**REPUBLIC OF AZERBAIJAN**

*On the rights of the manuscript*

# ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

## MIXED-LIGAND COMPLEXES OF IRON (III) AND COPPER (II) WITH HYDRAZONE ANDAROMATIC AMIN BASED REAGENTS IN PHOTOMETRICAL ANALYSIS


Specialty: 2301.01 – Analytical chemistry

Field of science: Chemistry

Applicant: **Chinara Allahverdi Mammadova**


**BAKU – 2022**

The dissertation work was carried out at the "Ecological Chemistry and Environmental Protection" research laboratory under the Department of Ecological Chemistry of the Faculty of Ecology and Soil Science of Baku State University and at the Department of Analytical Chemistry of the Faculty of Chemistry.

Scientific supervisors: – doctor of chemical sciences, professor
**Famil Musa Chiragov**
– doctor of chemical sciences, professor
**Namig Gurbat Shikhaliyev**.

Official opponents: of chemical sciences, professor
**Ali Zal Zalov**
doctor of chemical sciences, professor
**Elman Mahammad Movsumov**
doctor of philosophy in chemistry,
associate professor
**Fatali Elmar Huseynov**

Dissertation council ED 2.16 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at Baku State University

Chairman of the Dissertation council:
doctor of chemical sciences, professor
_____**Valeh Mehrali Ismaylov**

Scientific secretary of the Dissertation council:
doctor of philosophy in chemistry, …
associate professor
_____**Farid Nadir Naghiyev**

Chairman of the scientific seminar:
doctor of chemical sciences, professor
_____**Khalil Jamal Naghiyev**

## GENERAL CHARACTERISTICS OF WORK

**Relevance and development of the topic.** One of the most important problems of modern analytical chemistry is the synthesis of new coordination compounds with a wide range of practical applications and the study of their physicochemical properties. It is known from the literature that hydrazones and aromatic amine-based compounds have been widely used in the last few decades for the spectrophotometric determination of metal ions. Hydrazones act as multidentate ligands with transition metals to form colored complex compounds. These complexes are used for the selective and sensitive determination of metals. Aromatic amine-based compounds and their metal complexes are widely used as catalysts in various biological systems, in the production of polymers, dyes, pharmaceuticals and pharmaceuticals. Derivatives of hydrazone and their metal complexes are antibacterial, anti-tuberculosis, antifungal, antifungal, antiviral, anti-inflammatory, etc. has a number of broad-spectrum effects such as. Therefore, the synthesis of new reagents based on hydrazone and aromatic amines, spectrophotometric study of complex compounds formed with metal ions, the study of physical and chemical properties, the development of sensitive and selective methods for various objects are theoretically and practically relevant.

On the other hand, the study of the formation of various ligand complexes is a topical issue in the field of analytical chemistry. This is due to the fact that the use of multicellular complexes is accompanied by an increase in analytical parameters such as selectivity and sensitivity. This allows the development of design methods with high analytical performance for many elements.

**Object and subject of the research.** Synthesis of hydrazone and aromatic amine-based reagents. Development of photometric determination methods for iron (III) and copper (II) with synthesized reagents.

**Aims and objectives of the study.** The main purpose of the

study is the synthesis of hydrazone and aromatic amine-based reagents and the study of binary and mixed-ligand complexes formed by iron (III) and copper (II) with synthesized organic reagents, the development of spectrophotometric determination methods which allow their sensitive, selective determination at various sites.

In order to achieve the set goal, it is necessary to solve the following practical and theoretical issues:

- synthesis of hydrazone and aromatic amine-based reagents, their identification by various methods
- determination of dissociation constants of synthesized reagents, as well as stability constants of complexes formed by reagents with a number of metal ions
- study of complex compounds of synthesized reagents formed by iron (III) and copper (II) by various physicochemical methods
- spectrophotometric study of binary and mixed-ligand complexes formed by iron (III) and copper (II) of hydrazone and aromatic amine-based reagents
- development of spectrophotometric determination methods that allow sensitive, selective determination of iron (III) and copper (II) in various objects

**Research methods.** In order to achieve the set goal X-ray structure analysis (XRSA), nuclear magnetic resonance (NMR), infrared (IR) spectroscopy, potentiometric, conductometric, thermal, and spectrophotometric analysis methods were used .

**The main provisions of the defense:**

- 5 reagents based on hydrazone and aromatic amines were synthesized; they were identified by X-ray structure analysis, NMR, IR-spectroscopy methods. Monocrystals of two of the reagents were obtained, molecular and crystalline structures were studied by RQA method.
- the values of dissociation constants of the synthesized reagents were determined by the pH-metric titration method and the form of the reagents in the solution was studied. The stability constants of

the complexes formed by the reagents with a number of metal ions have also been determined.

- some of the complexes formed by the synthesized reagents iron (III) and copper (II) were studied by IR-spectroscopy and thermogravimetric analysis methods and their specific electrical conductivity was studied.
- basic spectrophotometric characteristics (molar absorption coefficient of complexes, determination of composition, optimal pH, interval of Ber's law) formed by hydrazone and aromatic amine-based reagents of iron (III) and copper (II) complexes were determined and stability constants were calculated.
- the effect of foreign ions and binders on the formation of complexes with iron (III) and copper (II) of new reagents based on hydrazone and aromatic amines was studied.
- methods for sensitive, selective photometric determination of iron (III) and copper (II) in various natural and industrial facilities have been developed.

**Scientific novelty of the research.**

- Synthesized hydrazone and aromatic amine-based reagents were used for the photometric determination of iron(III) and copper(II).
- The structure of the reagents was studied by NMR and IR spectroscopy methods.
- Crystal structure and crystallographic parameters of 3–((E)-2-hydroxybenzylidene)hydrozono) indolin-2-on and 2-(((1-(3-bromophenyl)ethylidene)-hydrazono) methyl reagents were studied by X-ray structure analysis method studied.
- The structure of some complex compounds formed by reagents with iron (III) and copper (II) has also been studied by IR spectroscopy and thermogravimetric analysis methods.
- Based on the results obtained during the study of complex compounds by physicochemical methods, it was determined that the complexes have high analytical properties.

- Methods for sensitive, selective photometric determination of iron (III) and copper (II) in various natural and industrial facilities have been developed.

**Theoretical and practical significance of the research.** Methods for the determination of iron (III) and copper (II) using synthesized hydrazone and aromatic amine-based reagents directly in various industrial and natural facilities, such as rocks, sea water, wastewater, Al-based alloys, various grades of iron (III) peas, buckwheat, bananas, beans, mushrooms, hips, wheat groats and white bread, using synthesized hydrazone and aromatic amine-based reagents have been developed.

**The applicant's personal contribution to the research.** The applicant was directly involved in the research. Analyzed the literature on the synthesis of hydrazone and aromatic amine-based reagents, their application in the analytical chemistry of iron (III) and copper (II). She took an active part in the implementation of experimental work. She has co-authored and commented on the research.

**Approbation and application.** Based on the materials of the dissertation, 25 scientific works were published. Seven of them are articles (2 of them are included in the Web of Science database), 19 are thesises. The results of the dissertation were presented at conferences held in Azerbaijan and Russia:

- VIII Republican Scientific Conference of Doctoral Students, Masters and Young Researchers “Actual Problems of Chemistry” dedicated to the 91st anniversary of the national leader H.Aliyev (Baku, 2014)

- IX Republican Scientific Conference of Doctoral Students, Masters and Young Researchers “Actual Problems of Chemistry” dedicated to the 92nd anniversary of the national leader H.Aliyev (Baku, 2015)

- XXVII Scientific Conference of Russian Youth "Problems of Theoretical and Experimental Chemistry" (Yekaterinburg, 2015)

- XI Republican Scientific Conference of Doctoral Students, Masters and Young Researchers “Actual Problems of Chemistry”

dedicated to the 94th anniversary of the national leader H.Aliyev (Baku, 2017)

- VI Republican Scientific Conference "Actual problems of ecology and soil science in the XXI century" dedicated to the 94th anniversary of national leader Heydar Aliyev (Baku, 2017)

- VIII Republican Scientific Conference "Actual problems of ecology and soil science in the XXI century" dedicated to the 96th anniversary of national leader Heydar Aliyev (Baku, 2019)

- XIII International Scientific Conference of Doctoral Students, Masters and Young Researchers "Actual Problems of Chemistry" dedicated to the 96th anniversary of the national leader Heydar Aliyev (Baku, 2019)

- XVI International Conference "Spectroscopy of Coordination Compounds" (Tuapse, 2019)

- III All-Russian Conference on Analytical Spectroscopy (Krasnodar, 2019)

- XXX Russian Youth Scientific Conference "Problems of Theoretical and Experimental Chemistry" (Yekaterinburg, 2020)

- XVII International Conference "Spectroscopy of Coordination Associations" (Krasnodar, 2020)

- VIII International Scientific Conference "Chemistry of Coordinating Compounds" dedicated to the 85th anniversary of the Department of Analytical Chemistry (Baku, 2020),

- II Republican Scientific Conference "Actual problems of ecology and soil sciences in the XXI century" dedicated to the 98th anniversary of the national leader H.Aliyev (Baku, 2021)

- Professor V.M. XXXI Russian Youth Scientific Conference "Theoretical and Experimental Chemical Problems" dedicated to the 90th anniversary of Zhukovsky (Yekaterinburg, 2021).

**Name of the organization where the dissertation work is carried out.** The dissertation work was carried out at the "Ecological Chemistry and Environmental Protection" research laboratory under the Department of Ecological Chemistry of the Faculty of Ecology and

Soil Science of Baku State University and at the Department of Analytical Chemistry of the Faculty of Chemistry.

**The total volume of the dissertation with a sign, indicating the volume of the structural units of the dissertation separately.** The dissertation consists of an introduction, five chapters, a conclusion and a list of references, covering 184 pages in A4 format. The results of the research are presented in 69 figures and 56 tables. The list of used literature includes 143 sources cited in the dissertation. The main part of the case consists of 161827 characters.

*The first chapter (53427 characters)* analyzes the literature of the last 10 years related to the research on the dissertation. Important analytical characteristics of the methods developed for the photometric determination of iron (III) and copper (II) are given. Analysis of the literature shows that organic reagents containing nitrogen and oxygen donor atoms are more commonly used in natural and industrial facilities for the determination of iron (III) and copper (II) by spectrophotometric methods.

*The second chapter (22921 characters).* The second chapter deals with the synthesis, identification of solutions, devices, reagents and determination of their physicochemical constants.

*The third chapter (19633 characters)* shows the study of the complex formation of reagents with iron (III) and copper (II) by various methods of physical and chemical analysis.

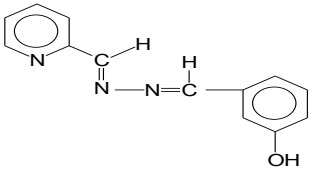
*Chapter Four (29408 characters).* The study of the formation of complexes with iron (III) and copper (II) reagents by spectrophotometric method is explained. The optimal conditions for the formation of the complex have been identified.

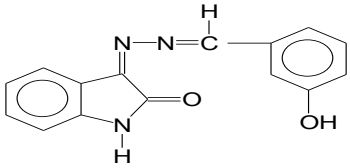
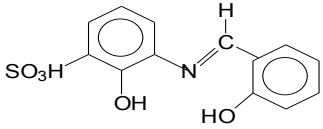
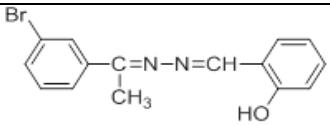
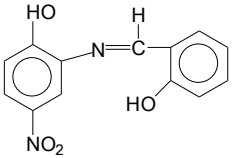
*In the fifth chapter (27702 characters)* the methods of photometric determination of iron (III) and copper (II) in the form of identical and different-ligand complexes in various natural and complex objects are given.

## MAIN CONTENT OF THE WORK. PHYSICAL AND CHEMICAL PROPERTIES OF REAGENTS

In the dissertation 5 organic reagents - synthesized on the basis of hydrazones - 2-((E)-(((E)-1-pyridine-2-il) ethylidene)hydrazono) methyl)phenol ($R_1$), 3-((E)-2-hydroxybenzylidene)hydrazo)indolin-2-on ($R_2$), 2-((1-(3-bromophenyl)ethylene)hydrazono)methyl) synthesized on the basis of phenol ($R_4$) and aromatic amines - (E) -2-hydroxy-3 - ((2-hydroxybenzilide)(amino)benzenesulfuric acid ($R_3$), 2 - (((4nitrophenyl)imino)methyl phenol ($R_5$) were used. Three of these reagents 2-((E)-(((E)-1-pyridine-2-il)ethylidene)hydrazono)methyl) phenol ($R_1$), (E)-2-hydroxy-3-((2-hydroxybenzylidene)(amino) benzene sulfuric acid ($R_3$) and 2- (((1-(3-bromophenyl)ethylidene) hydrazono)methyl)phenol) ($R_4$) are the first reagents synthesized by us. Two of the reagents ($R_2$ and $R_5$) are known from the literature as organic compounds. $1 \cdot 10^{-3}$ M and $2 \cdot 10^{-3}$ M solutions of reagents were used in the study. Solutions of reagents synthesized on the basis of hydrazones ($R_1$, $R_2$ and $R_4$) were prepared by dissolving their accurate samples in water-alcohol medium. Solutions of reagents synthesized on the basis of aromatic amines ($R_3$, $R_5$) were prepared by dissolving their exact samples in aqueous medium. The symbols, chemical formulas and names of the reagents used in the study are given in Table 1.

**Table 1.** Structural formula and names of synthesized reagents.

| Symbol | Chemical formula | Name |
|---|---|---|
| $R_1$ |  | 2-((E)-(((E)-1-pyridine-2-il) ethylidene)hydrazono) methyl)phenol |

| | | |
|---|---|---|
| $R_2$ |  | 3-((E)-2-hydroxy benzylidene) hydrazo)indolin-2-on |
| $R_3$ |  | (E)-2-hydroxy-3-((2-hydroxybenzylidene) (amino)benzene sulfuric acid |
| $R_4$ |  | 2-((1-(3-bromophenyl) ethylene) hydrazono)methyl |
| $R_5$ |  | 2-(((4nitrophenyl) imino)methyl phenol |

**Identification of reagents.** Infrared spectroscopy (IR), nuclear magnetic resonance (NMR) and X-ray structure analysis methods were used to study the composition and structure of the reagents synthesized during the study. As mentioned above, the infrared spectroscopy method was also used to obtain detailed information on the structure of the reagents. In order to identify the synthesized reagents, their IR spectra were taken. In interpreting the spectra, reference is made to available empirical data on the relationship between absorption bands and the structural elements of molecules. A comparison of the spectra of the reagents showed that in all cases a new absorption band appears in the spectra of the reagents in the region of 1590-1570 $cm^{-1}$, which can be attributed to the oscillations

of the azometine group. It is known from the literature that the oscillations of the azometine group are observed in the frequency range of 1560-1645 $cm^{-1}$. The absorption bands observed in the IR spectra in the frequency range 1270-1220 $cm^{-1}$ are the deformation oscillations of the hydroxy group (-OH) in the benzene ring. Absorption bands with a frequency of 2923 $cm^{-1}$ observed in the IR spectrum of each of the reagents confirm the presence of an aromatic ring. In addition, the absorption bands observed in the IR spectrum of reagents at 700-900 $cm^{-1}$ indicate the presence of an aromatic ring. Valence oscillations of pyridine in the IR spectrum of 2-((E)-(((E)-1-pyridine-2-il) ethylidene)hydrazono) methyl)phenol ($R_1$) are observed at a frequency of 1571 $cm^{-1}$ 3-((E)-2-hydroxybenzylidene) hydrazo)indolin-2-on ($R_2$) absorption band in the frequency range 3565 $cm^{-1}$ corresponding to the valence oscillations of the NH group of indole in its ($R_2$) IR spectrum and 1715 $cm^{-1}$ corresponding to the valence oscillations of the > C = O bond The absorption band in the frequency range $cm^{-1}$ was observed. In the IR spectrum of (E)-2-hydroxy-3-((2-hydroxybenzilide)(amino)benzenesulfuric acid ($R_3$), an absorption band in the frequency range 1160-1140 $cm^{-1}$ corresponding to the valence oscillations of the C-$SO_3$H bond was observed.

$^1$H and $^{13}$C NMR spectra were drawn to determine the structure of the synthesized reagents.

2-((E)-(((E)-1-pyridine-2-il)ethylidene)hydrazono)methyl)phenol ($R_1$)solution - 9 signals at room temperature in the spectrum $^1$H NMR in DMSO, three of which are triplet, three duplets and three singlets. The proton of the OH group is at 11.39 d.m. of the signal, and the proton of the azometine group is at 8.92 d.m (d), and the protons of the aromatic cycle are 6.97–8.68 d.m observed in the range.

$^1$H. NMR (DMSO -$d_6$,δ): 6.97(d,2H,2$CH_{ar}$); 7.39(t,1H, $CH_{ar}$); 7.49(t,1H, $CH_{ar}$); 7.67(d,1H,$CH_{ar}$); 7.87(t,1H,$CH_{ar}$); 8.21(d,1H,$CH_{ar}$); 8.68(s,1H,$CH_{ar}$); 8.92(s,1H,CH=); 11.39(s,1H,OH)

$^{13}$C. NMR (DMSO-$d_6$,δ): 14.94($CH_3$), 116.36($CH_{ar}$), 120.01 ($CH_{ar}$), 122.90($CH_{ar}$), 126.84($CH_{ar}$), 132.46($CH_{ar}$), 133.92($CH_{ar}$),

136.35($CH_{ar}$), 148.96($CH_{ar}$), 155.11($C_{ar}$), 159.38($C_{ar}$), 163.02($CH_{ar}$), 164.28($C_{ar}$), 167.21($C_{ar}$)

3-((E)-2-hydroxybenzylidene)hydrazo)indolin-2-on ($R_2$) NMR-spectrum can be concluded as follows: NMR 1H (DMSO-d6, δ, mh) 11.45 (d, OH-Ph), 8.81 (d, N = CH), 9.91 (d, NH), 6.81-7.71 (m, 4H, Ar). Observation of the signal at 11.25 d.m. (d) indicates that the proton of the OH group forms a strong hydrogen bond. The proton of the azomethine group is 8.81 d.m. (d), and the proton of the indole ring is NH 9.91 d.m. (d) is observed. The protons of the aromatic cycle are 6.81-7.71 d.m observed in the range.

From the spectra of $^{1}H$ and $^{13}C$ NMR of (E)-2-hydroxy-3-((2-hydroxybenzilide)(amino)benzene sulfuric acid ($R_3$) the following can be concluded:

$^{1}H$ NMR (DMSO -$d_6$,δ): 6.86-7.89(m,8H,2Ar); 9.02(s,1H,CH=); 9.82(s,1H, $OH_{ar}$); 13.98(s,1H,OH)

$^{13}C$ NMR (DMSO-$d_6$,δ): 117.12($CH_{ar}$), 117.14($CH_{ar}$), 119.24($CH_{ar}$), 120.19($CH_{ar}$), 128.71($CH_{ar}$), 132.84($CH_{ar}$), 133.62($CH_{ar}$), 135.64($C_{tert}$), 151.89($C_{tert}$), 161.26($C_{tert}$) , 162.32($C_{tert}$)

Using the X-ray diffraction method, 3-((E)-2-hydroxybenzilide)hydrozo)indolin-2-on ($R_2$) and 2-((1-(3-bromo phenyl)ethylidene)hydrozone)methyl)phenol ($R_4$) Molecular and crystallographic structures of reagents were determined:

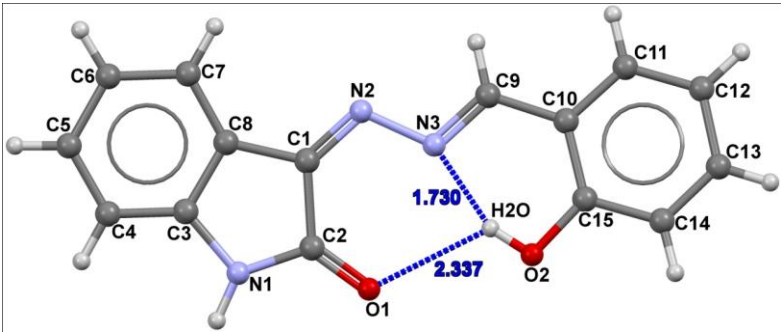



**Figure 1.** Molecular structure of $R_2$ reagent.

3-((E)-2-hydroxybenzylidene)hydrazo)indolin-2-on ($R_2$) mo - nocrystals are obtained by double recrystallization of the reagent in ethyl alcohol. For this purpose, the reagent is completely dissolved by heating in ethanol and then stored at room temperature. After about 1 week, the orange monocrystals of the reagent began to precipitate. The obtained crystals were filtered through filter paper and dried. The single crystal has a rhombic syngonium, consisting of 2 aromatic rings and a five-membered ring. The molecule has a plane structure. There are 2 intramolecular hydrogen bonds in the structure: the length of N3 ... $H_2O$ is 1,730 Å, the length of O1 ... $H_2O$ is 2,337 Å.

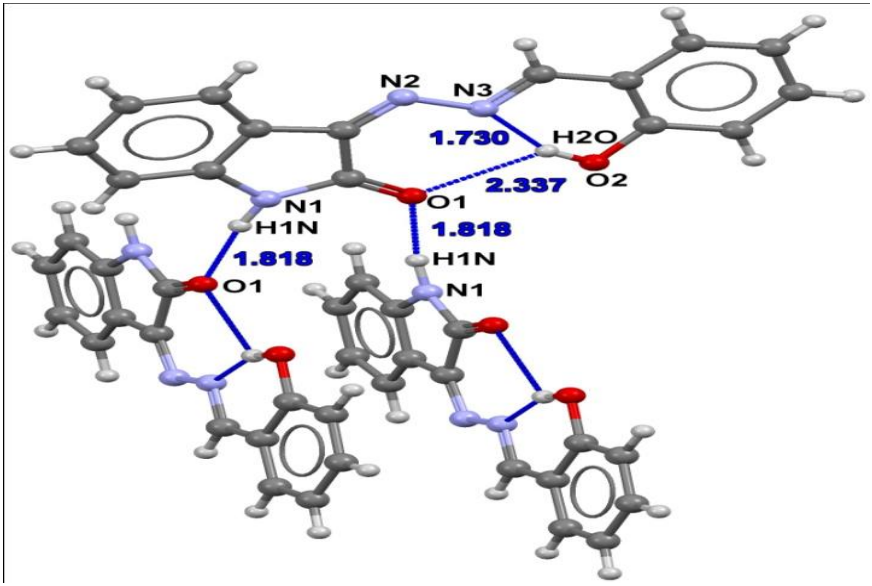



**Figure 2.** Crystallographic structure of reagent $R_2$.

In the crystal lattice, the molecules are joined together by an intermolecular hydrogen bond (O1 ... HN1 length 1,818 Å). Each molecule combines with other molecules in 2 intermolecular hydrogen bonds. Monocrystals of reagent 2- (((1-(3-bromophenyl)ethylidene)

hydrazono)methyl)phenol) ($R_4$) ($C_{15}H_{13}BrN_2O$) are obtained by double recrystallization of the reagent in ethyl alcohol. For this purpose, 2-(((1-(3-bromophenyl)ethylidene)hydrazono)methyl)phenol) ($R_4$) is heated in ethanol and kept at room temperature after complete dissolution. After about 4 days, the yellow, needle-like single crystals of the reagent began to precipitate. The obtained crystals were filtered through filter paper and dried. The single crystal has a monoclinic syngonium and consists of 2 aromatic rings. The compound contains Br ion. The molecule has a plane structure. There are 2 intramolecular hydrogen bonds in the structure: the length of H1 ... N2 is equal to 1,898 Å.

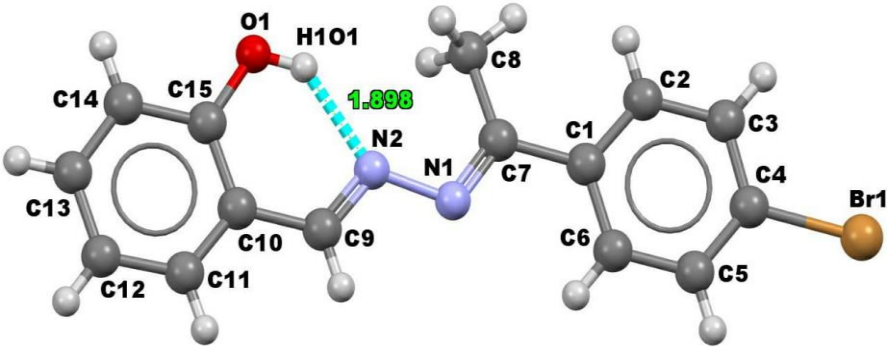



**Figure 3.** Molecular structure of $R_4$ reagent.

**Determination of dissociation constants of reagents.** The values of the dissociation constants of the reagents synthesized by the pH-metric titration method were determined and calculated according to Schwarzenbach's mathematical method. The remaining reagents are insoluble in water, except for $R_3$ and $R_5$. Therefore, the titration was performed in a water-alcohol medium.

The values of the dissociation constants of the reagents synthesized by the pH-metric titration method were determined.

**Table 2.** Values of dissociation constants of reagents

| | $pK_1$ | $pK_2$ |
|---|---|---|
| $R_1$ | 10,72± 0,06 | |
| $R_2$ | 9,48± 0,03 | |
| $R_3$ | 8,47± 0,03 | 9,38± 0,04 |
| $R_4$ | 9,66± 0,02 | |
| $R_5$ | 6,51± 0,04 | 8,63± 0,03 |

As can be seen from the table, three of the reagents used ($R_1$, $R_2$, $R_4$) are monobasic and two are bibasic weak acids ($R_3$, $R_5$), which are in molecular and ionic form depending on the pH value. We assume that (E)-2-hydroxy-3-((2-hydroxybenzilide)(amino) benzenesulfuric acid ($R_3$) and ), 2 - (((4nitrophenyl)imino)methyl phenol ($R_5$) $pK_1$ aminophenol fragment characterizes the process of separation of H + ions from OH groups, and $pK_2$ from OH groups in the salicylic aldehyde fragment, respectively. Determination of resistance constants of complexes formed by reagents studied with a number of metals by potentiometric titration method. By studying the stability constant, it is possible to determine the selectivity of the complex formation reaction in the presence of other complexing agents. It is known that the analytical characteristics of complex compounds with high stability are also high. Many methods are used to determine the durability of complex compounds. Among these methods, the pH-metric titration method, which is characterized by expressiveness and simplicity, is more widely used. The pH of the solutions used was also determined according to the Beyts equation. Complexes formed by reagents with some metals stability constants were determined by the mathematical method of Martel and Chaberak: The stability constants of the complexes formed by reagents synthesized on the basis of hydrazone and aromatic amines with a number of metals are given in Table 3.

**Table 3.** Stability constants of complexes formed by metals with reagents

| Reagent | $Fe^{3+}$ | $Cu^{2+}$ | $Ni^{2+}$ | $Co^{2+}$ | $Cd^{2+}$ | $Mn^{2+}$ | $Zn^{2+}$ |
|---|---|---|---|---|---|---|---|
| $R_1$ | 7,92±0,03 | 7,81±0,04 | 7,44±0,03 | 7,16±0,04 | 6,53±0,03 | 6,38±0,02 | 6,26±0,01 |
| $R_2$ | 9,23±0,04 | 7,12±0,05 | 6,45±0,04 | 6,24±0,06 | 5,75±0,06 | 5,35±0,05 | 5,16±0,04 |
| $R_3$ | 7,12±0,02 | 6,64±0,04 | 6,28±0,05 | 5,87±0,02 | 5,58±0,03 | 5,28±0,03 | 5,44±0,02 |
| $R_4$ | 7,82±0,04 | 7,62±0,03 | 7,46±0,01 | 6,85±0,03 | 6,60±0,02 | 6,41±0,04 | 7,30±0,05 |
| $R_5$ | 7,55±0,03 | 7,32±0,05 | 6,62±0,05 | 6,72±0,03 | 5,54±0,04 | 5,63±0,04 | 6,34±0,02 |

As can be seen from the results of potentiometric titration (Table 3), the durability of $R_1$-$R_5$ reagent complexes varies in the following order: Fe> Cu> Ni> Co> Zn> Cd> Mn> Mg> Ca

The change in the stability of the complexes in this order is due to the nature of the complexing agent (ion radius, ionization potential, hydration enthalpy, sedimentation pH, dehydration entropy, etc.) and the effects of functional groups. It is known that as the negative inductive effect of the functional groups of reagents decreases, the resistance of the complexes formed by them with metal ions increases. The durability of complexes also depends on the nature of the central atom, its position in the periodic table, the charge and the composition, structure and properties of the ligand. As can be seen from Table 3, the complexes formed with Fe(III) are characterized by higher resistance than the complexes formed by each of the $R_1$-$R_5$ reagents with other metal ions. This result allows the selective determination of iron (III) in various complex objects (ie in the presence of other ions) using reagents $R_1$-$R_5$.

Study of the synthesis, structure and properties of new solid complex compounds of iron(III) and copper(II). New complex compounds of Fe(III) and Cu(II) were obtained on the basis of synthesized reagents, their structure and properties were determined

by IR-spectroscopy and thermogravimetric analysis methods. Complex compounds were synthesized according to the following methodology. To the solution of the reagent in 50 ml of $2 \cdot 10^{-2}$ M ethanol is added 10 ml of an aqueous solution of $1 \cdot 10^{-2}$ M $FeCl_3$ with added $HNO_3$, and in copper complexes with an aqueous solution of $1 \cdot 10^{-2}$ M $CuSO_4 \cdot 5H_2O$. The reaction mixture is heated in a water bath at 70 ° C for 40 min. The solution is cooled and filtered, after a while the crystals separated from the filtered solution are recrystallized in ethanol and dried in vacuum at room temperature. Thermal decomposition of complex compounds of iron(III) and copper(II) with reagents synthesized by NETZSCH Proteus 6 was studied. The process of thermogravimetric and differential thermal analysis is carried out with the help of this device. In the thermogravimetric (TQ) analysis method, a change in mass depending on temperature (t) is observed and the dependence m = f (t) is established. Using this dependence, it is possible to determine the increase or decrease in the mass of the sample. For this reason, this method is widely used in the study of various physical (adsorption, desorption, sublimation, evaporation, etc.) and chemical transformations (oxidation, reduction, substitution, solid phase reaction, etc.). The thermal decomposition of complex compounds formed from 2-((E)-(((E)-1-pyridine-2-il) ethylidene)hydrazono)methyl)phenol ($R_1$) with copper(II), 3-((E)-2-hydroxybenzylidene)hydrazo)indolin-2-on ($R_2$) with copper(II) and iron (III), (E)-2-hydroxy-3-((2-hydroxybenzilide)(amino)benzene sulfuric acid ($R_3$)with iron (III) was studied. Thermal decomposition of the complex compounds we studied - Fe(III) -$R_2$ (1), Fe(III) -$R_3$ (2) and Cu(II) -$R_1$ (3) occurs in two stages: in the first stage, the separation of water molecules, and in the second stage decomposition of the anhydrous complex to metal oxides. It should be noted that the decomposition of anhydrous complexes occurs in parts. The end product of decomposition is metal oxides. In all cases, the maximum temperature of dehydration of water from complex compounds is 200°C. Thermal decomposition of the Cu (II) -$R_2$ complex occurs in three stages: the separation of water in the first and second stages, and the decomposition of the anhydrous complex in the third stage. Based

on the results of thermogravimetric analysis, the scheme of decomposition of compounds can be shown as follows:

1. $Fe(C_{15}H_{11}N_3O_2)\times 3H_2O \rightarrow FeC_{15}H_{11}N_3O_2 \rightarrow Fe_2O_3$

2. $Fe(C_{13}H_{12}O_5SN)\times 3H_2O \rightarrow FeC_{13}H_{12}O_5SN \rightarrow Fe_2O_3$

3. $Cu(C_{13}H_{11}N_3O)\times 3H_2O \rightarrow Cu\ C_{13}H_{11}N_3O \rightarrow CuO$

4. $Cu(C_{15}H_{11}N_3O_2)\times 2H_2O \rightarrow Cu(C_{15}H_{11}N_3O_2)\times H_2O \rightarrow CuC_{15}H_{11}N_3O_2 \rightarrow CuO$

The conductometric titration curves of solutions of metal salts with 3 - ((E) -2-hydroxybenziliden) hydrozo) indolin-2-on ($R_2$) and (E) -2-hydroxy-3 - ((2-hydroxybenziliden) (amino) benzenesulfonic acid ($R_3$) have been constructed. It has been found that during the conductometric titration of solutions of metal salts with reagents, the specific electrical conductivity of the system increases and decreases after the equivalence point. The decrease in electrical conductivity was explained by the protonation of the reagent. In all cases, depending on the nature of the metals, the change in electrical conductivity is as follows: Fe> Cu> Ni> Co> Zn> Cd> Mn> Ca

Iron(III) and copper(II) 3 - ((E) -2-hydroxybenziliden) hydrozo) indolin-2-on ($R_2$) and 2-((E)-(((E)-1-pyridine-2-il)ethylidene)hydrazono)methyl)phenol ($R_1$) formed binary (Fe(III) - $R_2$ and Cu(II) - $R_1$) and various ligand complexes (Fe(III) $R_2$-8-oxyquinoline, Fe(III) $R_2$- DFQ, Fe (III) $R_2$-DAM and Cu (II) $R_1$-TFQ, Cu(II) $R_1$-DFQ) special electrical conductivities in the buffer system were studied by the method of conductometric titration. Specific electrical conductivity was measured at the optimum complex formation pH of iron (III) and copper (II). As the volume of titrant (reagent) increases, the specific electrical conductivity of the system in the buffer environment begins to decrease and remains constant after reaching a certain value. In a buffer system, the value of the specific electrical conductivity is inversely proportional to the durability of the system, ie a system with a lower value of the specific

electrical conductivity is considered a more durable system. It was found that the specific electrical conductivity of mixed-ligand complexes in the buffer solution is small compared to binary complexes, ie their durability is higher than that of binary complexes. This suggests that the selectivity of such complexes in photometric determination, ie mixed-ligand complexes, will be higher than that of binary complexes.

Investigation of the complex formation of iron(III) and copper (II) with reagents. In the method of photometric analysis, their color combinations are used to develop the method of determination of metals. It has been visually determined that the reagents we synthesize form colored complexes with $Fe^{3+}$ and $Cu^{2+}$ ions. Based on the study of the stability constant and specific electrical conductivity of the complex compounds formed by these reagents with a number of metals, it was determined that the compounds with the highest resistance among the studied complex compounds are Fe(III) and Cu(II) complexes. Based on this, it is decided that these complexes should be superior to other complexes in terms of analytical parameters. Therefore, complex compounds formed by $Fe^{3+}$ and $Cu^{2+}$ ions with the studied reagents were studied by photometric method. It is known from the literature that the influence of third components on the binary complex is widely used in photometric analysis in order to increase the parameters of analytical reactions. As a third component, hydrophobic amines and surfactants are used in the study. The effects of many third-party components have been studied and only complexes of analytical importance have been studied. Surfactants and hydrofobic amines were used as the third component in the study. The structural formulas and names of the third components used in the study are as follows: cetylpyridine chloride (SPCl), cetylpyridine bromide (SPBr), cetyltrimethylammonium-bromide (STMABr), triton X-114, diphenylquanidine (DFQ), triphenylquanidine (triphenylquanidine)., diantipyrylmethane (DAM), diantipyrylphenylmethane (DAFM), diantipyrylpropylmethane (DAPM), 4-aminoantipyrine The binary and mixed-ligand colored complex compounds formed by the synthesized reagents ($R_1$-$R_5$) with

iron(III) and copper(II) were studied by spectrophotometric method. The optimal conditions for the formation of the complex have been identified. The effect of time, reagent and third component concentration, acidity of the environment on the formation of the complex was studied and spectrophotometric characteristics were calculated. The values of molar absorption coefficients of complex compounds and intervals of subordination to the degree graph were calculated. The ratio of the components of binary and mixed-ligand complexes was determined by isomolar series, Starik-Barbanel and equilibrium displacement methods. The Astakhov method was used to determine the number of protons released during complex formation. The spectrophotometric characteristics of the studied binary and different-ligand complex compounds of iron(III) and copper(II) are given in the following tables (Table 4 and Table 5).

**Table 4.** Spectrophotometric characteristics of the studied binary and mixed-ligand complex compounds of iron(III)

| Complexes | pH | $\lambda_{max}$, nm | $\varepsilon_{MeR}$ | M:R | Submission to Beer's law, mkg/ml |
|---|---|---|---|---|---|
| Fe(III)$R_2$ | 5 | 331 | 12500 | 1:2 | 0,448-1,792 |
| Fe(III)$R_2$-DAM | 3 | 376 | 18000 | 1:1:2 | 0,112-2,24 |
| Fe(III)$R_2$-8-oksixinolin | 4 | 467 | 22000 | 1:2:2 | 0,179-2,24 |
| Fe(III)$R_2$-DFQ | 3 | 369 | 16000 | 1:1:1 | 0,224-2,24 |
| Fe(III)$R_3$ | 4 | 353 | 10000 | 1:2 | 0,448-2,24 |
| Fe(III)$R_3$-DAFM | 1 | 378 | 13000 | 1:2:1 | 0,112-3,36 |
| Fe(III)$R_3$-8-oxyquinoline | 3 | 389 | 16000 | 2:2:1 | 0,112-2,24 |
| Fe(III)$R_3$SpCl | 3 | 374 | 16250 | 1:1:2 | 0,112 -4,48 |
| Fe(III)$R_3$- STMABr | 2 | 392 | 19000 | 1:1:1 | 0,112 -4,48 |
| Fe(III)$R_3$-TritonX-114 | 3 | 385 | 11000 | 1:2:1 | 0,224 – 2,24 |
| Fe(III)- $R_4$ | 5 | 464 | 12500 | 1:2 | 0,448-1,792 |
| Fe(III)$R_4$-DAPM | 3 | 387 | 13000 | 1:1:2 | 0,112-2,24 |
| Fe(III)$R_4$-DAM | 4 | 376 | 16250 | 1:2:1 | 0,179-2,24 |
| Fe(III)$R_4$-DAFM | 3 | 393 | 18000 | 1:1:1 | 1,64 – 3,14 |

**Table 5.** Spectrophotometric characteristics of the studied binary and mixed-ligand complex compounds of copper(II)

| Complexes | pH | $\lambda_{max}$, nm | $\varepsilon_{MeR}$ | M:R | Submission to Beer's law, mkg/ml |
|---|---|---|---|---|---|
| Cu(II)$R_1$ | 7 | 331 | 2280 | 1:1 | 0,410-5,12 |
| Cu(II)$R_1$-DFQ | 5 | 357 | 3150 | 1:2:2 | 0,256-5,12 |
| Cu(II)$R_1$- TFQ | 6 | 343 | 4800 | 2:2:1 | 0,256-5,12 |
| Cu(II)$R_2$ | 4 | 326 | 19500 | 1:1 | 0,256-1,536 |
| Cu(II)$R_2$-DAFM | 3 | 376 | 23250 | 1:2:2 | 0,128-1,536 |
| Cu(II)$R_2$-4-aminoantipyrine | 3 | 357 | 28500 | 1:2:1 | 0,128-2,048 |
| Cu(II)$R_5$ | 5 | 474 | 10000 | 1:2 | 0,51-3,07 |
| Cu(II)$R_5$- SPCl | 3 | 466 | 11250 | 1:2:1 | 0,26-2,56 |
| Cu(II)$R_5$- SPBr | 3 | 462 | 12000 | 1:2:1 | 0,51-2,56 |
| Cu(II)$R_5$-STMABr | 4 | 458 | 16750 | 1:1:1 | 0,15-2,05 |

As can be seen, the conditions for the formation of various ligand complexes are observed in a strongly acidic environment. In the presence of hydrophobic amines and surfactants, the molar absorption coefficients increase as the stability of the complexes formed by iron(III) and copper(II) increases. Therefore, it can be predicted that these reactions will be characterized by high selectivity. The maximum absorption spectrum of reactions involving third components shifts to an acidic environment relative to binary complexes. The maximum absorption of the complexes varies in the

range of 331-474 nm for copper complexes and 331-467 nm for iron complexes. As can be seen from Table 4, the optimal formation conditions of complexes with various ligands formed by iron(III) with $R_3$ reagent in the presence of DAFM and STMABr correspond to a more acidic (pH 1 and pH 2) environment. The highest molar absorption coefficients are observed in complexes with various ligands formed by iron(III) in the presence of DAM and 8-oxyquinoline with $R_2$ reagent, STMABr with $R_3$ reagent, and DAFM with $R_4$ reagent: Fe (III) $R_2$-8-oxyquinoline (22000), Fe( III) $R_2$-DAM (18000), Fe(III) $R_3$ - STMABr (19000), Fe(III) $R_4$-DAFM (18000). The composition of binary complexes formed by iron (III) with reagents $R_2$, $R_3$ and $R_4$ is 1: 2. Based on the spectra of the complexes obtained in the spectrophotometer, it was determined that the absorption spectra of the complexes change in the direction of both increasing and decreasing wavelengths relative to the absorption spectrum of the reagent, and batochrome and gibbsochrome shifts are observed. It is known from the literature that, depending on the nature of the functional groups included in the organic molecule, one aromatic nucleus is positively charged and the other is negatively charged, and π-complex is formed due to the interaction of these nuclei. As a result, a bathochrome shift is observed in the absorption spectrum of the ligand. As can be seen from Table 4, the absorption spectrum of the complexes formed by iron(III) with the $R_4$ reagent in the presence of third components is shifted in the direction of decreasing wavelength compared to the absorption spectra of the reagent and the binary complex, that is, gibbsochromic shift is observed. The absorption spectrum of complexes formed by iron(III) with reagent $R_3$ in the presence of in the presence of DAFM, 8-oxyquinoline, SpCl, STMABr and TritonX-114 and in the presence of third components with reagent $R_2$ changes its position in the direction of increasing wavelength compared to the absorption spectra of the reagent and the binary complex, that is, a bathochromic shift is observed. As can be seen from Table 5, the optimal formation conditions of the different-ligand complexes formed by copper(II) in the presence of DAFM and 4-aminoantipyrine with the $R_2$ reagent,

SPCl and SPBr with the $R_5$ reagent correspond to a more acidic environment than the different-ligand complexes formed by the $R_1$ reagent. The highest molar absorption coefficients are observed in different complexes formed by copper(II) with reagent $R_2$ in the presence of DAFM and 4-aminoantipyrine. The highest molar absorption coefficients are observed in different complexes formed by copper(II) with reagent $R_2$ in the presence of DAFM and 4-aminoantipyrine: Cu (II) $R_2$-DAFM (23250), Cu (II) $R_2$-4-aminoantipyrine (28500). The composition of the binary complexes formed by copper (II) with reagents $R_1$ and $R_2$ is 1: 1, and the composition of the binary complex formed with reagent $R_5$ is 1: 2. As can be seen from the table, in the absorption spectra of the complexes formed by copper(II) with reagents $R_1$ and $R_2$ in the presence of third components, the wavelength shifts in the direction of increasing relative to the absorption spectra of the reagent and binary complex, ie batochromic shift is observed. In the absorption spectra of the complexes formed by copper(II) $R_5$ reagent in the presence of third components, the wavelength changes in the direction of decreasing relative to the absorption spectra of the reagent and the binary complex, ie gibbsochrome shift is observed. In order to improve the analytical parameters of the studied complex compounds, the effect of third components on these complexes: surfactants, 8-oxyquinoline, 4-aminoantipyrine, diantipyrylmethane, diantipyrylphenylmethane, diantipyrilpropylmethane, diphenylquanidine, triphenylquanide was studied. It was found that the analytical parameters of the complex compounds formed by iron(III) and copper(II) with these reagents increase under the influence of third components.

The effect of cationic surfactants - cetylpyridine chloride, cetylpyridine bromide and cetyltrimethylammonium bromide and non-ionic surfactant - Triton X-114 on the complex compounds formed by metals with reagents was studied. It was found that cationic surfactants is associated with sulfo group and OH in reagents ($R_3$, $R_5$). electrostatic interaction (association is formed) and as a result the analytical parameters of the reaction increase. Due to the effect of cationic surfactants on the reagent, shifts in its light absorption

maximum are observed. Maximum delocalization of electrons of the reagent in the formed associations leads to the batochromic shift, which can be explained by an increase in the negative inductive effect of the sulfo group under the influence of cationic surfactants. Comparing the ratios of the components in the complexes and associations, it was shown that cationic surfactants interacts with the sulfo group.

Experience shows that the majority of binary and mixed-ligand complexes are formed in an acidic environment. Therefore, it is possible to predict that these reactions will be highly selective. The molar absorption coefficients of mixed-ligand complexes are also higher than those of the binary complex.. Therefore, it is possible to predict that these reactions will be highly selective. The molar absorption coefficients of mixed-ligand complexes are also higher than those of the binary complex. Studied the effect of foreign ions and masking substances on photometric determination of iron (III) in the form of binary and mixed-ligand complexes. It has been found that the low concentration of some ions prevents the determination of copper(II) and iron(III). In the presence of modified forms of reagents, the selectivity of the determination reactions increases. A comparison of the selectivity of the reagents studied in the literature for the photometric determination of iron(III) and copper(II) shows that the selectivity of the target is high with new reagents synthesized on the basis of hydrazone and aromatic amines, especially in the presence of modified reagents.

**Table 6.** Comparison of selectivity of methods for determination of different-ligand complexes formed by iron(III) in the presence of diantipyrylmethane and its homologues with $R_2$ - $R_4$ reagents

| Foreingn ions and masking substances | $FeR_2$-DAM | $FeR_3$.DAFM | $FeR_4$-DAM | $FeR_4$.DAPM | $FeR_4$-DAFM | 2-thenoyl - trifluoroacetone |
|---|---|---|---|---|---|---|
| Alkaline metals | * | * | * | * | * | |
| Alkaline earth metals | * | * | * | * | * | 100 |
| Ni(II) | 280 | 280 | * | * | * | 1 |
| Co(II) | 265 | 290 | * | * | * | 10 |
| Zn(II) | | 580 | * | * | * | |
| Mn(II) | 1250 | 360 | * | * | * | 10 |
| Cu(II) | mane olur | 285 | * | * | * | 1 |
| Cd(II) | 2200 | 480 | * | * | * | 10 |
| Al(III) | 1000 | 145 | 2410 | 2410 | 2710 | 1 |
| Bi(III) | 1200 | | 112 | 185 | 160 | |
| Cr(III) | 155 | 155 | | | | |
| Sn(IV) | | 160 | | | | |
| V(V) | | 273 | | | | |
| $MoO_4^{2-}$ | 250 | 200 | 857 | 857 | 925 | |
| $WO_4^{2-}$ | 700 | 980 | 1642 | 980 | 1660 | |
| $NO_3^-$ | | | | | | |
| $F^-$ | 2000 | 2000 | | | | 2 |
| Citric acid | 1500 | 380 | 250 | 250 | 250 | |
| Wine acid | 230 | 245 | 245 | 980 | 980 | 20 |
| Moçevina | | 325 | | | | |

*does not interfere

**Table 7.** Effect of foreign ions and masking substances on complex compounds formed by copper (II) $R_5$ reagent in the presence of SPCl, SPBr and STMABr

| Foreingn ions and masking substances | Cu(II)-$R_5$-SPCl | Cu(II)-$R_5$-SPBr | Cu(II)-$R_5$-STMABr | N,N'- di-(2-carboxyethy) 3,4-xylidine | 2,7-bis(azo2-hydroxy-3-sulfo-5-nitrobenzene)-1,8-dihydroxynaphthalene-3,6-disulfonate sodium salt |
|---|---|---|---|---|---|
| Na(I) | * | * | * | 1:1796 | * |
| K(I) | * | * | * | 1:3046 | * |
| Ca(II) | * | * | * | 1:312 | 625 |
| Ba(II) | * | * | * | 1:642 | 43 |
| Zn(II) | 1:1000 | 1:600 | 1:480 | 1:508 | 609 |
| Cd(II) | 1:380 | 1:350 | 1:280 | 1:875 | 813 |
| Mn(II) | 1:1810 | 1:1800 | 1:1620 | 1:43 | 172 |
| Ni(II) | 1: 220 | 1:200 | 1:220 | 1:461 | 18 |
| Co(II) | 1:600 | 1:600 | 1:220 | 1:276 | 19 |
| Al(III) | 1:2050 | 1:2010 | 1:1920 | 1:126 | 422 |
| Bi(III) | 1:160 | 1:50 | 1:77 | 1:163 | |
| Sn(III) | 1:430 | 1: 160 | 1: 210 | | |
| Ti(IV) | 1:326 | 1:180 | 1:42 | | |
| Mo(VI) | 1:800 | 1:360 | 1:300 | 1:450 | |
| W(VI) | 1:100 | 1:80 | 1: 50 | | |
| Moçevina | * | * | * | | |
| Tiomoçevina | 1:510 | 1:500 | 1:485 | | |
| $F^-$ | 1:250 | 1:300 | 1:250 | | 100 |
| Wine acid | * | * | * | | |
| Citric acid | 1:500 | 1:800 | 1:980 | 1:58 | |

*does not interfere

As we mentioned, the selectivity of determination reactions of modified forms of reagets increases. The highest selectivity is

observed in the different-ligand complex formed by Fe(III) in the presence of 8-oxyquinoline with the $R_2$ reagent and DAFM with the $R_4$ reagen, and Cu(II) in the presence of SPCl with the $R_5$ reagent. **Methods of spectrophotometric determination of iron(III) and copper(II) in various natural and industrial objects.** The methods developed for the spectrophotometric determination of iron(III) and copper(II) in the presented dissertation were used to determine copper(II) in mountain rocks, seawater, waste water, Al-based alloys, iron(III) in peas, buckwheat, bananas, beans, mushrooms, was applied for the spectrophotometric determination of hip, wheat semolina and white bread. The results of the appointment are shown in Table 8 and Table 9.

**Table 8.** Methods of spectrophotometric determination of copper (II) in environmental objects

| № | Objects | Reagent | Determined by photometric metod, % | Determined by AAS, % |
|---|---|---|---|---|
| I sample<br>II sample<br>III sample | Rocks | $R_1$ + TFQ | 0.57±0.10<br>0.89±0.12<br>4.09±0.18 | 0.579±0.014<br>0.900±0.013<br>4.060±0.016 |
| A 195-3<br>A 195-4<br>A 195-5 | Al-based alloys | $R_2$ | Passport results. | Photometric metod,, mkg/ml |
| | | | 0,14<br>0,11<br>0,04 | 0,14±0,002<br>0,11±0,003<br>0,04±0,002 |
| | *sea water | $R_2$ | Photometric metod,, % | AAS, % |
| | | | $(3,10\pm0,02)\cdot10^{-5}$ | $(3,11\pm0,01)\cdot10^{-5}$ |
| | **waste water | $R_5$ | $(4,04\pm0,01)\cdot10^{-5}$ | $(4,02\pm0,02)\cdot10^{-5}$ |

* Turkan settlement, Caspian Sea
** "Azerneftyag" PU

**Table 9.** Photometric determination of iron (III) in samples (n = 3, P = 0.95)

| The object being analyzed | Found Fe, % weight. | |
|---|---|---|
| | $R_2$-8-oxyquinoline | AAS |
| Banana | $(5,9\pm0,03)\times10^{-4}$ | $(5,94\pm0,05)\times10^{-4}$ |
| Buckwheat. | $(7,8\pm0,02)\times10^{-3}$ | $(7,88\pm0,06)\times10^{-3}$ |
| Peas | $(8,03\pm0,06)\times10^{-3}$ | $(8,12\pm0,03)\times10^{-3}$ |
| | | |
| | $R_1$+4-aminoantipyrine | AAS |
| Palmet | $(5,76\pm0,04)\times10^{-3}$ | $(5,62\pm0,07)\times10^{-3}$ |
| Simerenka | $(3,65\pm0,08)\times10^{-2}$ | $(3,73\pm0,11)\times10^{-2}$ |
| Fudji | $(2,24\pm0,06)\times10^{-2}$ | $(2,20\pm0,05)\times10^{-2}$ |
| | $R_3$+cetyltrimethylammonium bromide (STAmBr) | AAS |
| Beans | $(13,6\pm0,06)\times10^{-2}$ | $(14,1\pm0,03)\times10^{-2}$ |
| Mushroom | $(6,8\pm0,02)\times10^{-2}$ | $(7,1\pm0,01)\times10^{-2}$ |
| Rose hip | $(2,0\pm0,02)\times10^{-2}$ | $(2,2\pm0,04)\times10^{-2}$ |
| | Found, Fe,$x\pm Ɛ_a$, mg/kg | |
| | | |
| | $R_3$+ 8- oxyquinoline | AAS |
| Wheat groats | 69±1,7 | 70±1,5 |
| White bread | 34±0,04 | 35±0,03 |

Research shows that the proposed reagents are suitable for the photometric determination of iron (III) and copper (II).

## RESULTS

1. Analytical chemistry of iron(III) and copper(II) includes 5 organic reagents synthesized on the basis of hydrazone, aromatic amines and salicylic aldehyde. The structures of the reagents were determined by IR and NMR spectroscopic analysis methods, and the crystal structures of the two were studied by X-ray structural analysis. The values of the dissociation constants of the studied reagents were calculated and distribution diagrams were constructed depending on the pH.

2. The values of stability constants and specific electrical conductivities of complex compounds formed by these reagents with some metals were determined. Based on the results obtained from these studies, depending on the nature of the metals, the change of specific electrical conductivities and continuity constants was determined in the following order:

Fe>Cu>Ni>Co>Zn>Cd>Mn>Mg>Ca

3.The thermal stability of complex compounds (Cu(II)-$R_1$, Cu(II)-$R_2$, Fe(III)-$R_2$ and Fe(III)-$R_3$) was studied and the decomposition stages were determined. By comparing the IR-spectra of the ligand and complex compounds, it was determined which donor atoms and functional groups in the ligand formed bonds with the metal.

4. Binary and complex compounds of Fe(III) and Cu(II) with different ligands were studied by spectrophotometric method. Surfactants and hydrophobic amines were used as the third component. The optimal conditions of complex compounds were determined and the main spectrophotometric characteristics were calculated. It was determined that in all cases, the maximum yield of complex compounds with different ligands is shifted towards an acidic environment compared to the binary complex, and the molar absorption coefficient increases.

5. The ratio of metal-ligand and metal-ligand- third components in binary and different-ligand complex compounds was determined by various physicochemical analysis methods, and the number of protons separated from the ligand in complex formation reactions was

determined by the Astakhov method.

6. By comparing the main spectrophotometric properties of the developed methods, the highest sensitivity (Fe(III)$R_2$-8-oxyquinoline, Fe(III)$R_2$-DAM, Fe(III)$R_3$-STMABr, Cu(II)$R_2$-4-aminoantipyrine, Cu(II)$R_2$-DAFM) and high selectivity (Fe(III)$R_1$-DAM, Fe(III)$R_2$-DAM, Fe(III)$R_2$-8-oxyquinoline, Fe(III)$R_3$-SPCl, Fe(III)$R_4$-DAFM ,) methods were selected. These methods were compared with the most commonly used known methods for the determination of these metals in the literature. The proposed photometric methods for the determination of Fe(III) and Cu(II) are natural (peas, buckwheat, bananas, beans, hips and mushrooms, wheat groats and white bread) and industrial (mountain rocks, sea water, waste water, Al-based alloys) were applied in objects. The correctness of the developed methods was confirmed by addition, atomic-absorption spectroscopy methods and passport results.

**Published scientific papers on dissertation materials**.

**1.** Mammadova, Ch.A., Shikhaliyev, N.Q., Agayeva, N.T., Yusifli, A.M., Chiragov, F.M. Synthesis and analytical properties of asymmetric azines on the basis of salicylic aldehyde // VIII Republican Scientific Conference "Actual problems of chemistry", - Baku: - 07-08 May, - 2014, - p. 13-14.

**2.** Alieva, R.A., Mamedova, Ch.A., Alieva, F.S., Shikhaliev, N.G., Chiragov, F.M. Spectrophotometric study of copper(II) complexation with 2-((E)-(((E)-1-(pyridin-2-yl)ethylidene)hydrozono)methyl) phenol in the presence of N,N′-diphenylguanidine and N,N′,N″ - triphenylguanide // IX Republican Scientific Conference of doctoral students, masters and young researchers "Actual problems of chemistry", dedicated to the 92nd anniversary of the national leader H.Aliyev, - Baku: - 2015, - p.119.

**3.** Mamedova, Ch.A., Alieva, F.S., Shikhaliev, N.G., Chiragov, F.M. Spectrophotometric study of complex formation of copper(II) with 3-

((E)-2-hydroxybenzylidene) hydrozono) indolin-2-one // XXVII Russian Youth Scientific Conference "Problems of Theoretical and Experimental Chemistry", - Ekaterinburg: - April 22-24 , - 2015, - p. 150.

**4.** Tsintsadze, G.V. 2-((E)-(((E)-1-(pyridin-2-yl)ethylidene)hydro zono)methyl)phenol as a reagent for the spectrophotometric determination of copper(II) / G.V. Tsintsadze, Ch.A. Mamedova , F.S. Alieva [and others] // Chemical Journal of Georgia, - 2015. No. 1, - p. 16-20.

**5.** Mamedova, Ch.A. Determination of the dissociation constants of 2-((E)-(((E)-1-(pyridin-2-yl)ethylidene) hydrozono)methyl)phenol and the stability constants of its complexes with some metals / Ch.A.Mamedova, F.S. .Aliyeva, F.M. Chiragov [and others] // BU xəbərləri, - Bakı: - 2016. No. 3, - p. 27-30.

**6.** Mamedova, Ch.A. The structure of 3-((E)-2-hydroxybenzylidene) hydrozono)indolin-2-one and its use in the spectrophotometric determination of iron (III) / Ch.A. Mamedova, F.S. Aliyeva, F.M. Chiragov [and others.] // Bulletin of the Moscow State Regional University, Natural Sciences, - 2017. No. 2, - p. 81-89.

**7.** Mamedova, Ch.A. 3-((E)-2-hydroxybenzylidene)hydrozono) indolin-2-one as a reagent for the spectrophotometric determination of copper(II) // BU News, Natural Sciences Series, - 2017. No. 2, - s. 24-31.

**8**. Mamedova, Ch.A., Alieva, F.S., Rahimova, A.J. Study of the complexation of iron (III) with (E)-2-hydroxy-3-((2-hydroxybenzylidene) amino)benzenesulfo acid // XI Republican Scientific Conference of doctoral students, masters and young researchers "Actual problems of chemistry", dedicated to the 94th anniversary of the national leader H.Aliyev, - Baku: - 2017, - p.129.

**9.** Mamedova, Ch.A., Shikhaliev, N.G., Chiragov, F.M. Determination of trace amounts of iron in food // VI Republican Scientific Conference "Actual problems of ecology and soil sciences in the XXI century", dedicated to the 94th anniversary of national leader Heydar Aliyev, - Baku: - 2017, - p.17-18

**10**. Mammadova, Ch.A., Aliyeva, F.S., Chiragov, F.M., Shikhaliyev, N.Q. Investigation of analytical possibilities of complex compounds of Fe (III) reagents synthesized on the basis of salicylic aldehyde // I International Scientific Conference of Young Researchers, Baku Engineering University, − Bakı: − 2017, − s.134-135.
**11.** Mamedova, Ch.A., Alieva, F.S., Efendieva, N.N., Shikhaliev, N.G., Chiragov, F.M. Study of the complexation of iron (III) with 3-((E)-2-hydroxybenzylidene) hydrozono) indolin-2-one // Baikal School-Conference on Chemistry-2017, - Irkutsk: - 2017, - s.334-335.
**12.** Mamedova, Ch.A., Alieva, F.S., Shikhaliev, N.G., Chiragov, F.M. Spectrophotometric study of copper(II) complexation with 3-((E)-2-hydroxybenzylidene)hydrozono)indolin-2-one // XXVII Russian Youth Scientific Conference "Problems of Theoretical and Experimental Chemistry", - Ekaterinburg: - April 26-28 , - 2017, - p. 460-461.
**13.** Mamedova, Ch.A. Study of the complex formation of iron (III) with (E)-2-hydroxy-3-((2-hydroxybenzylidene) (amino)benzenesulfonic acid / Ch.A. Mamedova, F.S. Aliyeva, F.M. Chiragov [and others] // Proceedings of universities. Applied chemistry and biotechnology, - Irkutsk: - 2018. 8 (2), – c. 48-54.
**14.** Mamedova, Ch.A. Determination of trace amounts of iron in natural products // - Irkutsk: Izvestiya vuzov. Applied Chemistry and Biotechnology, - 2019. 9 (3), - p. 395-402.
**15.** Mamedova, Ch.A., Alieva, F.S., Shikhaliev, N.G., Chiragov, F.M. Determination of copper(II) in sea water // VIII Republican Scientific Conference "Actual problems of ecology and soil sciences in the XXI century", dedicated to the 96th anniversary of national leader H.Aliyev, - Baku, - May 3-4, 2019, - p.70.
**16.** Mamedova, Ch.A., Alieva, F.S., Mugalova, G.R., Shikhaliev, N.G., Chiragov, F.M. Spectrophotometric determination of iron(III) with (E)-2-hydroxy-3-((2-hydroxybenzylidene)(amino)benzene sulfonic acid // XIII International Scientific Conference of Doctoral Students, Masters and Young Researchers "Actual Problems of Chemistry" dedicated to the 96th anniversary of the national leader Heydar Aliyev, - Baku, - May 15-16, - 2019, - p.49- 50.

**17.** Mamedova, Ch.A., Alieva, F.S., Shikhaliev, N.G., Chiragov, F.M. Spectrophotometric determination of iron (III) with (E)-2-hydroxy-3-((2-hydroxybenzylidene) (amino)benzenesulfonic acid // XVI International Conference "Spectroscopy of Coordination Compounds", - Tuapse, - September 16 - 21, - 2019 , - p.223-224.
**18.** Mamedova, Ch.A., Shikhaliev, N.G., Chiragov, F.M. Determination of trace amounts of iron in wheat cut and bread // III All-Russian Conference on Analytical Spectroscopy, - Krasnodar, - September 29 - October 05, - 2019, - p.189.
**19.** Mamedova, Ch.A., Alieva, F.S., Shikhaliev, N.G., Chiragov, F.M. Study of the complex formation of iron (III) with (E) -2-hydroxy-3-((2-hydroxybenzylidene) (amino) benzene sulfonic acid // XXX Russian Youth Scientific Conference "Problems of Theoretical and Experimental Chemistry", - Yekaterinburg: - 2020, - page 176.
**20.** Mamedova, Ch.A., Shikhaliev, N.G., Chiragov, F.M. Definitions of copper in rocks // XVII International Conference "Spectroscopy of Coordination Compounds", - Krasnodar: - 2020, - p. 36.
**21.** Mammadova, C.A., Aliyeva, F.S., Chiragov, F.M., Shikhaliyev, N.Q. Spectrophotometric determination of iron (III) 2 - (((1- (3-bromophenyl) ethylidene) hydrazono) methyl) phenol // VIII International Scientific Conference "Chemistry of coordination compounds" dedicated to the 85th anniversary of the Department of Analytical Chemistry, - Baku: - 2020, - p.82.
**22.** Mammadova, Ch.A., Chiragov, F.M., Shikhaliyev, N.Q. Research and analytical application of complex compounds of reagents synthesized on the basis of salicylic aldehyde with Cu (II). // VIII International Scientific Conference "Chemistry of coordination compounds" dedicated to the 85th anniversary of the Department of Analytical Chemistry, - Baku: - 2020, - p.81.
**23.** Mamedova, Ch.A., Shikhaliev, N.G., Chiragov, F.M. Study of complex formation of copper (II) with 2-(((4-nitrophenyl)imino)methyl)phenol Bakı: − 2021, − s.26.
**24.** Gadzhieva, S.R., Mamedova, Ch.A., Shikhaliev, N.G., Chiragov, F.M. Study of the complex formation of iron (III) with 2-(((1-(3-bromophenyl)ethylidene)hydrozono)methyl) phenol // XXXI Russian

Youth Scientific Conference with International Participation "Problems of Theoretical and Experimental Chemistry", dedicated to the 90th anniversary of prof. V.M. Zhukovsky, - Yekaterinburg: - April 20-23, - 2021, - p. 98.

**25.** Gadzhieva, S.R., Mamedova, Ch.A., Shikhaliev, N.G., Chiragov, F.M. Determination of copper in aluminum-based alloys // XXXI Russian Youth Scientific Conference with International Participation "Problems of Theoretical and Experimental Chemistry", dedicated to the 90th anniversary of prof. V.M. Zhukovsky, - Yekaterinburg: - April 20-23, - 2021, - p. 99.

The defense will be held on 12th October 2022 at 11:00 at the meeting of the Dissertation council ED 2.16 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at Baku State University

Address: AZ 1148, Baku, Z. Khalilov str., 23, Main campus

Dissertation is accessible at the Baku State University's Library

Electronic versions of dissertation and its abstract are available on the official website of the Baku State University

Abstract was sent to the required addresses on 10 September 2022.

Signed to print: 22.06.2022
Paper format: 60×90 1/16
Volume: 39436
Number of hard copies: 20