), V(IV), Pd(II), Zr(IV), Al, Cd(II), Pb(II), Cr(III), Pt(II), W(VI), Bi(III), acetate, tartarate, sulfate, thiocarbamide, phtharide, thiosulfate; interfering ions Ni(II), Nb(V), Ti(IV), Fe(III), Ta(V), Hg(II), Mo(VI), Ag(I). The developed method is recommended for determining the content of Cu (II) in pharmaceutical, food, and plant samples [38].

Table 4. Analytical values of the obtained complex compounds

Complex	pH	λ(nm)	Δλ(nm)	$\varepsilon\cdot10^4$ L/mol·cm	lgβ	lgK_p	lgK_{ek}	Calibration range, μg/25mL
$Cu(DMF)_2(AF_1H)_2$	4,9-6,2	475	205	3,65	9,55	7,62	11,25	0,5–16
$Cu(DMF)_2(AF_2H)_2$	4,8-6,0	472	202	3,71	9,46	7,53	11,18	0,5–18
$Cu(DMF)_2(AF_3H)_2$	4,7-5,9	470	200	3,76	9,29	7,45	11,16	0,5-18
$Cu(DMF)_2(AF_4H_2)$	5,1-6,5	478	208	3,58	8,45	5,80	9,05	0,5-15
$Cu(DMF)_2(AF_5H_2)$	5,2-6,3	475	205	3,65	8,50	5,69	9,12	0,5-15
$Cu(DMF)_2(AF_6H_2)$	5,3-6,4	472	202	3,72	8,40	5,65	8,85	0,5-15
$Cu(DMMF)_2(AF_1H)_2$	5,3-6,5	478	202	3,80	10,64	7,71	12,13	0,5-18
$Cu(DMMF)_2(AF_2H)_2$	5,2-6,3	475	199	3,85	10,53	7,64	12,17	0,5-18
$Cu(DMMF)_2(AF_3H)_2$	5,0-6,2	82	206	3,92	10,25	7,53	12,09	0,5-20
$Cu(DMMF)_2(AF_4H_2)$	5,5-6,9	80	204	3,75	9,84	5,85	10,24	0,4-18
$Cu(DMMF)_2(AF_5H_2)$	5,6-6,8	475	199	3,85	9,72	5,74	10,15	0,4-18
$Cu(DMMF)_2(AF_6H_2)$	5,7-6,8	470	194	3,88	9,58	5,72	10,29	0,5-18
$Cu(DMBF)_2(AF_1H)_2$	5,7-7,1	480	200	3,90	11,05	7,85	12,85	0,4-20
$Cu(DMBF)_2(AF_2H)_2$	5,9-7,0	485	205	3,95	10,95	7,79	12,82	0,5-22
$Cu(DMBF)_2(AF_3H)_2$	6,0-7,2	472	192	3,05	10,86	7,66	12,75	0,5-22
$Cu(DMBF)_2(AF_4H_2)$	5,9-7,3	485	205	3,85	10,18	5,90	10,09	0,5-18
$Cu(DMBF)_2(AF_5H_2)$	6,1-7,4	483	203	3,90	1011	5,82	10,06	0,4-18
$Cu(DMBF)_2(AF_6H_2)$	6,2-7,4	480	200	3,96	9,95	5,77	10,12	0,4-18

In this article, the formation of a complex of the dinatrium salt of 4-hydroxy3- (4-sulfonato-1-naphthyl azo) -1-naphthalene sulfonate with the Cu (II) ion in aqueous solutions was studied by the spectrophotometric method. The sensitivity of the method for determining Cu (II) was determined under optimal conditions: (pH=5.95; ε=48077 L/mol·cm, C_M =1.28·10-5; Δλ=75 nm, $C_{Cu(II)}$ =5.0-50.0 μg/25mL). The influence of foreign ions was studied: non-interfering ions Al^{3+}, Ca^{2+}, NH_4^+, Cr^{3+}, F^-, NO_3^-, SO_4^{2-}, Cl^-, Mg^{2+}, Sn^{2+}, Br^-, PO_4^{3-} (1:1000). Interfering ions Fe^{3+} (1:10), Ni (II) (1:2); Pb^{2+} (1:5), Co^{2+}, EDTA, Cd^{2+} (1:1), Hg^{2+} (1:8), SCN^- (1:0.5). The proposed spectrophotometric determination method was used in the analysis of sample mixtures, and the obtained results were metrologically evaluated, and it was found that Sr = not more than 8.7 % [39].

Based on the results of research conducted by scientists, a spectrophotometric method for determining Cu (II) ions with N- (2-hydroxybenzoyl) -N'- (p-tosyl) -hydrazine (GBSH) in an ammonia medium has been developed. A graduated graph was constructed for the complexation of HBSH with Cu (II) ions under optimal conditions (λ= 401 nm, pH = 9.2, t = 30 min, HBSH= 3.75 ml). The Beer-Lambert-Beer law was observed in the range of 0.13-1.59 mg/25 mL. It was established that the actual molar light absorption coefficient for the complex compound of HBSG with Cu (II) ions in an ammonia medium is equal to ε=1480 L/mol·cm. The ratio of [Cu (II)]:[GBSG] in a solution of a molar complex compound is 1:1. Using the Babko method, the conditional stability constant of the HBSH complex with Cu (II) ions was calculated and amounted to $4.53\cdot10^{16}$. The accuracy and reproducibility of the developed spectrophotometric method were determined using statistical methods [40].

The article proposes a new inversion voltammetric method with modified complexing reagents and graphite-containing sensors for detecting copper and zinc ions. It has been shown that modifying the studied organic compounds improves their chemical and analytical properties. An inversion voltammetric method for determining copper and zinc ions using graphite-containing electrodes modified with EDTA has been developed. Optimal conditions for obtaining modified electrodes and determining copper and zinc using complexing electrodes have been determined. The developed method was tested on various types of actual samples [41].

In the research work, the electropolymerization of pyrrole on the electrode surface was carried out using the anionic ligand sulfosalicylic acid, then a new polymer membrane of a modified electrode was obtained for the specific determination of Cu (II) by complex formation and penetration into the composition of copper ions. The factors contributing to the binding of Cu(II) to the polymer membrane and to the reduction in the detected lowest concentration are the copper-binding ability of the ligand, over-oxidation, the applied potential, and the polymer structure on the modified electrode. The presence of Cu (II) inside the membrane was confirmed by X-ray spectral analysis. Differential pulse voltammetry of the anodic solution was recorded to quantitatively measure the Cu(II) concentration after the analyte reached its initial concentration inside the modified electrode. Potentiometric measurements were carried out to test the electrode's ability to function as an ion-selective electrode for direct measurement of Cu(II) concentration. It has been established that while Ag and Hg elements interfere with the analysis, others, such as Co^{2+}, Mn^{2+}, Ni^{2+}, Ba^{2+}, Zn, Al^{3+}, Cd^{2+}, and Pb^{2+}, do not interfere with the detection of Cu(II), even if they exceed 100 times. The electrode exhibited a stable and repeatable signal with a linearity interval from $1.0 \cdot 10^{-8}$ to $1.0 \cdot 10^{-3}$ M with a relative standard deviation of less than 0.9 %. The least detectable concentration of Cu (II) was $1.5 \cdot 10^{-9}$ M. It has been proven that the relative standard deviation for potentiometric measurements is 0.4 %, the linearity range is from $1.0 \cdot 10^{-8}$ to $1.0 \cdot 10^{-3}$ M, and the lowest detectable concentration is approximately $4.0 \cdot 10^{-9}$ with a response time of 8-40 s [42].

In the article, the developed method of extraction-spectrophotometric determination of copper with 1- (2-pyridylazo) -2-naphthal (PAN), distinguished by selectivity, sensitivity, simplicity, and speed, is recommended for the analysis of ores, concentrates, industrial solutions, wastewater, as well as materials with a complex chemical composition [43].

In this work, a highly selective and sensitive anodic stripping differential pulse polarographic method is proposed for determining the amount of Cu (II) ions in water samples. The method is based on the separation and preconcentration of Cu (II) on an Octadecyl-Bonded Silica (ODBS) membrane disk modified with a synthesized triazene ligand ([1- (ortho-acylbenzene) 3- (3,4-dichlorobenzene) triazene]). Various parameters were optimized, such as the pH of the aqueous solution (7-8), flow rate (10 mL min^{-1}), ligand amount (6.0 mg), and type of eluting solvent (0.1 mol/L nitric acid). The breakthrough volume exceeded 500 mL, the enrichment factor was 100, and the detection limit was 3.88 μg L^{-1}. The influence of various cationic interferences on the recovery percentage of copper ions was studied. The method was successfully applied for the determination of copper ions in various samples [44].

In this research, a new and simple Differential Pulse Polarographic (DPP) method for determining microelements in dried grapes was developed. This method allows the determination of small amounts of elements with high accuracy. Polarograms were obtained in the presence of digested grape samples at various electrolytes and pH values. With the addition of only one sample, it was possible to simultaneously separate and determine Pb, Cu, and Cr in potassium carbonate at pH 11. An ammonia buffer at pH 9.8 was found suitable for separating and detecting Ni and Zn peaks. It was reported that simultaneous determination of Bi, Fe, and Mo could be carried out in HAc-NaAc buffer at approximately pH 7 in the presence of EDTA [45].

In this work, the electrochemical behavior of the azo dye 4- (2-pyridylazo) Resorcinol (PAR) was studied using Square Wave Voltammetry (SWV), Differential Pulse Polarography (DPP), Direct Current Polarography (DCP), and Cyclic Voltammetry (CV) in Britton-Robinson buffer (pH 2.0-12.0). Based on polarographic and voltammetric results, a mechanism for the electrochemical reaction of the azo dye was proposed. Additionally, the electrochemical behavior of the copper (II) complex with PAR was investigated using SWV in 0.1 M KNO3 supporting electrolyte. The SWV behavior of the Cu (II) -PAR complex was determined at various metal and ligand concentrations in a KNO3 supporting electrolyte. The metal: ligand molar ratio and stability constant of the Cu (II) -PAR complex were found to be 1:2 and $5.42 \cdot 10^{10}$, respectively [46].

According to research conducted by scientists, new chemically modified carbon paste electrodes containing Copper Oxide Nanoparticles (CuO NPs) as a neutral ionophore and screen-printed electrodes were developed and studied as Cu(II) selective electrodes. The electrodes showed Nernstian responses to Cu(II) concentrations ranging from $5.3 \cdot 10^{-7}$ to $1 \cdot 10^{-2}$ and $6.1 \cdot 10^{-8}$ to $1 \cdot 10^{-2}$ mol L^{-1}. The detection limits were determined to be $5.3 \cdot 10^{-7}$ and $6.1 \cdot 10^{-8}$ mol L^{-1} for the modified carbon paste and screen-printed electrodes, respectively. It was found that electrodes using Dibutyl Phthalate (DBP) (electrode I) and Tricresyl Phosphate (TCP) (electrode II) as plasticizers had slopes of 29.65 ± 0.30 and 28.99 ± 0.60 mV/decade, respectively. The electrodes were satisfactorily applied for the determination of Cu (II) ions [47].

In this research, sixteen metal ions, namely Li, Co(II), Ni (II), Cu(II), Ca, Mn(II), Ba, Mg, Sr (II), Zn, Al, Cd, Pb(II), Cr(III), Fe(III), and Th (IV) were selected to study their interaction with folic acid using a potentiometric method. The stability constants of the formed complexes were calculated at an ionic strength of I = 0.2 M $NaNO_3$ in aqueous solutions at 25 ± 0.1°C. Depending on the nature of the ligand or metal ions, complexes with metal-to-ligand ratios of 1:1, 1:2, and 1:3 were formed. The order of stability constants for the binary complexes was investigated. The stoichiometry of the formed complexes was confirmed by conductometry. Additionally, the ionic equilibrium of the ligand and its complexes with various metal ions in solution was studied. It was found that the overall stability constants of the formed complexes followed the order: Co (II) > Ni (II) > Cu (II) > Mg > Mn (II) > Cd (II) > Ca. This was proven to be in accordance with the Irving-Williams series [48].

In the article, modified and unmodified solid-state titanium electrodes with selective, stable electrochemical and performance indicators for copper (II), zinc (II), and cadmium (II) cations were created. Potentiometric measurements were carried out using an Anion-4100 ion meter with an error of 0.001 V. It has been established that the preparation of solutions against the background of 1 mol/L of potassium nitrate allows for determination at constant ionic strength (I=1). In addition, it has been experimentally proven that the potential of the titanium electrode is practically independent of the chosen background concentration. Methods for determining copper (II), zinc (II), and cadmium (II) cations in formation waters have been developed. Potentiometric titration has shown the possibility of using titanium electrodes as indicators for the determination of copper, zinc, and cadmium in formation waters [49].

In this article, it was determined that the determination of copper ions in food products can be carried out potentiometrically using an EMK-Cu-01 electrode with an ion-selective indicator from $1\cdot10^{-5}$ to $1\cdot10^{-2}$ mol/dm^3 against a background of 0.05 M KNO_3 + 0.02 M NaF. The developed method made it possible to determine copper in aqueous solutions of electrolytes with a relative error of no more than 3.75 % and a relative standard deviation of less than 7.0 % [50].

In this work, when titrating the prepared solutions of $Cu(NO_3)_2$ (pH=2.38), at concentrations of $1\cdot10^{-5}$ and $2\cdot10^{-5}$ mol/dm^3, compounds with a copper-glutathione ratio of 1:2 were obtained. On the titration curves, a characteristic refraction is observed, the pH value of which varies from 2.38 to 2.44 [51].

The authors note that 2-Mercapto-5-Benzimidazolsulfonic Acid (MBS), including non-covalent Cu(I), Ag(I), Au(I), and Pt(II) on the silicon surface, is proposed as a reagent for detecting low-temperature fluorescence.

The luminescence and luminescence excitation spectra of metal complexes with MBS in solutions and on the sorbent surface are located in the range of 250-400 nm and 450-700 nm, respectively. The developed luminescent and sorption-luminescence methods were used for the determination of copper, silver, gold, and platinum with a detection limit of 0.001 - 0.01 µg per 0.1 g of sorbent for natural and industrial objects [52].

In the article, it was found that the results of a comprehensive study of the luminescence spectra of a sensitive element in the presence of an analyte of various concentrations show the possibility of both qualitative and quantitative determination of the concentration of metal ions in water. Methods for increasing the sensor system's sensitivity and selectivity are considered. The possibility of creating a sensor system based on chitosan films modified with luminescent indicators, providing measurements of the concentration of silver and copper ions with a detection limit of 10^{-7} mol/L and 10^{-6} mol/L, respectively [53].

In this work, the complexation of copper with 2-Hydroxy-5-T-Butylphenolazobenzene was studied by atomic absorption and spectrophotometric methods. Optimal conditions for complex formation have been studied. Extraction-atomic absorption and extraction-photometric methods for determining copper have been developed, and the influence of foreign ions on it has been established [54].

Table 5. Description of Cu (II) complexes

Complex	pH	λ(nm)	$\varepsilon\cdot10^4$ L/mol·cm	Interfering ions	Calibration range, µg/25mL
Cu(II) + sodium diethyldithiocarbamate (Na-DDTC)	1,5-6	435-440	0,17	Ag(I)-30; Hg(II)-50; Bi(III)-30; Pb(II)-50; Ni(II)-100; Fe(III)-10;Mn(II)-50	1-15
Cu(II) + 2-hydroxy-5-tert-butylphenylazobenzene	9-9,3	500	2,2	Ag(I)-100; Hg(II)-100; Ni(II)-400; Co(II)-350; Cd(II)-300; Zn-300; Bi(III)-500	0,1-20

4. Spectrophotometric and Other Physicochemical Methods for Determining the Zn ion

The article discusses the interaction between Zinc and Chromium(III) salts. The effect of temperature on the Nature Of Chromium (III) and zinc salts with various organic reagents was analyzed, and the complex-forming properties of these elements were compared with other elements. Analytical characteristics of the complexes formed by the Zn ion were studied (Table 6) [55].

Table 6. Spectrophotometric characteristics of colored zinc compounds

Reagent	pH	λ_{MR}	λ_R	Δλ	molar ratio	$\varepsilon\cdot10^4$ L/mol·cm	K_M
Xylenol Orange (XO)	5,8	585	440	145	1:1	31200	$1{,}0\cdot10^{-7}$
Methylthymol Blue (MB)	5,0	596	434	162	1:1	20000	$2{,}0\cdot10^{-7}$
Pyrocatechol Violet (PCV)	7,5	610	480	130	1:1	13400	$3{,}5\cdot10^{-7}$

In this work, a rapid and straightforward method for spectrophotometric determination of Zn ions using 2,7-Dinitroso-1,8-Dioxynaphthalene-3,6-Disulfonic Acid (DNDOKS-S, S-3,6) is proposed. It has been demonstrated that the reagent interacts with Zn ions to form a complex with a Zn-DNDOKS-S, S-3,6 ratio of 1:2.

The spectral characteristics of the Zn complex with the DNDOKS-S, S-3,6 reagent were studied (Table 7). Optimal conditions for detecting Zn ions have been determined. Physicochemical characteristics, statistically processed results, and the application of the method in analysis are presented [56].

Table 7. Spectral characterization of DNDOKS-S,S-3,6 (HR) and its complex with Zn(II) (MR)

Complex color	pH	λ_{max}, nm		Δλ	C_M^{2+}, μg/25 mL	C_M^{2+}, mol/L	Ā	Sensitivity according to Sendel μg/cm^2
		MeR	HR					
Complex Zn(II) with R (ℓ=1.0 cm, n=5)								
Red-yellow	6,73	490	550	60	10	$6{,}12 \cdot 10^{-6}$	0,406	0,0007

In the article, the interaction of zinc ions with one of the triphenylmethane dyes, m-cresolphthalexone C, was studied, differing in light absorption spectra, the ratio of reaction components, and other properties, as well as varying pH values (pH 5 and 7). The causes of the observed color reactions were discussed. Table 8 shows the simplest ratios of metal and reagent, ε, and stability constants of zinc's complex compounds with m-cresolphthalexone C [57].

Table 8. Simplest ratios of metal and reagent, ε, and stability constants of zinc's complex compounds with m-cresolphthalexone C

Reagent	pH	λ_{MeR}	λ_R	Δλ	mole ratio	ε L/mol·cm
I	5	580	450	130	1:2	35200
II	7	490	580	-90	1:1	24000

Table 9. Result of the research

Complex	pH	Δλ	$\varepsilon \cdot 10^4$ L/mol·cm	lgβ	Molar ratio of components
Zn(II):drotaverine:PAN pyridylazonaphthol	9	30	0,41	5,14	1:1:1

As a result of the research conducted by the authors, it was established that the components of the resulting three-component system undergo a chemical reaction in the ratio Zn:drotaverine:PAN = 1:1:1. ε and the instability constant of the obtained complex compound were calculated (Table 9). The main spectrophotometric characteristics of the obtained three-component system are presented in the table [58].

The article describes a simple, fast, sensitive, and new spectrophotometric method for assessing zinc in pharmaceutical preparations. The method is based on the reaction between Zn and the newly synthesized reagent [4,5-diphenyl-2- ((1E) - (4- (1- (2-phenylhydrazono) ethyl) phenyl) di-azenyl) -4H-imidazole] (DFHEDFI). The optimal conditions for complex formation were determined: molar ratio (M:L) of 1:2, λ=520 nm, pH 7.5. A reddish-pink complex was formed with ε=4400 L/mol·cm, R^2=0.9996. Beer's law was observed for Zn in the range of 0.5-27 μg/25ml, and the stability constant was determined to be $1 \cdot 10^{12}$ L mol^{-1}. For seven repeated measurements, the relative standard deviation, relative error, and recovery values were found to be 1.5 %, -0.778 %, and 99.22 %, respectively. The proposed method was applied to determine Zn in zinc sulfate capsules, and the results were compared with those obtained by the atomic absorption method [59].

The spectrophotometric method developed during the study is based on the formation of a Zn-hesperidin complex in 70 % methanol at pH 3.12, with maximum light absorption at λ_{max}=283 nm. The method of equimolar solutions confirmed the complex stoichiometry as Zn:hesperidin = 2:1. The stability constant of the complex was determined by the Bjerrum method, with a value of lgβ=17.01 at pH 3.12. The linearity range for the developed method is 0.61-7.32 μg/25ml, R^2 = 0.9882. The proposed method meets all target requirements and has been successfully used for the determination of hesperidin in tablets with a recovery value of 92.2 %, as well as in commercial orange juices [60].

The article studied the complex formation of N-butanoyl-N'- (p-toluenesulfonyl) -hydrazine (BSH) with Zn ion by precipitation. Zn was quantitatively isolated in the pH range of 7.4 - 10.1. The study of molar ratios [Zn]:[BSH] was carried out using saturation, equilibrium shift, and Asmus methods. The results were confirmed by extraction-photometric and conductometric titration methods. It was proven that the obtained data show [M (II)]:[BSH] ratios of 1:1 and 1:2 [61].

This work developed a very simple, sensitive, highly selective, and extraction-free spectrophotometric method for determining low concentrations of Zn. A new analytical reagent, 4,4'-bis- (2,3,4-trihydroxyphenylazo) -biphenyl (BTFAB), was proposed for direct, extraction-free spectrophotometric determination of Zn. In an aqueous medium, BTFAB reacts with Zn to form a brown chelate with a molar ratio of 2:1 (Zn: BTFAB). The optimal conditions were studied at λ=540 nm, with the complex remaining stable for 24 hours. The ε and S.b.c. values were ε=23000 L/mol·cm and 5 μg/cm^2, respectively. The linear calibration graph for Zn was obtained in the range of 0.1-30 μg/mL. The influence of more than 30 foreign cations, anions, and complexing agents was studied. The method is highly selective for Zn and has been successfully applied to various drinking and wastewater samples. The authors have demonstrated the method's high accuracy [62].

This study is aimed at developing a new spectrophotometric method for determining Zn and Cu (II) using a new chromogenic reagent, the sodium salt (HR) of [4-amino-5-hydroxy-6-[(5-methyl-2-pyridyl) azo]-3-sulfo-1-naphthyl]sulfonic acid. A new organic HR reagent has been synthesized. The complex compounds of Zn (II) and Cu(II) with HR were 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. It has been established that the HR reagent interacts instantaneously with Zn and Cu (II) at pH 6.5 and pH 4.0, and the absorption of the solution is stable for 70 and 1440 minutes, respectively. The stoichiometry of the complexes using isomolar series, Asmus line, equilibrium shift, and spectrophotometric titration methods determined the metal-ligand ratio of 1:2 for Zn and Cu. To determine the charge of the complex, the solution was passed through a column containing the cations KU-2 and KRS-10, as well as 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 oxygen-OH group, the nitrogen atoms of the pyridine ring, and the N=N group. To assess the stability constant (Kstable), the dilute Babko method was used, which was found to be at the level of $1.44 \cdot 10^{21}$ ($\lg\beta=21.16$) and $2.97 \cdot 10^{17}$ ($\lg\beta=17.47$) for Zn and Cu complexes, respectively. The proposed spectrophotometric method showed that the concentrations of zinc (II) and copper (II) can be considered as 1.0-18.0 and 0.50-6.50 μg/25mL, respectively, which have molar absorption of $4.2 \cdot 10^4$ L/mol·cm and $2.04 \cdot 10^4$ L/mol·cm, respectively. Similarly, the resulting complexes were stable over a range of pH values, allowing the simultaneous determination of two metals. The proposed spectrophotometric method was used in the analysis of sample mixtures, industrial alloys based on aluminum, and natural water, and the obtained results were studied metrologically (Sr 4.3 %) [63].

In the article, a spectrophotometric method for determining the Zn ion with 8-hydroxyquinoline-2-carboxylic acid was developed. Analytical parameters $\lambda=450$, pH=6.17, molar ratio of components 1:2, $\varepsilon=4400$ L/mol·cm, $\lg\beta=7.3$, $Q_{min}=12$ μg/mL, Sr= 2.0 % [64].

In this work, the optimal conditions for spectrophotometric determination of the Zn ion with 1- (5-benzyl-2-thiazolyl) -azo-2-naphthol (BTAN) were studied (pH=8.0). It was established that the molar ratios of the components Zn: BTAN=1:2. The calibrated graph was manifested in the range of 2.5-40 μg/25mL. It was established that $Q_{min}=4$ μg/25mL and $R^2=0.9985$ [65].

The work presents the results of the simultaneous determination of zinc, mercury, and cadmium ions in an aqueous solution by the voltmetric method. To obtain analytical signals of all three elements, a silver indicator electrode and perchloric acid background were used. The dependence of the height of analytical signals on the concentration of zinc ions in the analyzed system was established in the concentration range from $5 \cdot 10^{-5}$ mol/L to $5 \cdot 10^{-3}$ mol/L. Using the logarithmic scale, the logarithmic dependence for the current values and concentrations of standard zinc solutions was determined. This type of dependence on zinc ions under the studied conditions was obtained for the first time [66]. The article examines the comparative behavior of indicator electrodes based on shungite, silicon, and germanium for a three-electrode inversion scheme of voltammetric analysis of aqueous solutions containing lead, copper, zinc, cadmium, cobalt, and nickel ions [67].

This article discusses the conditions and presents the results of the voltametric analysis of meltwater from the snow cover by the content of heavy metals in various districts and suburban areas of the city of Kemerovo. It has been experimentally established that under the conditions of determining manganese ions using naked voltammetry, it is possible to detect heavy metal ions - zinc, cadmium, lead, and copper. The influence of accumulation potential and other registration parameters on the magnitude of analytical signals of metals was studied. Graduated graphs of the dependence of the metal hill flow on metal ion concentration have been constructed. The calibration dependence was established on the background electrolyte - sodium sulfite, a three-electrode cell, a mercury film electrode as an indicator electrode, and a silver chloride electrode as an auxiliary electrode, as well as corresponding inscriptions. The average zinc and manganese content in the samples varied from 1.5 to 8 μg/L, determined at the level of other metals [68].

In the research work carried out by the authors, the processes of complexation of sulfonyl (GTS) derivatives of thiophenes with Cu(II), Co(II), Ni(II), Zn, and Cd ions in ammonia solutions were studied. Using isomolar series and conductometric titration methods, the [M(II): GTS] =1:2 ratio was determined; the composition of the complexes isolated by the preparation was confirmed by IR spectra and elemental analysis data [69].

In the article, one of the sensitive and inexpensive methods used in the analysis of water bodies is ionometry, which is associated with the introduction of new ion-selective electrodes into potentiometric analysis practice. An optimized membrane composition for the production of a zinc-selective electrode based on polyvinyl chloride modified with 2-mercaptobenzothiazole (MPBT) has been proposed. The slope of the electrode function was estimated at 30.1 ± 0.3 mV. Based on the dependence of the electrode potential on the logarithm of the concentration of zinc ions for the selected membrane composition, it was determined that the recommended electrode model operates in the concentration range of $1 \cdot 10^{-5}$-$1 \cdot 10^{-1}$ mol/L, and the detection limit is 0.65 mg/L. The potentiometric selectivity coefficients of the zinc-selective electrode for various ions were determined [70].

In this research work, imidazole and acridine derivatives were extensively studied, which indicates that the quantitative determination of elements as a result of complex formation determines high selectivity and efficiency. The possibilities of using new organic reagents for fluorimetric determination of

Zn and Ag (I) microquantities in various objects were studied [53].

This article provides an overview of the literature covering wastewater and heavy metals in waste, as well as their properties. The toxicological properties of heavy metals - copper, zinc, and iron - are considered, and data on their effects on living organisms are presented. Also, general information is provided on scientific research, including modern physicochemical methods for the detection of heavy and toxic metal ions, such as Zn, Cu(II), and Ni(II) in water. It is substantiated that the use of several analysis methods for the detection of heavy metals in water allows for express, highly sensitive, selective analysis [71].

In the article, the conditions for conducting elemental analysis (nitric acid concentration, monochromator crack width, flame stabilization time) were selected to ensure compliance with pharmacopoeial requirements for the determination of Zn in insulin (0.8 mg/dm^3, for a standard Zn solution with a concentration of $Sr \leq 1.4$ %). The coefficient of correlation of the ranked graph is not less than 0.99. A comparison of the results of measuring the Zn content in the studied samples was carried out when using hydrochloric or nitric acid as a solvent. Comparison of the modified method with the pharmacopoeia did not reveal significant differences in the results of Zn determination when replacing hydrochloric acid with nitric acid [72].

The article notes that the method of separating metals together with mercury into a layered system: water-antipyrine-sulfosalicylic acid-potassium thiocyanate is applied to the surface of a graphite electrode placed in a three-electrode cell, forming the lower phase of an ionic organic liquid, part of which is saturated with 0.1 mol/L of KSCN. The mercury accumulation potential was applied without delay, for -1.4 V for 30 seconds, and then in anode scanning mode, the voltammogram was recorded in a square-wave mode in the region from -1.20 to +0.20 V in the form of anode oxidation peaks of zinc, copper, cadmium, and lead [73].

In this work, the determination of copper, zinc, arsenic, and selenium in certified standard samples of complex alloy nickel alloys was carried out using inductively coupled plasma mass spectrometry (ICP-MS). The method of melting the sample and preparing it for analysis is presented. Element detection limits, % (by mass): 0.00005 Cu; 0.00005 Ce; 0.00007 Zn; 0.0001 As; range of determined concentrations - from 0.00002 to 0.0401% (by weight); Sr not more than 0.05 [74].

In the article, a two-cloud point procedure for simultaneous preliminary concentration and separation of heavy metal ions (Cd(II), Ni(II), Co(II), Pb(II), Zn, and Cu(II)) was developed using inductively coupled plasma optical emission spectrometry in water samples. The process is based on the formation of complexes of the metal ion with 8-hydroxyquinoline (8-HQ) in a phase rich in the surfactant Triton X-114. Under optimal conditions (pH=7.0, Triton X-114=0.05 % (w/v), 8-HQ=$2.0 \cdot 10^{-4}$ mol L^{-1}, HNO_3=0.8 $molL^{-1}$), the detection limits of Cd(II), Ni(II), Co(II), Pb(II), Zn and Cu(II) ions were 0.01, 0.04, 0.01, 0.34, 0.05 and 0.04 µg/ml, respectively. At 100 µg/ml, the values of the relative standard deviation for 10 repetitions were below 6.0 %. The proposed method can be successfully used to determine Co(II), Cd(II), Pb(II), Ni(II), Zn, and Cu(II) ions in water [74].

In this study, a new carbon paste electrode modified with a ligand synthesized in the laboratory, N1-hydroxy-N1, N2-diphenyl-benzamidine (GDFBA) and multilayer carbon nanotubes (MCCNT) (GDFBA–MCCNT/CPE) was created. The modified electrode was used for preliminary concentration and voltametric determination of Zn ions using a square-wave anode cleaning voltmeter (KWACV). Preliminary concentration of Zn on the electrode surface was carried out in a 0.1 mol/L Brinton Robinson (B-R) buffer solution (pH 6) for 120 s at a potential of -1.30 V relative to Ag/AgCl, then purified for 120 s. The positive potential of TAPVC was scanned after 10 seconds. Under optimized experimental conditions, the proposed electrode showed a broader linear dynamic response for Zn in the concentration range of 0.02-10.00 µM with a detection limit of 2.48 nM. This is due to the remarkable metal-chelating properties and good conductivity of the ligand, as well as the large surface area of the PCUNT, which significantly improved the sensitive performance of the nanocomposite modified electrode. The selectivity of the electrode was studied by assessing the interference effect of various foreign ions on the maximum Zn flux. The method demonstrated high reproducibility with a relative standard deviation of 3.1 %. This method was used to determine Zn ions in water samples. The reduction values in the tested samples were found to be 98.50-106.0 %, which indicates good accuracy of the proposed electrode. In addition, the electrochemical behavior of GDFB in acetonitrile and aqueous solutions was studied [75].

In the article, a new luminescent Zn ion detection chemisensor based on thiophene-dicarbohydrazide was synthesized and well-tested. It has been established that the chemosensor has high emission upon complexation with the Zn ion. This activated fluorescent recognition was preconceived in a DMSO/H_2O (6:4 v/v) medium. The coupling constant was calculated to be $1.15 \cdot 10^4$ M. The detection limit was considered to be $1.51 \cdot 10^{-7}$ mol/L, which is significantly lower than the permissible level of Zn (70 µM) in drinking water. The 1:1 binder stoichiometry of the chemosensor N'2, N'5-bis ((3-hydroxynaphthalene-2-yl) methylene) thiophene-2,5-dicarbohydrazide (GNTH) Zn complex was determined by the Jobs method. It is noted that the observed luminescent enhancement can be detected using a chelation-enhanced fluorescent mechanism for ignition emission [76].

5. Spectrophotometric and other Physicochemical Determination of Ni (II) ion

In the research work, a new reagent was synthesized at the Department of Organic Chemistry of Omsk State University, which can be used for spectrophotometric determination of Ni (II) and Cu (II). It has been established that complexes with these cations are sufficiently stable and have an intense color. It was established that under conditions of a 3-fold increase in the reagent content, solutions of Cu(II) and Ni(II) complexes obey the Beer-Lambert-Beer law with a metal concentration in the range of $4.2 \cdot 10^{-6}$ - $4.2 \cdot 10^{-5}$ mol/L and a pH of 0.99. The developed method is recommended for the determination of these metals [77]. In this work, the complexation of nickel(II) ions with 2,7-dinitroso-1,8-dioxynaphthalene-3,6-disulfuric acid was studied by the spectrophotometric method. Identification of the reagent was carried out using elemental analysis and IR spectroscopy.

Optimal conditions for the formation of a complex compound have been found. It has been established that the complex compound is formed in an alkaline medium (pH=8.5-9.5). The complexing form of nickel Ni (II) was established by the Nazarenko method. The ratio of the components in the complex (Ni:P) was 1:2. Based on the obtained data, spectrophotometric methods for determining nickel (II) ions in various objects have been developed [78].

Table 10. Influence of the third components

Complex	pH	λ	$\varepsilon \cdot 10^4$	lgβ	Molar ratio of components	Calibration range, μg/mL
Dibromethylcarboxyazo	-	625	10380	-	1:2	0,01-0,79
Ni– FDMPAP	7	411	6250	4,24±0,04	1:2	0,37-2,78
Ni(II)–FDMPAP–DAPFM	6	321	12800	4,75±0,05	1:2:1	0,37-2,78
Ni(II)– FDMPAP –OX	6	315	18000	4,98±0,03	1:2:4	0,23-2,83

In this article (Table 10), the influence of the third components, dianthypyrylphenylmethane (DAPFM) and oxyquinoline (OX), on the complexation of nickel (II) with 3-(1-phenyl-2,3-dimethylpyrazolone-5) -azopentadione-2,4 (FDMPAP) was studied [81].

In the article, a spectrophotometric method for determining Ni (II) ions with 5- (2-bromo-5-methoxybenzylidene) thiazolidin-2,4-dione (BMBT) was developed. A graduated graph was constructed for the complexation of BMBT with Ni (II) ions under optimal conditions (λ= 482 nm, pH =7.1-8.9). The Beer-Lambert-Beer law was observed in the range of 0.3-13 μg/25 mL. It was established that for the complex compound of BMBT with Ni (II) ions in an ammonia medium, ε=17500 L/mol·cm. It has been established that the ratio [Cu (II)]:[GBSG] in a solution of a molar complex compound is 1:2. The convergence and accuracy of the developed spectrophotometric technique were determined using the method of mathematical statistics [80].

This [81] is a fast and straightforward spectrophotometric method for determining Ni (II) using sulfosalicylic acid. The obtained complex is pink, the molar ratio of components is 1:1, and the complex has a maximum absorption at λ = 510 nm. The region of obeyance to Beer's law was calculated as 2-20 μg/25mL, S.s. 0.083 μg/cm^2, and ε=669 L/mol·cm. Analysis of various alloys was carried out satisfactorily. In the article, Esomeprazole is a new chromogenic reagent used for the direct spectrophotometric determination of nickel (II). Esomeprazole formed a greenish-yellow complex with nickel (II) at pH=5. The method obeyed Beer's law in the range of 0.139-1.394 μg·mL^{-1}, S.s. 0.0029 μg/cm^{2,} and ε=24000 L/mol·cm. The method is helpful in determining nickel in peanuts and sesame seeds, determined in the following order [82].

In this study, the concentrations of cobalt (II) and nickel (II) in complexes with 1- (2-pyridylazo) -2-naphthol were calculated in an aqueous micellar medium with a mass fraction of 2% sodium dodecyl-bis (oxyethylene) sulfate. The stoichiometry of the complexes was established at pH=4.01 using the method of isomolar series: Co (II): PAN=1:2 and Ni (II): PAN=1:2; their graphs are presented. For the joint determination of cations, calculation methods such as the Additional Addition Method (ADM) and the Linear Least Squares Method (LME) were used. ECCU made it possible to evaluate the random error caused by the presence of the interfering component and convert it into a systematic error that can be minimized. It was calculated that Sr does not exceed 9.0 % [83].

In the article, the interaction of nickel(II) and cobalt(II) ions in aqueous solutions with Nitrilotrimethylphosphonic Acid (NTMPC) was studied by the spectrophotometric method. Homogeneous ligand complexes with different proton compositions were found: in all the found complex particles, the molar ratio of metal: ligand was 1:1. Complete stability constants were determined, and the fractional distribution of the formed Nickel (II) and Cobalt (II) complexonates was calculated depending on the acidity of the medium [84].

In the study, Ni (II) 2-Hydroxyl-5-Iodothiophenol (GYTF) and Diphenylguanidine (DFG) formed a well-chloroform-separating triple complex. It is noted that complex nickel with a composition of 1:2:2 (Ni: GYTF: DFG) and a two-phase stability constant lgβ=6.62 can be used for selective, sensitive, and reliable extractive spectrophotometric determination. Maximum absorption wavelength 480 nm, ε $2.64 \cdot 10^4$ L/mol·cm, S.s.. 2.23 μg cm^{-2}, the optimal pH range is 4.5-6.8, the detection threshold is 0.02 μg/mL, the linearity range is 0.07-3.6 μg/ml, and the value of Sr ≤1.8% of the developed method is not exceeded. To assess the complex application of the Spectrophotometric determination of Ni (II), the influence of extraneous ions was studied. The results showed that excessive amounts of alkaline, alkaline earth, and rare earth elements, as well as F-, SO_3^{2-}, Br^-, Cl^-, SO_4^{2-}, and $C_2O_4^{2-}$, did not interfere at all with Ti(VI). Fe(III), Mo(VI), Cu(II), and Nb(V) ions interfere. The developed method was used for the determination of nickel in the geological sample, carnallite [85].

The article creates optimal conditions for the spectrophotometric method of determining Ni (II) with Chlorophosphonazo-III (XFA-III) and successfully determines the nickel content in water samples. In a buffer environment of Acetic Acid-Sodium Acetate at pH=5.5, XFA-III and Ni (II) formed a green-blue complex with a maximum absorption wavelength of 620 nm. The Ni (II) content is in the range of 0.1-3.5 μg/mL, and a good linear relationship of absorption is shown. The method was calculated to be ε= $1.40\cdot10^4$ L/mol·cm and Q_{min}=0.075 μg/ 25mL. The influence on foreign ions was studied (maximum 5% error) (m/m): SiO_4^{2-}, CH_3COO^-, Cl^-, SO_4^{2-}, F^-, Br^-, PO_4^{3-} (100), B^{3+}, I^-(50), Ag^+, Cd^{2+} (15); Mg^{2+} (4), Al^{3+}, Cu^{2+}, Fe^{3+}, Zr^{4+} (0.5): Ce (IV), Mo (VI) (0.4); Cr (VI) (0.3); Fe^{2+}, Zn, W (VI) (0.2); Ti (IV) (0.1); Mn^{2+}, Co^{2+}, MnO_4^- (0.05) Ca^{2+}, Ba^{2+}, Sr^{2+}, La^{3+} (0.02) ratios did not interfere [86].

In this work, the Ni (II) ion reacted with Isonicotinohydroxamine Acid (IHC) at pH=8.5 and formed a 1:2 lemon-green complex. The complex has a maximum absorption at 610 nm with ε=1.44·104 L/mol·cm. Beer's law was observed in the range of 0.32-4.80 μg/25mL. S.b.c. was 0.004 μg cm^{-2}. At Q_{min}=3.20 μg/25 mL, Sr=1.1 % (n=6). The tolerance limits for interfering ions have been discussed. To optimize reaction conditions, all variables were studied. The effectiveness of the proposed method was demonstrated by the successful application of nickel detection in water, wastewater, and alloys, and its accuracy and reproducibility were determined [87].

In this study, a new, simple, sensitive, and fast spectrophotometric method for determining the low content of Ni (II) is proposed. It has been established that the method is based on complex formation with a 1:2 ratio. 1- (4′-Pyrazolone-azo) 2,7-Naphthalendiol (PANDOL) was obtained as a new reagent. It was studied that the complex has maximum absorption at λ=514 nm and ε=20000 L/mol·cm. Graded graphical correlation was found in the range of 0.1-2.0 μg/mL. The accuracy and reproducibility of the method for determining various known amounts of Ni (II) were tested. To verify the selectivity of the method, the influence of various ions on the determination of Ni (II) was also studied. The value of the product stability constant is $1.3\cdot10^7$. The proposed method was successfully used in the analysis of synthetic mixtures and tea samples without initial concentration or separation [88]. In the article, 3-Hydroxy-3-N-Propyl-1- (4-Sulfonamidophenyl) Triazen was used for the Spectrophotometric determination of nickel (II) at 400 nm, and the pH was maintained from 6.9 to 7.3. Beer's law obeys in the range from $1\cdot10^{-5}$ to $6\cdot10^{-5}$ mol/L, ε=6743 L/mol·cm and S.s.=8.61 μg cm^{-2}. Ni (II) up to 100 μg has also been successfully detected in the presence of various interfering cations and anions. The reagent formed a 1:2 complex with Ni(II). The composition of the complex was determined by the Joube method. The stability constants, determined by two different methods, were 9.57 and 9.53, respectively [89].

In this work, a Spectrophotometric method for determining Ni (II) using 5-Bromo-2-Hydroxy-3-Methoxybenzaldehyde-P-Hydroxybenzoyl Hydrazone (5-BGMBAPGBG) was developed. Ni (II) reacts with 5-BGMBAPGBG at an acidic pH of 4.0-8.0, forming a green complex. The complex has maximum absorption at λ=440 nm. The spectrum of the second-order derivative of the complex showed peaks of λ=475 nm and λ=447 nm and zero points of λ=404.5 nm and λ=462.4 nm. It was noted that the amplitudes of the peaks linearly change with the concentration of Ni (II) at pH 6.0. They are subject to the equations A_{475} = 22.5476 C + 0.002 and A_{447} = 32.260 C + 0.046. Beer's law was observed in the range of 0.18-2.93 μg/ml at λ=475 and λ=447 nm. The correlation coefficients are 0.99996 at λ=475 nm and 0.99995 at λ=447 nm. For eleven determinations, Sr was 0.0734 at λ=475 nm and 0.0957 at λ=447 nm. The influence of various ions on the derivative amplitude has been studied. The method has been successfully used to determine Ni(II) in alloys, vegetable oil, and leaf samples [90].

The article developed a high-concentration, simple, inexpensive, and environmentally safe method for separating and determining low levels of nickel through UV/Vis Spectrophotometry in some environmental samples, such as wastewater from the city of Rushima in Iraq. The optimal conditions for the surfactant Triton X-100 (as a non-ionic surfactant) at λ=345 nm depended on several experimental parameters, such as the pH level of the solution, the reaction time of Triton X-100, the concentration of selenium, temperature, and metal concentration. The proposed method has a linear region of 10-60 $\mu g/ml^{-1}$, and the recovery of the analyzed substance is calculated to be within the range of 98-101 %. It was studied that the detection limits for Ni (II) are 0.535 $\mu g/mL^{-1}$, the correlation coefficient (R) =0.9991, Sr =0.22 %, and pH=10 [91].

In this work, it is shown that it is possible to determine the composition of four types of metal ions (Cu, Fe, Cr, Ni) simultaneously using multi-wave spectrophotometry. Measurement interferences of typically present Mg, Ca, and Zn ions were considered, and the best absorption wavelengths of four metal ions were found. The molar absorption coefficient at a special wavelength was determined, and an entirely linear equation was established. To verify the correctness of the linear equations, the prepared mixed solution of Cu, Fe, Cr, and Ni was measured by this method, and the result showed that the relative error can be controlled within ±5 %. Considering that the composition of metal ions can vary in various real samples, the lower limit of detection of this method was studied. The results of the experiments show that the content of Cu, Fe, Cr, and Ni is $Q_{min}=5\cdot10^{-4}$ mg/mL, $1\cdot10^{-3}$ mg/mL, $5\cdot10^{-3}$ mg/mL, $5\cdot10^{-3}$ mg/mL. respectively, and the possibility of obtaining a reliable result of quantitative analysis with a higher concentration of samples [92].

In the article, a new reagent, O-Chlorophenylazo-Bis-Acetoxime (OXFABAO) was used for the Spectrophotometric determination of Ni (II). Nickel formed a greenish-yellow complex with the reagent 1:2 (Ni: :P), soluble in ethanol. The working wavelength was obtained in the range of pH=7.3-7.9 at 370 nm (ε=2451 L/mol·cm). Beer's law was obeyed in the range of 0.117 - 0.939 μg/25mL, and S.b.c was 23.09 μg/cm^2. The values of lgβ, determined by two different methods, are 8.95 and 8.76, respectively. The influence of 24 types of foreign ions was studied [93].

In this work, the newly synthesized 2,4-Dihydroxybenzaldehyde Thiosemicarbazone (DGBATSK) was used as a chromogenic reagent in an aqueous Triton X-100 micellar medium at pH 7. The absorbance in the selected wavelength pair was observed with the addition of a standard solution of 463 and 500 nm. The obtained results showed that Ni (II) and Co (II) can be determined simultaneously at a concentration ratio of 5:1 to 1:5. For a solution containing Ni (II) and Co (II) at $5.0\cdot10^{-5}$ M, Sr was 1.86 % and 4.4 %, respectively. The influence of various ions on the determination of Cobalt (II) and Nickel (II) [94].

In this method, developed by the authors, Hydrazone compounds were used as selective and sensitive analytical reagents. It reacted with Nickel (II) at a pH of 9.0 and room temperature in an aqueous solution, forming yellowish M:L (1:1) complexes. Maximum absorption λ=410 nm and ε values of 5.92·104 L/mol·cm were determined. Beer's law was valid in the range from 0.1467 to 1.760 μg/mL of Ni (II). The newly developed methods have been successfully applied for the determination of Nickel (II) in Alloy samples [95].

The article examines a simple, sensitive, and selective method for the Spectrophotometric determination of Ni (II) in water samples. Analytical ions were collected in a red-colored complex with 1- (2-Pyridylazo) -2-Naphthol (PAN) on a membrane filter, and absorption spectra of the colored membrane filters were obtained. To optimize sensitivity, the influence of the pH value, sample volume, and PAN content was investigated. The mixing of other common ions was eliminated using appropriate masking agents. Absorption has a linear relationship with the concentration of Ni (II) in the range from 0.3 to 1.5 μg/mL^{-1} and from 2 to 10 μg/mL^{-1}, and the correlation coefficients (R^2) are 0.9871 and 0.9954. Under optimal conditions, the detection threshold was 0.1 μg/l. It was calculated that the recovery for the restored samples ranges from 95.0 % to 101.5 %, and the relative Sr from 2.8 % to 4.1 % [96].

In this work, the analytical characteristics of the method, such as the detection limit, linear region, Sr, and relative standard error under optimal conditions, are calculated. The calibrated graphs were linear in the range of 5-300 μg/mL^{-1} and 10-320 μg/mL^{-1}. Q_{min}=2.43 and 2.83 μg mL^{-1} were calculated for Co (II) and Ni (II), respectively. The influence of specific foreign ions has been studied. The developed method was successfully used for the simultaneous determination of Co (II) and Ni (II) in water samples [97].

The article describes the method of the first derivative Spectrophotometry for the simultaneous determination of Co (II) and Ni (II) with Alizarin red S in the presence of Triton X-100. The absorption region was investigated at wavelengths λ=549.0 nm for Co (II) and λ=546.0 nm for Ni (II). Linearity was obtained by the first derivative spectrophotometric method in the presence of each other in the range of 0.291-4.676 μg/mL of Ni (II) and 0.293-4.124 μg/mL of Co (II). The influence of various ions on possible interference was studied [98].

In this study, a simple Spectrophotometric method for determining Ni (II) using Isatin-3-Semicarbazone (ISC) as an analytical reagent was developed. The ISC was synthesized and characterized by elemental and spectral analysis. Ni (II) was isolated quantitatively (99.80 %) in isoamyl alcohol from an aqueous solution with a pH range of 5.5 - 7.2. Isoamyl alcohol extract showed a peak intensity at λ=500 nm. Beer's law is obeyed by the Ni (II) concentration in the range of 1.0-6.0 μg/mL. It was calculated that S.s. and ε were 7.32 μg cm^{-2} and 8014.07 L/mol·cm, respectively. The composition of the extracted species was 1:2 (Ni: ISK) according to the methods of isomolar series and molar ratio. The degree of interference of various foreign ions has been studied. The developed Spectrophotometric method was successfully used to determine Ni (II) in Alloy samples [99].

In this article, a method has been developed for measuring the micro-concentrations of Nickel and Cobalt in aqueous solutions and natural water using the method of pulse inversion Chronopotentiometry with sufficient reproducibility and accuracy in accordance with the criteria of metrological certification [100]. The article presents the results of Potentiometric Titration of a Ni (II) containing solution with a Sodium Diethyldithiocarbamate (DDTC-Na) solution. The effectiveness of electrochemical analysis depends on the presence of the most suitable indicator system. The feasibility of using known ion-selective electrodes as sensors for nickel ions has been investigated. It is noted that the optimal conditions for the Potentiometric determination of Ni (II) have been studied [101]. In this work, presented by the researchers, it was found that nickel can be successfully detected in a weakly alkaline medium only using glassy carbon and shungite electrodes. It has been established that the analytical signal of the last electrode is also several times higher than the signal from the glassy carbon electrode. It has been shown that, unlike cobalt ions, semiconductor electrodes based on Silicon and Germanium do not respond to the presence of Nickel ions, which can be used to develop a selective voltammetric method for determining Nickel and Cobalt in one solution using several types of indicator electrodes [102; 545-551]. In this article, studied by scientists, a sensitive and fast method for determining nickel in food products based on atomic absorption spectrometry has been developed. The test results showed that Sr was 0.020 mg/kg. The developed method was successfully used to assess the Ni(II) content in food products [103].

In this study, reliable and straightforward methods of Chelatometric Titration of Cu (II), Ni (II), and Pb (II) ions in the flow injection analysis mode using conductometric determination are proposed. The possibility of separate titration of these ions in the mixture (molar ratio 1:1) has been proven. If the volume of the dosed sample was 200 mL, then the range of the determined content was (0.006-0.6) mg/L. It is noted that the relative error was 10-20 % [104].

In the article, the sample solution was dissolved with HCl before loading to determine Ni, Mg, Cr, Al, and Co using ICP-MS. After studying the spectral sounds for the selected elements, the correct analytical spectral lines were selected. Adding the same amount of Fe as the samples in the mixed standard solution can eliminate matrix mixing. The results of the experiments showed that the reduction factors of Mg, Ni, Al, and Co are 96.83 % -105.23 %, and Sr does not exceed 3.3 % [105].

In this study, parameters (for example, the pH value of the sample, the flow rate of the sample and eluent, the type and volume of the elution solution, as well as the presence of interfering ions) influencing the simultaneous pre-concentration of Ni (II), Pb (II), and Cd (II) ions were studied and optimized. Under optimal experimental conditions, the detection limits of this method for Pb (II), Ni (II), and Cd (II) ions in real solution were 0.32, 0.17, and 0.04 μg/mL^{-1}, respectively. Q_{min} 2.0 μg/mL of lead and nickel, 1.0 μg/mL of cadmium were calculated. For seven repeated determinations of Pb (II), Ni (II), and Cd (II) ions, the average absorbances of 0.074, 0.151, and 0.310 were calculated, respectively, and the Sr values of 1.7 %, 1.5 %, and 1.2 %. The developed method was used to determine small amounts of lead, cadmium, and nickel in biological and water samples [106]. The article developed a solid-phase extraction method for the determination of Copper, Nickel, and Zinc ions in natural water samples. This method is based on the adsorption of Copper, Nickel, and Zinc on multilayer carbon nanotubes impregnated with Di- (2-Ethylhexylphosphoric Acid) (D2EHPA) and Tri-N-Octylphosphine Oxide (TOFO). The influence of such parameters as the pH value of the aqueous solution, the amount of adsorbent, the flow rate of the sample and eluent, matrix effects, and the concentration of D2EGFK-TOFO was studied. Desorption studies were conducted with 2 mol/L HNO_3. The concentrations of copper, nickel, and zinc were determined by flame atomic absorption spectrometry.

The results showed that the maximum adsorption of Copper, Nickel, and Zinc occurs at a pH of 5.0 with a multilayer carbon nanotube of 500 mg. The three-sigma detection limits were 50 μg/L for copper, 40 μg/L for nickel, and 60 μg/L for zinc. It was established that the highest enrichment factors are the adsorption capacity of multilayer carbon nanotubes D2EGFK-TOFO, which is 4.90 mg/g for copper, 4.78 mg/g for nickel, and 4.82 mg/g for zinc. The developed method was used in practice for the determination of Ni (II), Cu (II), and Zn in electrocoating wastewater and real water samples with satisfactory results (Sr < 10 %) [107].

The purpose of this work is to determine Fe, Cu, Ni, and Zn in samples of vegetable oils using high-precision flame atomic absorption spectrometry of a constant source. The main lines were selected for all the studied metals, and the detection limits (3s, n=10) were 0.12, 0.62, 0.58, and 0.12 mg/kg for Fe, Cu, Ni, and Zn, respectively. The relative standard deviation ranged from 5 % to 11 % in samples containing 0.25 and 1.5 μg/mL of each metal, respectively. Recovery ranged from 89% to 102%. The proposed method was used to determine Fe, Cu, Ni, and Zn in soybean, olive, and sunflower oils [108].

In this article, a precise and straightforward Electroanalytical method for determining the simultaneous content of Nickel and Zinc in industrial wastewater using polarography is established. With this method, it was possible to determine the amount of Nickel and Zinc simultaneously. The polarogram recorded for industrial wastewater in Potassium Thiocyanate as a supporting electrolyte showed two cathodic peaks at -0.67 V and -0.98 V relative to the Saturated Calomel Electrode, which was confirmed by the standard addition method to consist of Nickel and Zinc. For Nickel and Zinc, the linear dynamic range ranged from 2.795 μg/mL to 18.214 μg/mL and from 3.114 μg/mL to 20.293 μg/mL, respectively [109].

6. Degree of Investigation of the Problem

A significant contribution to the development of Spectrophotometric determination of metal ions, as well as Cu (II), Zn, and Ni (II) ions, was made by foreign scientists: A.N. Vernigora, Y.N. Guskova, K.V. Katrich, and N.D. Shepina, I.V. Misnik, A.Z. Zalov, Y. Karaman, T.A. Ali, A.F. Mohammed, S.J. Baqir, L. Zhao, E. Tesfaye, A. Sreekanth, T.V. Antonova, S. A. Chernenko, B. Ranganath, O.I.

Yurchenko, A.S. Batrak, X.D. Li, Q.Z. Zhai, H.J. Mohammed, R. Khanam, S. Khan, R. Dashora, A. Giri, T.S. Reddy, N. Chandrasekhar, P.A. Borade, A.S. Gupta, V.D. Barhate, V.A. Funtikov, E.V. Shtrans, O. Modern Uzbek scientists also occupy a worthy place in this scientific field. In particular, as a result of scientific research conducted in recent years by Academician Sh.T. Tolipov and his students R.Kh. Djiyanbayeva, N.B. Babaev, A.T. Tashkhodzhaev, T.K. Khamrakulov, A.M. Gevorgyan, K.Z. Rakhmatullaev, I.P. Shesterova, Kh.Kh. Turaev, O.F. Fayzullaev, N.T. Turabov, E. Abdurakhmanov, Z.A. Smanova, Z.Z. Yakhshiyeva, A.M. Nasimov, and other scientists have achieved significant successes in the synthesis of new organic analytical reagents and their introduction into practice. In the course of the research, the sensitivity, selectivity, and accuracy of the analysis methods using the proposed reagents were increased to a high level, and the possibilities of their wide application were scientifically proven. However, research in ecological and analytical analyses for the Spectrophotometric determination of Cu (II), Zn, and Ni (II) ions using new organic reagents has not been sufficiently studied in practice(Table 11-13).

Table 11. Optimal conditions for determining Cu (II) and comparison of some analytical characteristics

№	Name of reagent	pHopt	Molar ratio Cu:R	Beer's law validity range	ε_{real}, $L\cdot mol^{-1}\cdot cm^{-1}$	References
1	N-benzoyl-N′-(phenylsulfonyl)hydrazine	11.5	1:01	0.3 – 1.90 mg / 25 mL	2759	[29]
2	3-((E)-2-hydroxy-benzylidene)hydrazono)indolin-2-one	4.0	1:01	0.5 – 6.5 µg / 25 mL	13000	[30]
3	Indigo	2.2	1:02	5.0 – 70.0 µg / 25 mL	41000	[31]
4	1-phenyl-2-[2-hydroxy-3-sulfo-5-nitrophenylazo]butadione-1,3	3.0	1:02	6.0 – 76.0 µg / 25 mL	14000	[32]
5	Sodium salt of 2,7-bis(azo-2-hydroxy-3-sulfo-5-nitrobenzene)-1,8-dihydroxynaphthalene-3,6-disulfonic acid	3.0	1:02	3.0 – 58.0 µg / 25 mL	10400	[36]
6	1-(2-methoxyphenylamino)-3-methoxypropan-2-ol	5.4 – 6.8	1:02	1.0 – 16.0 µg / 25 mL	43200	[38]
7	Disodium salt of 4-hydroxy-3-(4-sulfonato-1-naphthyl azo)-1-naphthalene sulfonate	5.95	1:02	5.0 – 50.0 µg / 25 mL	48000	[39]

Table 12. Optimal conditions for determining Zn (II) and comparison of some analytical characteristics

№	Name of reagent	pHopt	Molar ratio Zn:R	Beer's law validity range	ε_{real}, $L\cdot mol^{-1}\cdot cm^{-1}$	References
1	Xylenol orange	5,8	1:02	5.0 – 20.0 µg / 25 mL	31200	[55]
2	Methylthymol blue	5,0	1:02	5.0 – 25.0 µg / 25 mL	20000	
3	Pyrocatechol violet	7,5	1:02	8.0 – 25.0 µg / 25 mL	13400	
4	2,7-dinitroso-1,8-dioxynaphthalene-3,6-disulfonic acid	6,73	1:02	2.0 – 35.0 µg / 25 mL	19305	[56]
5	m-cresolphthalein complexone (S)	7,0	1:01	3.0 – 20.0 µg / 25 mL	24000	[57]
6	[4,5-diphenyl-2-((1E)-(4-(1-(2-phenylhydrazono)ethyl)phenyl)diazenyl)-4H-imidazole]	7,5	1:02	0.5 – 27.0 µg / 25 mL	4400	[59]
7	Sodium salt of 4-hydroxy-3-(4-sulfonato-1-naphthylazo)-1-[4-amino-5-hydroxy-6-[(5-methyl-2-pyridyl)azo]-3-sulfo-1-naphthyl]sulfonic acid	6,5	1:02	1.0 – 18.0 µg / 25 mL	42000	[64]

Table 13. Optimal conditions for determining Ni (II) and comparison of some analytical characteristics

№	Name of reagent	pHopt	Molar ratio Ni:R	Beer's law validity range	εmax, L·mol⁻¹·cm⁻¹	References
1	2,7-dinitroso-1,8-dioxynaphthalene-3,6-disulfonic acid	9.15	1 : 2	5.0 – 55.0 μg / 25 mL	23585	[78]
2	5-(2-bromo-5-methoxybenzylidene)thiazolidine-2,4-dione	7.1–8.9	1 : 2	0.3 – 13.0 μg / 25 mL	17500	[80]
3	Sulfosalicylic acid	7.2	1 : 1	2.0 – 20.0 μg / 25 mL	669	[81]
4	Esomeprazole	5.0	1 : 2	3.0 – 35.0 μg / 25 mL	24000	[82]
5	Xylenol orange (Chlorophosphonazo-III)	3.5	1 : 2	2.5 – 87.5 μg / 25 mL	14000	[86]
6	Isonicotinic hydroxamic acid	8.5	1 : 2	8.0 – 120.0 μg / 25 mL	14400	[89]
7	1-(4′-pyrazol-azo)-2,7-naphthalenediol	6.95	1 : 2	2.5 – 50.0 μg / 25 mL	20 000	[88-112]

7. Conclusion

Analysis of the literature studied during the research shows that in some existing methods, in cases of high sensitivity, selectivity is low, and in cases of high selectivity, sensitivity is low. Therefore, the development of fast, sensitive, selective, express, and inexpensive methods for determining Cu (II), Zn, and Ni (II) ions is still a pressing problem. Numerous studies have been conducted using many organic reagents for the Spectrophotometric determination of Cu (II), Zn, and Ni (II) ions. However, not all of them are specific or sensitive, since the functional-analytical groups in the molecules also react to a certain extent with the cations of other metals. Further efforts of researchers are aimed at improving known methods, mainly increasing their sensitivity and selectivity, which requires the selection of masking agents to eliminate the influence of interfering elements, as well as the search for new sensitive and selective reagents. Determination of Cu (II), Zn, and Ni (II) ions is carried out by Gravimetric, Titrimetric (Oxidation-Reduction Methods, Precipitation, Complex Formation), Photometric, Spectrophotometric, Atomic Absorption, Atomic Emission, Electrochemical, Catalytic, and Radioactivation Methods. In this work, the methods of Spectrophotometric analysis are widely covered. Methods based on organic reagents are important for determining the quantity of Cu (II), Zn, and Ni (II) ions by the spectrophotometric method.

Authors' Declaration

We hereby confirm that all the Figures and Tables in the manuscript are ours.

Ethical Clearance

The local ethical committee at the Termez Institute of Engineering and Technology and Termez State University approved the project.

Authors' Contribution Statement

N.Sh.S. conducted the research, T.Kh.Kh. the conception, design, and drafting, N.B.A was responsible for the acquisition of data, Sh.R.S. did the interpretation; K.Sh.A. participated in the conception, design, and drafting, and all the authors took part in revision and proofreading.

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