

REPUBLIC OF AZERBAIJAN

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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

**STUDY OF ANALYTICAL POSSIBILITIES OF ORGANIC
REAGENTS SYNTHESIZED BASED ON BENZOYLACETON**

Specialty: 2301.01 – Analytical chemistry

Field of science: Chemistry

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Baku – 2024

The work was performed at Baku State University, the department of Analytical Chemistry

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

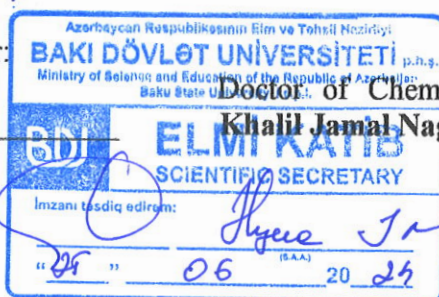
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GENERAL CHARACTERISTICS OF THE WORK

Actuality of the work and degree of development. Due to their ability to form chelates, β -diketones and their derivatives form stable complex compounds with metals. Based on these properties, they are considered as promising organic reagents in analytical chemistry.

It is used in separation and concentration of metal ions from alkyl-, Schiff- and azo derivatives of β -diketones, photometric and extraction-photometric determination of colored complex compounds with metals¹. It is used in the separation of metals in gas chromatography from fluorine-containing β -diketones.

The colored complex compounds formed by this class of reagents with iron (III), copper (II), vanadium (V) and many rare earth elements were studied by photometric method and the effect of third components was studied to increase the analytical parameters of these compounds such as selectivity and sensitivity².

The complex compounds obtained on the basis of these reagents are used in medicine as an oxygen carrier, antibiotic, as a catalyst in a number of chemical reactions, as well as in micro and optoelectronics.

Photometric determination methods using these reagents have been developed to determine many metals in natural and industrial objects.

Taking all this as a basis, it should be noted that the synthesis of azo compounds based on benzoylacetone, the study of the complex compounds they form with metals, and the study of their analytical possibilities are an actual problem.

¹ Tahani, I.K. Synthesis, characterization and biological activity of some metal complexes of benzoylacetone schiff base // *European Chemical Bulletin*, - 2014. 3(9), - p.878-882.

² Kopylovich, M.N. (E)-2-(2-(2-hydroxyphenyl) hydrazono)-1-phenylbutane-1,3-dione: Tautomerism and coordination to copper (II) / Maximilian Kopylovich, Kamran Mahmudov, Matti Haukka [et al.] // *Inorganica Chimica Acta*, - 2011. - p.175–180.

The object and subject of the research. Synthesis of organic reagents based on benzoylacetone. Development of highly selective photometric determination methods for the determination of iron (III) and copper (II) in natural objects with these reagents.

Research goals and objectives. It consists of the development of methods of solidification of complex compounds formed by synthesized reagents with a number of metals and the development of photometric determination methods with high selectivity for the determination of iron (III) and copper (II) in natural objects using these reagents.

To achieve the set goal, the following issues were resolved:

- Synthesis of Schiff and azo derivatives of benzoylacetone;
- Determination of the structure and properties of the synthesized reagents;
- Studying the extraction possibilities of complex compounds formed by a number of metals with these reagents (R₁-R₄);
- Study of stability constant and specific electrical conductivity of complex compounds;
- Spectrophotometric study of the colored complex compounds formed by these reactants with Fe (III) and Cu (II) ions: determining the optimal formation conditions, the interval of obedience to Beer's law, the ratio of components in the complex;
- Development of highly selective photometric determination methods of iron (III) and copper (II) and their application in natural objects;

Research methods. X-ray structure analysis (XSA), nuclear magnetic resonance (NMR), infrared spectroscopy (IR), potentiometric, conductometric, thermal and spectrophotometric analysis methods were used while performing the research work.

The main provisions defended:

- Synthesis of azo compounds and Schiff bases based on benzoylacetone, their research by NMR and IR-spectroscopy method. Studying the structure of reagents by X-ray structure analysis method;
- determination of the dissociation constants of the synthesized reagents by the pH-metric titration method and the

stability constants of the complex compounds formed by them with a number of metals, and the determination of special electrical conductivity by the conductometric titration method;

- Studying the extraction possibilities of the complex compounds formed by R₁-R₄ reagents with some metals in different solvents and determining the solvent with a higher extraction yield;

- Investigation of the binary and complex compounds with various ligands formed by the investigated reactants with Fe (III) and Cu (II) ions and study of their main spectrophotometric characteristics;

- Investigating the effect of foreign ions and shielding substances on the studied complex formation reactions of Fe (III) and Cu (II);

- Among the photometric methods developed for the determination of Fe (III) and Cu (II), the methods with higher selectivity are selected and applied for their determination in objects with complex composition;

Scientific novelty of the research.

- For the first time, methods of spectrophotometric determination of Fe (III) and Cu (II) ions in complex objects were developed using organic reagents synthesized on the basis of benzoylacetone.

- 13 reagents were synthesized on the basis of benzoylacetone and the crystal structure of five of these reagents was studied by X-ray structure analysis method and it was determined that the obtained reagents are in hydrazo tautomeric form.

- Extraction capabilities of complex compounds formed by R₁-R₄ reactants with a number of transition metals in various organic solvents (CCl₄, C₆H₆, CH₃Cl, isobutanol) were studied and it was determined that Fe (III) complexes have a higher extraction yield in CCl₄ solvent environment. Based on the obtained results, it was possible to separate iron (III) from a mixture of other metals with reagents.

- Solid complexes formed by R₁, R₅, R₁₁ and R₁₂ reagents with Fe (III) and Cu (II) ions were studied by infrared spectroscopy and thermal analysis methods. With the IR-spectroscopic analysis

method it was determined which groups in the reagents are involved in the reaction with metal ions, and with the thermogravimetric analysis method, it was determined that the complex compounds are decomposed in 2 stages: - in the first stage, water molecules are separated from the composition of the complexes, and in the second stage, the complexes themselves are decomposed.

- Basic analytical parameters (sensitivity, selectivity, accuracy) of binary and amines formed with the reactants of Fe (III) (R₅, R₁₁-R₁₃) and Cu (II) ions (R₉-R₁₂), complex compounds with various ligands formed in the presence of surfactants characterizing spectrophotometric quantities were calculated.

- Based on the results of the study of complex compounds, it was found that complex compounds with different ligands have a high analytical parameter - selectivity during spectrophotometric determination.

Theoretical and practical significance of research. Methods of photometric determination of Fe (III) and Cu (II) in natural objects were developed using synthesized reagents. These methods were applied for their determination in sea water, copper-based alloy, mountain rock, buckwheat, peas, mushrooms, onions, bananas, apples, varieties.

Approval and application of work. 19 theses and 8 articles related to the topic of the dissertation were published, 1 invention was patented. The materials of the dissertation work were reported and discussed at the following conferences: "Chemistry of Coordination Compounds" VI Republican scientific conference dedicated to the 80th anniversary of the "Analytical Chemistry" department (Baku, 2015), I international scientific conference of young scientists (Ganja, 2016), "Modern Nature Actual problems of science" International Scientific Conference (Ganja, 2017), Baikal School-Chemistry Conference-2017 (Irkutsk, 2017), V International Bergman Conference, "Physical and chemical analysis in education, science and technology" (Makhachgala, 2017), "Modern problems of chemistry and pharmacy" International VI All-Russian conference (Cheboksar, 2017), "Chemistry of Coordination Compounds": Current Problems of Analytical Chemistry International scientific

conference dedicated to Academician Rafiga Aliyeva's 85th anniversary (Baku, 2017), "Nagiyev Readings" scientific conference dedicated to Academician M. Nagiyev's 110th anniversary (Baku, 2018) , "Chemistry - achievements and perspectives" International scientific-methodical conference dedicated to the 85th anniversary of Academician Givi Vasilievich Tsintsadze (Tbilisi, 2018), "Current problems of modern natural and economic sciences" International scientific conference (Ganja, 2018), National leader H. XIII International scientific conference of doctoral students, masters and young researchers dedicated to the 96th anniversary of Aliyev's birth "Actual problems of chemistry" (Baku, 2019), XI All-Russian scientific conference "Ecoanalytics-2019" on the analysis of environmental objects (Perm, 2019), Nakhchivan State University Republican Scientific Conference "Modern View of Chemistry" (Nakhchivan, 2019), VIII International Scientific Conference "Chemistry of Coordination Compounds" dedicated to the 85th anniversary of the "Analytical Chemistry" Department (Baku, 2020), National Leader Heydar Aliyev's birth XIV International Scientific Conference "Actual Problems of Chemistry" of doctoral students, master's students and young researchers dedicated to the 98th anniversary (Baku-2021).

The name of the institution where the dissertation work was performed. The presented work was carried out in accordance with the scientific research plan conducted by the Department of Analytical Chemistry of the Faculty of Chemistry of Baku State University "In the direction of synthesis of new organic reagents and the study of their interaction with inorganic ions (State registration 01870009955).

The total volume of the dissertation with a sign indicating the volume of the structural sections of the dissertation separately. The dissertation consists of 176 pages written in A4 format, consisting of introduction, five chapters, conclusion and used literature. The dissertation consists of 171699 characters. The results of the conducted research are given in 63 pictures and 41 tables. The list of used literature includes 169 sources.

In the introductory part (mark 9552) actuality of the work and degree of development, the object, subject, goals and tasks of the research, research methods, the main propositions defended, the scientific innovation of the research, the theoretical and practical importance of the research, the approval and application of the work, the personal contribution of the applicant in the conducted research information has been provided.

In the first chapter (57112 marks) the literature data of the last 10 years and the analysis of literature data are given.

In the second chapter (22795 marks) the preparation of solutions, devices, synthesis of reagents and their research by physico-chemical analysis methods are given.

In the third chapter (mark 25353) there is a study of complex compounds formed by nitrogen derivatives of benzoylacetone with a number of metals.

The fourth chapter (mark 27690) provides a spectrophotometric study of binary and complex compounds with various ligands formed by iron (III) and copper (II) with organic reagents synthesized on the basis of benzoylacetone.

In the fifth chapter (17674 marks) the development of methods of photometric determination of iron (III) and copper (II) in various natural and industrial objects is given.

The applicant's personal contribution to the research conducted. Directly in the collection and analysis of literature data on the determination of iron (III) and copper (II), the synthesis of benzoylacetone-based reagents and their complexes with the same and different ligands with Fe (III) and Cu (II) metals, the preparation of natural objects for analysis, and the development of determination methods attended. She put her forward opinions in single-authored and other articles related to research work.

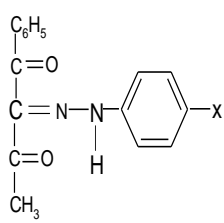
MAIN CONTENTS OF THE WORK

Synthesis, identification and determination of physico-chemical constants of reagents

During the research, 13 reagents synthesized on the basis of benzoylacetone were used. In the experiment, reagents R₉, R₁₀ were dissolved in water, and other reagents were dissolved in ethanol. The formula, conventional symbol, name and relative molecular mass of the reagents used are given in table 1.

Table 1.

Structural formula, name and relative molecular mass of reagents.

The formula of the reagents and conditional sign	Name	Relative molecular mass
R ₁ -R ₄ (X=F, Cl, Br, I) 	2-(2-(4-Fluorophenyl)hydrazinylidene)-1-phenylbutane-1,3-dione (R ₁) 2-(2-(4-Chlorophenyl)hydrazinylidene)-1-phenylbutane-1,3-dione (R ₂) 2-(2-(4-Bromophenyl)hydrazinylidene)-1-phenylbutane-1,3-dione (R ₃) 2-(2-(4-Iodophenyl)hydrazinylidene)-1-phenylbutane-1,3-dione (R ₄)	284 300,5 345 392
R ₅ :X= F R ₆ :X= Cl R ₇ :X= Br R ₈ :X= OH	(Z)-3-((4-Fluorophenyl)amino)-1-phenylbuten-2-1-one (R ₅) (Z)-3-((4-Chlorophenyl)amino)-1-phenylbuten-2-1-one (R ₆) (Z)-3-((4-Phenyl)amino)-1-bromophenylbuten-2-1-one (R ₇) (Z)-3-((4-Hydroxyphenyl)amino)-1-phenylbuten-2-1-one (R ₈)	255 271,5 316

$ \begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{C}=\text{O} \\ \\ \text{C}-\text{H} \\ \\ \text{C}-\text{N}-\text{C}_6\text{H}_4-\text{X} \\ \\ \text{CH}_3 \end{array} $		253
<p>R₉: X=OH, Y=SO₃H, Z=NO₂ R₁₀: X=OH, Y=SO₃H, Z=Cl</p> $ \begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{C}=\text{O} \\ \\ \text{CH}-\text{N}=\text{N}-\text{C}_6\text{H}_3(\text{X}, \text{Y}, \text{Z}) \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_3 \end{array} $	<p>1-phenyl-2-[2-Hydroxy-3-sulfo-5-nitro-phenylazo]butadione-1,3 (R₉) 1-phenyl-2-[2-Hydroxy-3-sulfo-5-chlorophenylazo]butadione-1,3 (R₁₀)</p>	407 320,5
<p>R₁₁</p> $ \begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{C}=\text{O} \\ \\ \text{CH}-\text{N}=\text{N}-\text{C}_6\text{H}_3(\text{HO}, \text{NO}_2) \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_3 \end{array} $	1-phenyl-2-(2-Hydroxy-4-nitrophenylhydrazo)butadione-1,3	295
<p>R₁₂</p> $ \begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{C}=\text{O} \\ \\ \text{HC}-\text{N}=\text{N}-\text{C}_6\text{H}_5(\text{OH}) \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_3 \end{array} $	1-phenyl-2-[2-Hydroxyphenylazo] butadione-1,3	282
<p>R₁₃</p> $ \begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{C}=\text{O} \\ \\ \text{CH}-\text{N}=\text{N}-\text{C}_6\text{H}_3(\text{OH}, \text{COOH}) \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_3 \end{array} $	1-phenyl-2-(3-Hydroxy-4-carboxyphenylazo)-butadione 1,3	326

As the third component cation surfactants - cetyltrimethylammonium bromide (CTMABr), cetylpyridine bromide (CPBr), cetylpyridine chloride (CPCl); organic compounds containing nitrogen - 1,10-phenanthroline (Phen), 2,2'-dipyridyl (Dip), diantipyrylmethane (DAM), diantipyrylphenylmethane (DAPM), diantipyryl-o-oxyphenylmethane (DAOPM) and ethylenediamine (ED) were used .

The solutions of the salts used in the work were prepared based on the methods known in the literature.

The reagents were synthesized based on the methodology known in the literature.

Identification of reagents. The reagents were identified by X-ray structural analysis (XSA), Nuclear magnetic resonance (NMR), Infrared spectroscopy (IR) and spectrophotometric analysis. The reagents were purified by recrystallization and their purity was checked by paper chromatography.

Single crystals of the reagents were grown by recrystallization from ethanol solution. In order to get correct information about the structure of the newly synthesized compounds, five of the reactants studied by X-ray structure analysis were 2-(2-(4-Fluorophenyl)hydrazinylidene)-1-phenylbutane-1,3-dione (R₁), (Z)-3-((4-Fluorophenyl)amino)-1-phenylbuten-2-1-one (R₅), (Z)-3-((4-Chlorophenyl)amino)-1-phenylbuten-2-1-one (R₆), (Z)-3-((4-Phenyl)amino)-1-bromophenylbuten-2-1-one (R₇), (Z)-3-((4-Hydroxyphenyl)amino)-1-phenylbuten-2-1-on (R₈) structure was studied.

The experiment was carried out on a BRUKER SMART APEX II CCD (MoK α -radiation graphite monochromator, φ and ω scanning) diffractometer.

Crystallographic parameters of C₁₆H₁₃FN₂O₂ (R₁) crystal: a=6.0571(3) Å, b=15.9031(7) Å, c=14.8651(7) Å, $\alpha=90^\circ$, $\beta=94.386(2)^\circ$, $\gamma=90^\circ$, monoclinic syngonia, V=1427.71(12) Å³, P2₁/n, Z=4, d_{cal}=1.323 mg/m³, adsorption coefficient 0.097 mm⁻¹, crystal size 0.30·0.20·0.20 mm³, R₁=0.1261, wR₂=0.2667.

The lengths of the interatomic bonds in the molecule were compared with the corresponding bonds in the International table of

crystallography, and the compatibility of the values of single and double bonds was determined.

It was determined by the XSA method that the reagent R₁ consists of 2 aromatic rings, methyl, carbonyl and -NH-N= groups. There are intermolecular and intramolecular hydrogen bonds in the crystal lattice. In the crystal, an intramolecular hydrogen bond is formed between the -NH-group and the CO group, and its length is 1.876 Å. The intermolecular hydrogen bond in the compound F atom and the H atom of the -CH₃ group and its length is 2.630 Å.

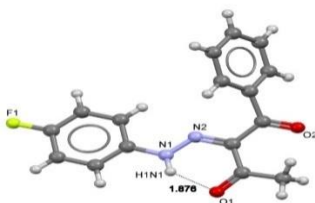


Figure 1. Molecular structure of the reagent 2-(2-(4-Fluorophenyl)hydrazinylidene)-1-phenylbutane-1,3-dione (R₁).

It is known from the literature that this class of reactants exists in three tautomeric forms: keto-azo, enol-azo and hydro-azo. As can be seen from Figure 1, the compound is in the hydrazo form in the solid state.

Molecular structure of synthesized Schiff-based derivatives of benzoylacetone. The crystal structure of four reagents synthesized using halogenated and hydroxy derivatives of aniline was studied. It should be noted that these reagents are known in the literature and have been studied by the IR-spectroscopic method and certain ideas about their structures have been put forward. Since these reagents are in different tautomeric forms, their single crystals were grown and their structures were determined by X-ray structure analysis method in order to get accurate information about their structures.

Among them, R₅-R₈ jets are reported below.

Crystallographic parameters of C₁₆H₁₄FNO (R₅) crystal: a=6.4596(13) Å, b=28.676(4) Å, c=7.2110(14) Å, α=90°, β=91.231(8)°, γ=90°, monoclinic syngonia V=1335.4(4) Å³, P21/n, Z=4, d_{cal}=1.270 mg/m³, adsorption coefficient 0.089 mm⁻¹, crystal size 0.320 · 0.230 · 0.170 mm³, R₁ = 0.2161, wR₂ = 0.3052.

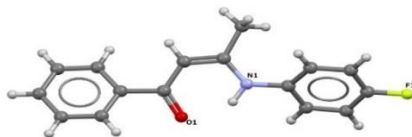


Figure 2. Molecular structure of the reagent (Z)-3-((4-Fluorophenyl)amino)-1-phenylbuten-2-one.

In the R_5 crystal, the molecules are arranged in layers in the same direction (Figure 2). There are both intramolecular and intermolecular hydrogen bonds in the crystal. The crystal has monoclinic syngonia. The length of the intramolecular hydrogen bond N(1)-H(1N1)...O(1) is 2.642(4) Å, and the intermolecular hydrogen bond C(10)-H(10C)...O(1) is 3.405(4) Å. All of these types of jets have a similar structure.

Parameters of $C_{16}H_{14}ClNO$ (R_6) crystal: (0.180 · 0.130 · 0.17 mm³), a=6.4192(12) Å, b = 7.185(4) Å, c = 30.1840(14) Å, $\alpha=90^\circ$, $\beta=90.830(8)^\circ$, $\gamma=90^\circ$, monoclinic syngonia, V=1371.4(4), Z=4, adsorption coefficient 0.276 mm⁻¹ crystal size (0.180 · 0.130 · 0.17 mm³), $R_1 = 0.1034$, $wR_2 = 0.2306$.

The crystalline structure of (Z)-3-((4-Chlorophenyl)amino)-1-phenylbuten-2-one (R_6) reagent, which was synthesized by methods different from the investigated reagents, is known in the literature³.

The molecular structure of the reactant (Z)-3-((4-Chlorophenyl)amino)-1-phenylbuten-2-one (R_6) is as follows (Figure 3):



Figure 3. Molecular structure of the reagent (Z)-3-((4-Chlorophenyl)amino)-phenylbuten-2-one.

³ Ziller, J. W. Synthesis, Characterization and Crystal Structure of (Z)-3-(4-Chlorophenylamino)-1-Phenylbut-2-En-1-One / Joseph Ziller, Patil Siddappa, Diego Gonzalez-Flores [et al.] // Journal of Chemical Crystallography, - 2012. - p.543-548.

The synthesized reagent (R₇) was also investigated by XSA method (Figure 4).

Parameters of C₁₆H₁₄BrNO (R₇) crystal: (0.120 · 0.160 · 0.200 mm³), a = 6.4676(13) Å, b = 28.652(4) Å, c = 7.217(14) Å, α=90°, β=91, 15(8)°, γ=90° monoclinic syngonia, V=1396.4(4) Z=4, d_{Cal}=1.573 mg/m³, adsorption coefficient 3.069 mm⁻¹, crystal size (0.120 · 0.160 · 0.200 mm³), R₁ = 0.1123, wR₂ = 0.2118. The molecular structure of (Z)-3-(4-Phenyl)amino)-1-bromophenylbuten-2-1-one reactant is as follows:



Figure 4. Molecular structure of the reagent (Z)-3-((4-Phenyl)amino)-1-bromophenylbuten-2-1-one.

Parameters of C₁₆H₁₅NO₂ (R₈) crystal: a = 6.451(11) Å, b = 28.669(4) Å, c = 7.209(14) Å, α= 90°, β=91.21(2)°, γ= 90° monoclinic syngonia V=1328.4(4)Å³, P21/n, Z=4, d_{Cal}=1.260 mg/m³, adsorption coefficient 0.083 mm⁻¹, crystal size (0.190 · 0.160 · 0.15 mm³), R₁ = 0.0758, wR₂ = 0.1196.

The molecular structure of (Z)-3-((4-Hydroxyphenyl)amino)-1-phenylbuten-2-1-one reagent is as follows (Figure 5):

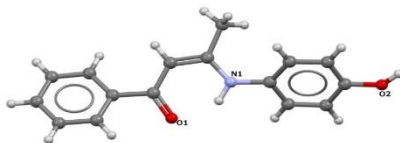


Figure 5. Molecular structure of the reagent (Z)-3-((4-Hydroxyphenyl)amino)-1-phenylbuten-2-1-one.

The crystal structure of the R₁₁ reagent was studied by employees of Baku State University and is known in the literature.

The synthesized reagents were simultaneously identified by NMR and IR spectroscopy methods.

The results of NMR spectroscopy of reactants $C_{16}H_{13}FN_2O_2$ (R_1), $C_{16}H_{14}FNO$ (R_5) are shown.

1H NMR analysis of the reactant $C_{16}H_{13}FN_2O_2$ (R_1): 2.31 (s, 3H, CH_3), 6.77–7.86 (5H, C_6H_5 and 4H, C_6H_4), 13.27 (s, 1H, HN). δ : 2.24 (s, 3H, CH_3), 6.77–7.86 (5H, C_6H_5 and 4H, C_6H_4), 14.44 (s, 1H, NH). ^{13}C 1H NMR (100.61 MHz, DMSO- d_6). δ : 26.4 (CH_3), 112.3 (Ar-NH-N), 128.4, 128.6, 133.1, 133.7 and 135.5 (Ar-H), 137.8 (C = N), 139.7 (Ar-C = O), 141.8 (Ar - F), 191.7 and 194.9 (C = O). δ : 31.1 (CH_3), 114.6 (Ar - NH - N), 126.5, 128.8, 134.4, 135.2 and 135.9 (Ar-H), 139.2 (C = N), 141.2 (Ar - C = O), 145.1 (Ar-F), 196.1 and 198.2(C=O).

1H NMR analysis of the reagent $C_{16}H_{14}FNO$ (R_5): (1H NMR in DMSO- d_6 , TMS as internal standard, δ (ppm)): 2.18 (s, 3H, CH_3), 5.61 (s, 1H, CH), 6.94–7.82 (5H, C_6H_5 and 4H, C_6H_4). ^{13}C 1H NMR (100.61 MHz, DMSO- d_6). δ : 28.5 (CH_3), 82.4 (CH = C), 116.4, 122.3, 127.3, 129.2 and 130.7 (Ar - H), 135.2 (Ar - C = C), 144.1 (Ar - N = C) and 147.9 (Ar -F).

Since the molecular structures of the synthesized reactants were studied by the X-ray structure analysis method, we also conducted IR spectroscopic analyzes of the reactants of several of them (R_1 , R_3 , R_4).

In order to get some information about the structure of these reactants, the IR spectra of these reactants were taken and compared with the spectra of the starting materials - benzoylacetone and amines - taken for synthesis. In the spectrum of all nitrogen derivatives of benzoylacetone, a new absorption band is observed in the region of 1508-1560 cm^{-1} , unlike the original substances. This band proves the presence of an azo group in the synthesized reactants. It is known from the literature that the absorption band is observed in the frequency range of 1650-1400 cm^{-1} , depending on the atoms and groups to which the azo group is combined. In the spectra of azomethine derivatives of benzoylacetone, a new absorption band observed in the region of 1544 cm^{-1} indicates that the compound contains a C=N group.

Based on literature data, -C=N 1560-1545 cm^{-1} , -N=N- 1400-1650 cm^{-1} , C-F 1400-1000 cm^{-1} , C-Cl 800-600 cm^{-1} , C-Br 600-500

cm⁻¹, -COOH- 3000-2500 cm⁻¹, -OH group 1200 cm⁻¹, -C=O 1680-1630 cm⁻¹, methyl group in ketone 1360 cm⁻¹, Ar-CO- 1690 cm⁻¹, The oscillation frequency of C-I-500 cm⁻¹ groups occurs. Synthesized in compounds -C=N 1544 cm⁻¹, C-F 1029-1325 cm⁻¹, C-Cl 765-698 cm⁻¹, C-Br 505 cm⁻¹, -N=N- 1508-1560 cm⁻¹, -C =O 1647 cm⁻¹, methyl group in ketone 1325 cm⁻¹, C-I-503 cm⁻¹, -COOH- 2859 cm⁻¹, -OH group 1246 cm⁻¹.

Determination of dissociation constants of reagents. One of the important analytical characteristics of organic reagents is their dissociation constant. The dissociation constants of the reactants we studied were determined by the potentiometric titration method, and calculations were made according to Schwarzenbach's mathematical method.

It should be noted, that the dissociation constants of reactants R₅-R₈ are known in the literature. After studying the structure of these reagents by the X-ray structure analysis method, it was found that their structures differ from the previously known structures, that is, the Schiff base formation reaction takes place in the carbonyl group, which is close to the methyl group. Therefore, we considered it appropriate to redefine the dissociation constants of these reactants. To determine the values of dissociation constants, R₁-R₈ reagents and water:ethanol mixture solutions were used. The solutions of the reagents were titrated with standard alkaline KOH (3:7) solutions and based on the obtained results, titration curves were constructed in pH-V_{Base} coordinates. The equivalent point was observed as the number of titratable groups contained in the reagents. The -lg values of the dissociation constants of the reactants are given in table 2. As can be seen from the values of the dissociation constants, as the electronegativity value of the substituents increases, the value of pK_a decreases, that is, the acidity property of the reactant increases. It should be noted that the basic property of azo compounds is higher than the basic property of azomethine derivatives.

It was determined that reactants R₁-R₈ are monobasic, R₉-R₁₂ are dibasic, and reactant R₁₃ is tribasic.

Table 2.
Dissociation constants of reagents.

Reagents	Dissociation constant (pK)
R ₁	8,84±0,05
R ₂	8,87±0,06
R ₃	8,98±0,04
R ₄	9,11±0,05
R ₅	8,58±0,05
R ₆	8,61±0,04
R ₇	8,65±0,06
R ₈	8,77±0,05
R ₉	pK ₁ =6,10±0,04, pK ₂ =9,12±0,05
R ₁₁	pK ₁ =6,49±0,05, pK ₂ =10,22±0,04

The negative decimal logarithmic values of the dissociation constants of the reactant R₁₃, which is a tribasic acid, are pK₁=6.13±0.06, pK₂=8.73±0.04, pK₃=10.43±0.06.

Determination of stability constant of complex compounds by potentiometric titration method. One of the most important characteristics of complex compounds is its stability constant. Parameters characterizing analytical reactions also depend on the stability of complex compounds. Complexes with a high stability constant are widely used for analytical purposes. Complexes with high stability are of particular importance for the determination of small amounts of metal ions. Determination of stability constants of complex compounds formed by organic reagents used in photometric determinations with metals is of special interest. Because, by determining the stability constants, it is possible to predict the selectivity of analytical reactions in advance.

The potentiometric titration method used to study the stability of complexes stands out for its simple device provision, high accuracy, and expressivity.

The stability constants of the complex compounds formed by the R₁-R₈ reagents used in the study with Fe (III), Cu (II), Ni (II), Co (II), Cd (II) and Zn (II) ions were studied. The titration was performed at room temperature. According to the result obtained

from the titration, the titration curves between pH and V_{KOH} were established and it was determined that the titration curves of the complex compounds are formed in an acidic environment compared to the titration curves of the reactants. This is due to the separation of the proton during the formation of the complex in the solution. The more acidic the titration curves of the complexes are formed in relation to the titration curve of the reactant, the more stable that complex is. Among the titration curves of metals, the titration curve of iron is the most formed in acidic medium in all cases.

The results of the calculations are shown in the table 3.

Table 3.

Stability constants of complexes formed by reactants with a number of metals.

R	Fe ³⁺	Cu ²⁺	Ni ²⁺	Co ²⁺	Zn ²⁺	Cd ²⁺
R ₁	9,8±0,04	8,85±0,05	7,75±0,04	5,23±0,06	6,1±0,05	5,3±0,06
R ₂	10,3±0,04	8,33±0,05	5,74±0,06	5,79±0,04	7,3±0,06	6,8±0,06
R ₃	6,3±0,06	5,51±0,06	5,45±0,05	4,32±0,04	5,48±0,05	5,05±0,06
R ₄	10,7±0,06	8,59±0,05	6,04±0,06	5,94±0,04	7,2±0,06	6,1±0,05
R ₅	6,63±0,04	6,57±0,04	5,15±0,06	5,37±0,05	5,57±0,03	5,63±0,05
R ₆	7,43±0,03	6,66±0,04	5,16±0,06	5,39±0,05	5,59±0,04	6,60±0,05
R ₇	7,47±0,02	6,69±0,04	5,19±0,05	5,41±0,06	5,61±0,05	6,63±0,03
R ₈	7,57±0,05	6,78±0,03	5,26±0,03	5,49±0,02	5,69±0,04	6,72±0,06

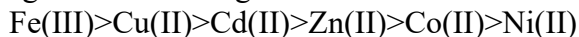
Iron (III) and copper (II) complexes have the highest stability in all cases, as can be seen from the values of the stability constants of the complex compounds.

The conductometric titration method was used to determine the specific electrical conductivity of the complex compounds and the M:R ratio. Chloride salts of metals Fe (III), Cu (II), Ni (II), Co (II), Cd (II) and Zn (II) were used during the titration. The titration of complex compounds was carried out in a buffer solution medium. During conductometric titration in buffer solution medium, the specific electrical conductivity of the system decreases. This is due to the absorption of hydrogen ions released during the complex formation reaction by the buffer solution and the transfer of metal

ions to the composition of the complex. Based on the titration results, titration curves were constructed in $\frac{R}{M}$ - χ coordinates.

Based on these curves, it was determined that as the volume of the titrant increases, the specific electrical conductivity of the solution decreases and remains constant when it reaches a certain value. This is explained by the fact that as each portion of the reactant is added, it reacts with the metal ions in the solution and forms a complex compound. As the titration continues, the amount of metal ions in the solution decreases, and in the end, it completely becomes part of the complex. Therefore, the value of electrical conductivity remains constant after the equivalence point. The reagent itself does not conduct electricity.

According to the conductometric titration curves, depending on the nature of the metals, the change in specific electrical conductivity varies according to the following order.



Extraction of chelate compounds used for the separation of metal ions is considered the most cost-effective method. Through this method, by changing the medium, one can separate a number of metals from other metals or metal ions included in a group from certain mixtures. Therefore, this method is considered an ideal method for the separation of metals due to its simplicity and expressiveness.

β -Diketones and their derivatives are also widely used in metal extraction because they form chelate complexes with metals. Extraction of complex compounds formed by R1-R4 reactants synthesized on the basis of benzoylacetone with Fe (III), Cu (II), Ni (II), Co (II), Cd (II), Zn (II), Mn (II) was studied. The possibilities of extraction of the complex compounds formed by these reactants with metals in various organic solvents were studied and it was determined that the extraction yield was the highest in CCl_4 among the used solvents. Extraction of the complexes in a non-polar solvent indicates that these complexes are uncharged. Based on the results obtained from the experiment, the dependence of the extraction yield on the nature of the metals was determined based on the dependence

established for each metal between the logarithmic value of the distribution coefficient and the pH.

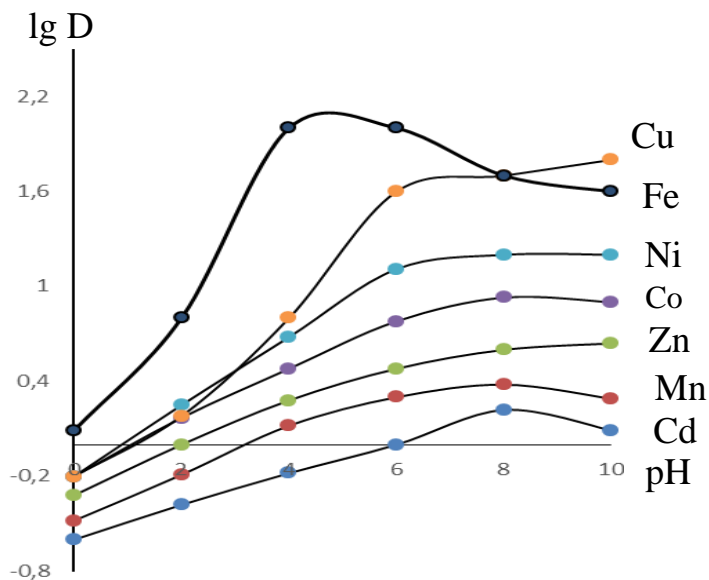


Figure 6. Distribution coefficient of elements for reactant R_1 dependence between logarithmic values of $\lg(D)$ and pH.

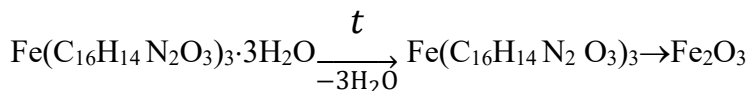
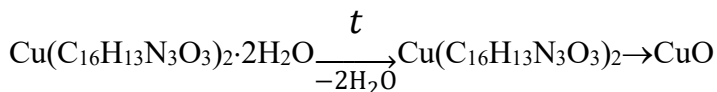
Figure 6 shows the dependence of logarithmic value $\lg(D)$ and pH of the extraction of complex compounds formed by the R_1 reactant with metals.

As can be seen from the figure, iron (III) is the best extracted among these metals. Iron (III) is maximally extracted at pH-3.5. The logarithmic value of the distribution coefficient is equal to 2 and does not change until pH-6. After pH 6, a decrease is observed due to the hydrolysis of iron.

In copper extraction, the logarithmic value of the distribution coefficient increases after pH 6. The logarithmic value of that pH distribution coefficient is equal to 1.6. With increasing pH, the logarithmic value of the distribution coefficient increases after pH-6 and becomes equal to 1.8 at pH 10. At pH-3.5, the logarithmic value

of the distribution coefficient of nickel is equal to 0.3, for cobalt it is 0.2, for zinc it is 0.1, and for manganese it is equal to 0.05. For cadmium, it is a smaller price. The maximum value of the logarithmic distribution coefficient for nickel, cobalt and cadmium occurs at pH-8. For zinc and manganese, it gets the highest value at pH-9. Analyzing them, we come to the conclusion that when the complexes formed by the R1 reactant with the mentioned metals are extracted with CCl4, the extraction phase of iron (III) at pH 3.5 is 100%, copper (II) is 30%, nickel (II) is 20%. , cobalt (II) -15%, zinc (II) - 5%, manganese (II) -3%. According to the experimental results, it was determined that depending on the nature of the metals, the extraction yield varies in the order of Fe>Cu>Ni>Co>Zn>Mn>Cd.

Synthesis and investigation of properties of new complex compounds of iron (III) and copper (II). The method of solid state synthesis of complex compounds formed by iron (III) and copper (II) with R₁, R₅, R₁₁ and R₁₂ reagents has been developed. Synthesized complex compounds were studied by thermogravimetric and IR spectroscopic analysis methods. It was determined by the method of thermogravimetric analysis these complex compounds decompose in 2 stages. Decomposition schemes of complex compounds can be written as follows.



The crystal structure of the complex compound formed by Cu (II) with R₁₂ reagent was studied. The complex compound is in dimer form Cu₂(L)₂. In the compound, the distance between Cu-Cu atoms is 3.0247(7) Å, and the Cu-O distance is 1.938(2) and 1.940(2) Å. Cu(1)-O(1)-Cu(1) and O(1)-Cu(1)-O(1) angles are 102.49(10) and 77.51(10)°. The structure of the Cu(II) complex, which we also

synthesized with the R₁₁ reagent, is probably the same as in the given literature and is shown below⁴ (Figure 7).

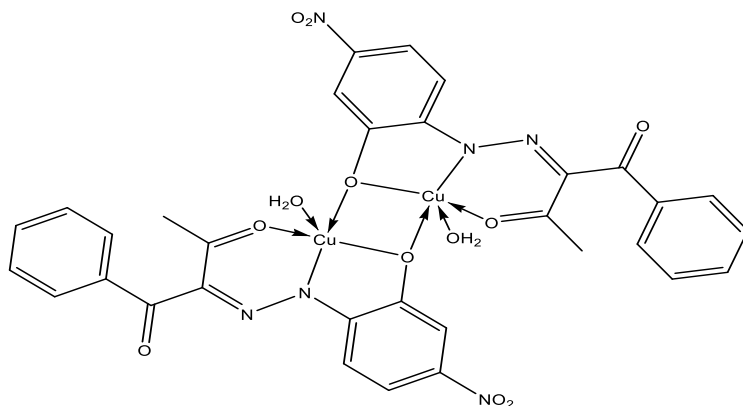


Figure 7. Mechanism of complexation of 1-Phenyl-2-(2-hydroxy-4-nitrophenylhydrazo)-butadione-1,3 (R₁₁) reactant with Cu (II) metal.

By the IR spectroscopic analysis method it was determined which groups are involved in complex formation. No difference is observed in the IR spectra of complex compounds formed by iron (III) and copper (II) with R₁, R₅ reagents. Based on the X-ray structure analysis method, it was determined that these reactants are in the hydrazo form.

According to IR spectroscopy, it was determined that the peaks appearing in the absorption bands of 1534 cm⁻¹ and 1525 cm⁻¹ correspond to C=N, and the peaks appearing in the absorption bands of 2927 cm⁻¹ and 3185 cm⁻¹ correspond to the valence vibration of the -NH group.

⁴ Mahmudov, K.T. Arylhydrazones of methyleneactive compounds: coordination chemistry, organic transformations, catalytic and analytical applications: / Doctor of chemical sciences, dis. / - Baku, 2012. – p.351.

In the carbonyl group, a shift is observed in the second carbonyl group in two different areas $\nu(\text{CO})$ 1629 cm^{-1} and 1638 cm^{-1} and $\nu(\text{C}=\text{O}\dots\text{H})$ corresponding peaks at 1595 cm^{-1} and 1598 cm^{-1} frequency observed in the field. In complex compounds, the peaks of the mentioned groups shift towards 1594 cm^{-1} and 1597 cm^{-1} in the carbonyl group. These shifts indicate that these groups are involved in coordination with the metal.

Also, the presence of the valence vibration of the OH group at $3200\text{--}3600\text{ cm}^{-1}$ indicates the presence of a water molecule in the complex. Analytical application of reagents in the determination of iron (III) and copper (II). As a result of the experiment, it was determined that iron (III) ion forms an intensely colored complex compound with reagents R₅, R₁₁-R₁₃, and copper (II) ion with reagents R₉-R₁₂. Therefore, the complex combination formed by these reactants with these metal ions was studied spectrophotometrically. In order to increase the analytical parameters of binary complex compounds, the effect of hydrophobic amines phenanthroline, ethylenediamine, α,α' -dipyridyl, diantipyrylmethane and its derivatives diantipyrylphenylmethane, diantipyryl-*o*-oxyphenylmethane, cationic surfactants CSS – cetylpyridine chloride, cetylpyridine bromide, cetyltrimethylammonium bromide on the binary complex was studied. According to the literature, the mechanism of formation of the complex with different ligands is as follows, and we assume that it was obtained in other complexes with different ligands:

It was determined that increasing in the stability of complexes with different ligands due to the effect of the third component, certain changes occur in the light spectrum of the compounds and in the optimal pH.

Thus, bathochromic shift occurs at the maximum illumination of complex compounds, and the optimal pH shifts to an acidic environment.

The ratio of components in binary and mixed-ligand complexes was determined by isomolar, Starik-Barbanel and equilibrium shift methods. The number of hydrogen ions released during the complex formation reaction was determined by the Astakhov method. Based

on the obtained results, the structure of the complex formed by Cu (II) with R₉ in the presence of surfactant can be described as follows (Figure 8):

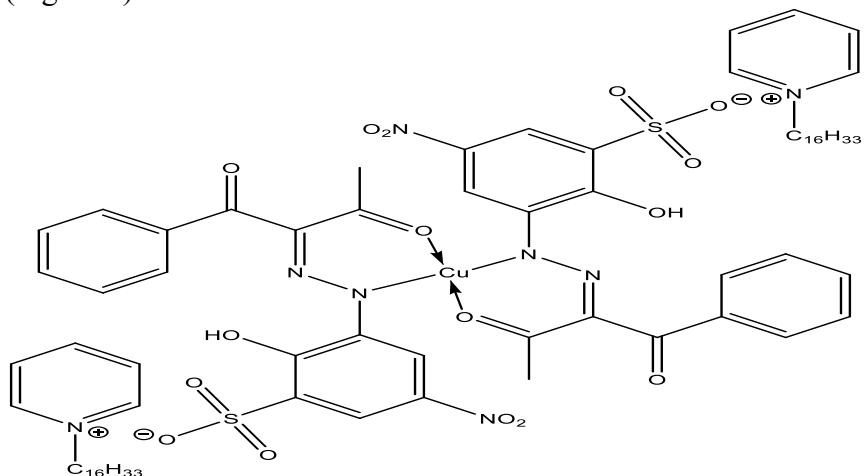


Figure 8. Mechanism of complex formation of Cu (II) metal with reagent R₉ in the presence of cationic surfactants.

Experiments show that complexes with different ligands are formed in acidic environment compared to binary complexes. Therefore, it can be predicted that these reactions will have high selectivity. The molar absorption coefficients of the studied complex compounds with different ligands are also higher than the binary complex.

The effect of concentration of reagents on complex formation was determined and various spectrophotometric characteristics were calculated.

The statistical characteristics of photometric determination methods developed for Fe (III) R₁₂ and R₁₃, and Cu (II) - for R₉ reagent were calculated. Based on the calculated results, the standard and relative standard deviation were calculated and it was determined that the proposed methodology is accurate, correct and reliable.

The main spectrophotometric characteristics of the reactions we will apply for iron (III) and copper (II) are shown in table 4. In the table, binary and complex compounds with various ligands formed by iron (III) R₅ and R₁₁-R₁₃, copper (II) R₉-R₁₂ reagents were studied by photometric method. The results of the study pH_{opt}, λ_{max}, molar absorption coefficient, the ratio of components in the complexes, the stability constants of the complexes, and the values of the interval obeying Beer's law are shown in Table 4.

Table 4.

Some characteristics of complexes formed by iron (III) and copper (II) with azo derivatives of benzoylacetone.

Complex	pH _{opt}	λ _{opt}	ε·10 ⁴	lgβ	The ratio of components	The interval of obedience to Beer's law is mcg/ml
Fe(III)-R ₅	5,0	418	1,000	9,34±0,09	1:2	0,22-11,20
Fe(III)-R ₅ -DAM	3,0	458	1,275	11,68±0,13	1:2:2	0,17-6,72
Fe(III)-R ₅ -DAPM	3,0	482	2,000	10,66±0,14	1:2:2	0,11-11,20
Fe(III)-R ₅ -DAOPM	3,0	487	1,500	10,10±0,10	1:2:2	0,17-6,72
Fe-R ₁₁	5,0	440	2,680	5,11±0,03	1:1	1,12-2,24
Fe-R ₁₁ -CPCl	3,0	463	3,900	10,70±0,03	1:1:1	0,112-1,12
Fe-R ₁₁ -CPBr	3,0	456	3,362	10,40±0,03	1:1:1	0,56-1,12
Fe-R ₁₁ -CTMABr	3,0	482	2,920	10,10±0,03	1:1:1	0,56-1,12
Fe-R ₁₂	5,0	425	1,786	4,96±0,03	1:2	0,11-2,74
Fe-R ₁₂ -DAM	2,0	455	2,260	9,09±0,03	1:2:2	0,11-3,36
Fe-R ₁₂ -DAPM	3,0	434	2,670	10,87±0,04	1:2:1	0,11-6,72
Fe-R ₁₂ -DAOPM	3,0	448	2,860	11,91±0,1	1:2:2	0,11-5,6
Fe-R ₁₃	5,0	397	0,750	4,57±0,05	1:1	0,224-2,24
Fe-R ₁₃ -DAM	3,0	402	1,200	10,23±0,03	1:1:1	0,112-6,72
Fe-R ₁₃ -DAPM	3,0	405	1,425	11,48±0,03	1:1:1	0,112-8,96
Fe-R ₁₃ -	3,0	400	1,050	9,20±0,01	1:1:1	0,112-2,24

DAOPM						
Cu-R ₉	3,0	444	1,400	6,04±0,12	1:2	0,25-3,07
Cu-R ₉ -ED	2,0	461	2,200	10,16 ±0,14	1:2:2	0,12-2,56
Cu-R ₉ -Fen	3,0	468	1,850	9,12 ±0,09	1:2:2	0,18-2,56
Cu-R ₉ -α,α'- dip	3,0	471	1,720	9,44 ±0,13	1:2:2	0,18-2,56
CuR ₉ -CPCl	2,0	456	2,300	11,24±0,12	1:2:2	0,12-2,56
CuR ₉ -CPBr	2,0	454	2,200	10,82±0,10	1:2:2	0,12-2,56
CuR ₉ - CTMABr	2,0	461	2,500	12,04±0,09	1:2:1	0,12-2,56
CuR ₁₀	4,0	451	1,375	5,76±0,03	1:2	0,25-3,07
CuR ₁₀ -CpBr	3,0	475	1,920	11,46±0,05	1:2:2	0,14-2,58
Cu-R ₁₁	4,0	456	0,975	4,90±0,04	1:2	0,25-6,14
Cu-R ₁₁ -CPCl	2,0	468	1,500	10,36±0,03	1:2:2	0,13-5,12
Cu-R ₁₁ -CPBr	3,0	484	2,150	11,26±0,05	1:2:2	0,13-2,56
Cu-R ₁₁ - CTMABr	3,0	476	1,750	10,52±0,04	1:2:2	0,13-3,07
Cu-R ₁₂	5,0	434	1,500	4,36±0,03	1:2	0,25-3,74
Cu-R ₁₂ -CPCl	4,0	463	1,800	8,91±0,05	1:2:2	0,13-2,56
Cu-R ₁₂ -CPBr	4,0	447	1,700	8,95±0,03	1:2:1	0,15-2,56
Cu-R ₁₂ - CTMABr	4,0	452	2,250	9,26±0,04	1:2:2	0,13-2,56

As can be seen from the table, the optimal conditions of the mixed-ligand complex formed by the effect of the third component shift towards the acidic environment. Therefore, it can be predicted that the selectivity of this complexation reaction is higher than that of the binary complex, and a bathochromic shift occurs in the maximum absorption spectrum of complexes with different ligands compared to the binary complex. This situation is observed in all studied complexes. As the stability of complexes with various ligands formed by iron (III) and copper (II) in the presence of hydrophobic amines and surfactants increases, molar absorption coefficients also increase. In complexes with different ligands, the interval of subordination to the rank graph starts from a smaller density.

Masking agents are used to eliminate the effect of foreign ions that interfere with the determination during the analysis.

The effect of foreign ions on the binary and mixed-ligand complexation reactions of Fe (III) and Cu (II) with the reagents was studied, and the effect of shielding agents studied in order to eliminate the influence of interfering ions. Calculations of experimental results are given in the table (Tables 5-6).

Table 5.

Effect of external ions and shielding agents on complexes formed by iron (III) DAM and its derivatives with 1-phenyl-2-[2-hydroxy-phenylazo]butadione-1,3 reagent in the presence and absence of DAM.

Ion or substance	Fe-R ₁₂	Fe-R ₁₂ -DAM	Fe-R ₁₂ -DAFM	Fe-R ₁₂ -DAOFM
Alkali metals	*	*	*	*
Alkaline-earth metals	*	*	*	*
Ni(II)	1700	1765	1720	1650
Co(II)	1500	1700	1650	2000
Zn(II)	430	670	780	850
Mn(II)	285	328	320	500
Cu(II)	3	8	8	5
Cd(II)	1200	1667	1650	1550
Al(III)	100	260	300	200
Cr(III)	139	155	158	140
Sn(IV)	120	180	175	165
V(V)	30	50	51	45
Sb(V)	16	20	25	30
F ⁻	200	220	220	500
Citric acid	260	345	350	370
Alcoholic acid	580	1000	1000	900
Na ₂ HPO ₄	720	844	855	816

*-does not interfere

Table 6.

Effect of external ions and shielding agents on complex formations of copper (II) with R₉ reagent in the presence and absence of hydrophobic amines and CSS.

Ion or substance	R ₉	R ₉ -ED	R ₉ -Fen	R ₉ - α,α' -dip	R ₉ -CPCI	R ₉ -CPBr	R ₉ -CTMABr
Na	*	*	*	*	*	*	*
K	*	*	*	*	*	*	*
Ca	*	*	*	*	*	*	*
Zn	*	*	*	*	*	*	*
Cd	*	*	*	*	*	*	*
Mn	*	*	*	*	*	*	*
Ni	46	78	65	65	118	115	115
Co	277	324	310	305	364	340	345
Al	*	*	*	*	*	*	*
Sm	*	*	*	*	*	*	*
Fe(III)	9	5	5	5	6	5	3
Ga(III)	547	597	570	560	647	610	600
In(III)	539	605	580	580	645	620	620
Bi(III)	33	84	70	70	124	110	110
Sn(IV)	186	240	215	210	280	255	250
Hf(IV)	351	420	390	375	460	430	415
Ti(IV)	375	480	450	455	520	490	495
Zr(IV)	711	790	755	765	830	795	805
Mo(VI)	150	204	180	180	244	220	220
W(VI)	287	375	340	340	415	380	380
C ₂ O ₄ ²⁻	104	150	120	130	190	160	170
EDTA	10	17	14	15	57	54	55
Tiomochevina	59	73	64	60	113	104	100
Citric acid	985	1120	1010	1005	1170	1160	1055
Na ₂ HPO ₄ ·12H ₂ O	703	740	710	720	790	760	770
Alcoholic acid	279	310	305	300	350	345	340
F ⁻	281	315	310	310	355	350	350

*-does not interfere

The developed methods were applied for the determination of iron (III) in different samples of apples and onions, and copper (II) in sea water, copper-based alloy, mountain rocks, buckwheat, peas, bananas and mushrooms (Table 7).

Table 7.

Results of photometric determination of the amount of iron (III) and copper (II) in various natural objects.

Analyzed samples	It has been found Fe %.	
	R ₁₂ +Diantipyryl-phenylmethane	AAS
Apple (Severyanka)	$(5,60 \pm 0,07) \cdot 10^{-3}$	$(5,63 \pm 0,09) \cdot 10^{-3}$
Apple (Syganka)	$(2,48 \pm 0,06) \cdot 10^{-2}$	$(2,45 \pm 0,10) \cdot 10^{-2}$
Apple (Golden Delishes)	$(3,36 \pm 0,04) \cdot 10^{-2}$	$(3,32 \pm 0,03) \cdot 10^{-2}$
	R ₁₃ +Diantipyryl-phenylmethane	
Hovsan onion	$(5,34 \pm 0,03) \cdot 10^{-1}$	$(5,20 \pm 0,08) \cdot 10^{-1}$
Red onion	$(2,82 \pm 0,04) \cdot 10^{-1}$	$(2,89 \pm 0,06) \cdot 10^{-1}$
	It has been found Cu, %	
	R ₉ +CTMABr	
1 sample of pyrite	0,65±0,10	0,600±0,006
2 sample of pyrite	0,93±0,13	0,910±0,003
3 sample of pyrite	4,15±0,12	4,19±0,004
	R ₉ +ED	
Sea water (Turkan settlement)	$(3,74 \pm 0,03) \cdot 10^{-5}$	$(3,78 \pm 0,01) \cdot 10^{-5}$
	R ₁₁ +CPBr	
Banana (Gro-Michel)	$(3,40 \pm 0,03) \cdot 10^{-3}$	$(3,46 \pm 0,05) \cdot 10^{-3}$
Mushroom (Champinion)	$(3,15 \pm 0,02) \cdot 10^{-3}$	$(3,2 \pm 0,06) \cdot 10^{-3}$
Pea (Getman)	$(3,33 \pm 0,06) \cdot 10^{-3}$	$(3,5 \pm 0,03) \cdot 10^{-3}$
	R ₁₂ +CTMABr	
Banana (Gro-Michel)	$(3,47 \pm 0,03) \cdot 10^{-3}$	$(3,49 \pm 0,05) \cdot 10^{-3}$
Buckwheat (Oranta)	$(2,40 \pm 0,02) \cdot 10^{-3}$	$(2,46 \pm 0,06) \cdot 10^{-3}$
Pea (Getman)	$(3,34 \pm 0,06) \cdot 10^{-3}$	$(3,38 \pm 0,03) \cdot 10^{-3}$

Results

1. 13 reagents were synthesized based on benzoylacetone. The individuality of the reagents was confirmed by IR and NMR spectroscopic analysis methods. The crystal structure of five of these reactants was studied by X-ray analysis method and it was determined that the reactants are in the hydrazo tautomeric form.
2. Complex compounds formed by these reactants (R_1 - R_4) with series transition metals Fe (III), Cu (II), Co (II), Ni (II), Zn (II), Cd (II), Mn (II) the possibilities of extraction in different organic solvents - carbon-4-chloride, benzene, chloroform and isobutanol - were studied. It was determined that the extraction yield of complex compounds is the highest when CCl_4 is used. In all cases, the best extracted ion is Fe^{3+} . It was determined that Fe^{3+} ion can be separated from a mixture of other metals with R_1 and R_2 reagents.
3. The complex compounds formed by iron (III) and copper (II) with synthesized reagents were studied using the spectrophotometric method, the optimal conditions were determined, the main analytical characteristics of the complexes were determined, and the mechanism of complex formation was studied. The stability constants and specific electrical conductivities of complex compounds were studied by potentiometric and conductometric titration methods. It was determined that the iron (III) complex has the highest continuity constant and the lowest value of specific electrical conductivities.
4. Third components were used in order to increase the analytical parameters of complex compounds formed by iron (III) and copper (II) with reagents synthesized on the basis of benzoylacetone. It was found that the optimal pH valued formation of the mixed-ligand complex formed by the effect of the third component shifts towards an acidic environment, a bathochromic shift occurs in λ_{max} compared to the binary complex, the value of the molar absorption coefficient and

the stability constant increases. Complexes with different ligands have been proven to have higher analytical characteristics than complexes with the same ligand.

5. At the same time, the effect of foreign ions on the reactions of the formation of binary and mixed-ligand complexes of shielding substances was studied. Based on the obtained results, it was determined that complexes with different ligands are characterized by higher selectivity for determination of iron (III) and copper (II).
6. Methods of spectrophotometric determination of iron (III) and copper (II) ions have been developed. The developed methods were applied for the determination of mentioned metals in natural objects such as sea water, copper-based alloy, mountain rock, banana, mushroom, buckwheat, pea, apple, and onion varieties. It has been found to have high repeatability and reliability, as well as being simple and express.

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