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SPECTROPHOTOMETRIC DETERMINATION OF IRON(III) WITH 1,2-BIS((4-OXOPENTANE-2-ILIDEN)AMINE)ETHANE

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Complexation of iron(III) with 1,2-bis((4-oxopentane-2-iliden)amine)ethane in the presence of third components - 1,10-phenantroline, 4-aminoantipyrine and sodium dodecylsulfate is investigated by spectrophotometric method and high selective method of its definition in natural objects is worked out. It was found that in the presence of third components iron(III) forms different liganded complexes with the reagent, where in bathochromic shift is observed in the absorption spectrum and the maximum yield moves to acidic environment compared to binary complex. Effects of reactive components, time and temperature to the forming of different liganded complexes id studied and their stoichiometry is defined by different methods. It has been shown that definition of iron(III) with 1,2-bis((4-oxopentane-2-iliden)amine)ethane in the presence of 1,10-phenantroline is highly selective. The designed method is used for definition of iron in volcanic rocks of Lesser Caucasus of Kalbajar region of Azerbaijan Republic.

Keywords: *iron(III), 1,2-bis((4-oxopentane-2-iliden)amine)ethane, 1,10-phenantroline, different liganded complex, volcanic rocks*

For spectrophotometric definition of iron (III) in natural and industrial objects chelating organic reagents, which consist of donor atoms of Nitrogen and Oxygen, are widely used [1 - 3]. Due to the biggest chemical and analytical characteristics different liganded complexes of these reagents with iron(III) have great practical value [3 - 5].

The main purpose of this work is investigation of complexation of iron(III) with 1,2-bis((4-oxopentane-2-iliden)amine)ethane in the presence of 1,10-phenantroline, 4-aminoantipyrine and sodium dodecylsulfate as a third component and working out of highly selective methods of its definition in natural objects.

Experimental part

Reagents. Standart $1{,}0\cdot10^{-1}$ M solution of iron(III) is prepared by dissolving of calculated hitch of metallic iron by method [6]. $5{,}0\cdot10^{-3}$ M working solutions are received through dilution of initial solution with distilled water before its using.

In this work $5{,}0\cdot10^{-3}$ M solutions of 1,2-bis((4-oxopentane-2-iliden)amine)ethane (R) and $1{,}0\cdot10^{-2}$ M solutions of third components - 1,10-phenantroline (Phen), 4-aminoantipyrine (Ant) and sodium dodecylsulfate (DDS) were used. Reagent, 1,10-phenantroline and 4-aminoantipyrine solutions were prepared by dissolving of corresponding hitches in ethanol and natrium dodecylsulfate in distilled water. All the used reagents had qualification not less than reagent grade. For creating necessary acidity acetate-ammonia buffer solutions (pH 3-11) and HCl (0-2) were used.

Equipment. Optimal density of solutions is measured on the spectrophotometer "Lambda-40" with computer software (Perkin Elmer firm) and on the photoelectrocolorimeter KFK-2 in the cuvettes with layer thickness 1,0 cm. pH value of solutions was measured with pH-meter pH-121 with glass electrode.

Results and discussions

Iron(III) forms colored complex compound with reagent in acidic environment at pH interval 1,0-7,0 with maximum of light absorption at λ=402 nm, and reagent itself absorbs in this environment at λ=336 nm. The maximum yield of complex is observed at pH 4,5-5,0. In the presence of third components different liganded complexes Fe(III)-R-Phen, Fe(III)-R-Ant, Fe(III)-R-DDS are formed, wherein the bathochromic shift is observed compared to the spectrum of binary complex and maximum yield of complexation moves to the acidic environment. Maximal absorption of complexes Fe(III)-R-Phen, Fe(III)-R-Ant and Fe(III)-R-DDS is observed at 420, 412 and 413 nm respectively. The yield of different liganded complexes Fe(III)-R-Ant and Fe(III)-R-DDS is maximum at pH 4,0-4,4 and pH 3,8-4,2 for Fe(III)-R-Phen. Color of reagent and complexes depend on acidity of environment, therefore absorption spectras have been studied on the background of control experiment (R+Th.c.) during complexation. It was found that optical density of different liganded complexes of iron(III) on the background of control experiment is maximum at 400 nm.

Effect of concentration of reactants, temperature and time to complexation of binary and different liganded complexes have been studied . It was found that all the complexes of iron(III) are formed immediately after mixing of solutions and have high stability. So if binary complex is stable during 2 hours and boiling till 60°C, then different liganded complex is stable during over than one day and boiling till 80°C. The yield of binary complex iron(III) is maximum at concentration of reagent 6,0·10^{-4} M and optical density of its solution is stable at 3,0-7,0 fold molar excess of reagent. The maximum yield of different liganded complexes Fe(III)-R-Phen, Fe(III)-R-Ant, Fe(III)-R-DDS is observed at the concentration of reagent 5,0·10^{-4} M and 4,0·10^{-4} M concentration of third components. Optical density of solutions of different liganded coplexes is constant at 2,5-8,0 fold molar excess of reagent and 2,0-10,0 fold molar excess of third components.

The stoichiometry of components it the compound of colored complexes of iron(III) has been found with the isomolar series method, Starik-Barbanel`s relative yield method and equilibrium shift method [7]. All the methods have shown that, the stoichiometry of components in the compound of binary complex is 1:2 and 1:1:1 in different liganded complexes (Table 1). The number of protons displaced during complexation have been defined by Astakhov`s method and specified stoichiometry of components in complexes have been confirmed [8].

Table 1

Chemical and analytical characteristics of Fe(III) complexes with 1,2-bis ((4-oxopentane-2-iliden)amine)ethane

Complex	pH_{opt}	λ_{max}, nm	$\Delta\lambda$, nm	$\varepsilon \cdot 10^3$ (at λ_{max})	C_R/C_{Fe}	$C_{th.c.}/C_{Fe}$	lgβ	Components stoichiometry	Linearity range of calibration graph, mg/ml
Fe-R	4,5-5,0	402	66	0,55±0,01	3,0-6,0		9,95±0,20	1:2	2,24-11,2
Fe-R-Phen	3,8-4,2	420	84	0,70±0,02	2,5-8,0	2,0-10	17,46±0,27	1:1:1	1,12-11,2
Fe-R-Ant	4,0-4,4	412	76	1,15±0,02	2,5-8,0	2,0-10	16,72±0,26	1:1:1	0,84-13,4
Fe-R-DDS	4,0-4,4	413	77	0,80±0,01	2,5-8,0	2,0-10	13,19±0,24	1:1:1	1,12-11,2

The stoichiometry and stability constant of binary complex Fe(III)-R were defined with the curve intersection method. Results were confirmed and it was found that lgβ(Fe-R)=9,95±0,20. Considering molar stoichiometry in different liganded complexes their stability constants have been determined. It was found that in the presence of third components stability of complexes greatly increases: lgβ(Fe-R-Phen)=17,46±0,27; lgβ(Fe-R-Ant)=16, 72±0,26; lgβ(Fe-R-DDS)=13,19±0,24.

Calibration graph is linear at the range 2,24-11,2 mg/ml Fe(III) for the Fe(III)-R complex, 1,12-11,2 mg/ml for Fe(III)-R-Phen and Fe(III)-R-DDS and 0,84-13,4 mg/ml for Fe(III)-R-Ant. Molar light absorption coefficients of complexes Fe(III)-R, Fe(III)-R-Phen, Fe(III)-R-Ant and Fe(III)-R-DDS at λ_{opt} are $(0{,}55\pm0{,}01)\cdot10^3$, $(0{,}70\pm0{,}02).10^3$,$(1{,}15\pm0{,}02)\cdot10^3$ and$(0{,}80\pm0{,}01)\cdot103$ respectively.

Studying the effects of foreign ions and masking agents on the results of determination of iron(III) have shown that, in the presence of third components selectivity of reaction greatly increases. The method of determination of Fe(III) with the reagent in the presence of 1,10-phenantroline has the highest selectivity. So over than 5000 fold amount of alkaline, alkaline earth and rare earth elements don`t interfere the determination of Fe(III) in the Fe(III)-R-Phen different liganded complex form; 1000 fold amount of Cu(II), Co(II), Zn(II), Ni(II), Cd(II), Mn(II), Mg(II), Pb(II), Cr(III), Al(III), Th(IV), U(VI); 500 fold amount of Ga(III), In(III), Bi(III), Sb(III), Ti(IV), V(V), Nb(V), Ta(V), F^-, HPO_4^{2-}, $C_2O_4^{2-}$; 100 fold amount of Zr(IV), Hf(IV), Mo(VI) and W(VI).

The designed method is used for determination of iron in volcanic rocks of Lesser Caucasus of Kalbajar region of Azerbaijan Republic.

Analysis. The sample rock weight with 5,0 g of mass is dissolved in the mixture of 20 ml HF + 15 ml HCl + 5 ml HNO_3 in the glassy cup. The received paste is processed with 4-5 ml of HNO_3 at 60-70°C till the complete distillation of HF. Precipitate is dissolved in distillated water, filtrated in 50 ml capacity flask and diluted to mark. The aliquot part of solution is placed in 25 ml capacity volumetric flask, 2,5 ml of $5{,}0\cdot10^{-3}$ M solution of reagent, 1,0 ml of $1{,}0\cdot10^{-2}$ M of 1,10-phenantroline are added and brought to mark with pH 4,0 acetate-ammonia buffer solution. Optical density of solution is measured on the photoelectrocolorimeter KFK-2 at 400 nm in the cuvettes with layer thickness 1,0 cm on the background of control experiment. The amount of iron is found on the pre-built calibration graph. Results of determination of iron volcanic rocks are shown in the Table 2.

Table 2

Results of determination of iron volcanic rocks (n=5, P=0,95)

Rock samles	Licensed compound amounts, %	Found Fe, %	S_r
I	TiO_2 - 0,75; Fe_2O_3-4,52 (Fe – 3,164); FeO – 0,88; (Fe – 0,684); CaO – 5,88; MgO – 1,50; P_2O_5 – 0,72; MnO – 0,02; K_2O – 4,00; Na_2O – 5,40; In_2O_3 – 0,01; Ga_2O_3 – 0,00945; Se_2O_3 – 0,01; SeO_3 – 0,05; REE – 0,70; H_2O – 0,29; SiO_2 – left.	3,840±0,106	0,024
II	TiO_2 - 0,70; Fe_2O_3-4,68 (Fe – 3,276); FeO – 0,74; (Fe – 0,684); CaO – 5,88; MgO – 1,10; P_2O_5 – 0,71; MnO – 0,02; K_2O – 3,92; Na_2O – 5,60; In_2O_3 – 0,01; Ga_2O_3 – 0,0102; Se_2O_3 – 0,01; SeO_3 – 0,05; REE – 0,30; H_2O – 0,13; SiO_2 – left.	3,861±0,093	0,021

REFERENCES

1. *Упор Э., Мохаи М., Новак Д.* Фотометрические методы определения следов неорганических соединений. М.: Мир, 1985. 359с.
2. *Умланд Ф., Янсен А., Тириг Д., Вюнш Г.* Комплексные соединения в аналитической химии. М.: Мир. 1975, 531с.
3. *Dawson M.V., Lyle S.J.* // Talanta. 1990. V.37. №12. p.1189-1191.
4. *Новопольцева В.М., Учватова О.В., Осипов А.К., Нищев К.Н.* // Журн. аналит. химии, 2007, т.61, №8. с.808-811.
5. *Нагиев Х.Д., Эспанди Ф.Э., Алиева Р.А., Гюллярли У.А., Чырагов Ф.М.* // Аналитика и контроль. 2013. Т. 17. №1. с.107-111.
6. *Коростелев П.П.* Приготовление растворов для химико-аналитических работ. М.: Наука, 1964, 261с.
7. *Булатов М.И., Калинкин Н.П.* Практическое руководство по фотометрическим методом анализа Л.: Химия, 1986, 432с.
8. *Астахов К.В., Вериникин В.Б., Зимин В.И., Зверькова А.А.*// Журн. неорган. химии, 1961, т.6. с. 2069-2076.

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DƏMİRİN(III) 1,2-BİS((4-OKSOPENTAN-2-İLİDEN)AMİN)ETANLA SPEKTROFOTOMETRİK TƏYİNİ

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Üçüncü komponentlər – 1,10-fenantrolin, 4-aminoantipirin və natrium doselsulfat iştirakında dəmirin(III) 1,2-bis((4-oksopentan-2-iliden)amin)etanla kompleks əmələ gətirməsi spektrofotometrik metodla tədqiq edilmiş və təbii obyektlərdə onun təyini üçün yüksək seçiciliyə malik metodikalar işlənilib hazırlanmışdır. Müəyyən edilmişdir ki, üçüncü komponentlər iştirakında dəmir(III) reaktivlə müxtəlifliqandlı kompleks birləşmələr əmələ gətirir ki, bunun da nəticəsində udma spektrində binar kompleksin udma spektri ilə müqayisədə batoxrom sürüşmələr və maksimum çıxımın daha turş mühitə doğru sürüşməsi müşahidə edilir. Müxtəlifliqandlı komplekslərin əmələ gəlməsinə komponentlərin qatılığının, vaxt və temperaturun təsiri öyrənilmiş və tərkibi müxtəlif metodlarla təyin edilmişdir. Müəyyən edilmişdir ki, dəmirin(III) 1,10-fenantrolin iştirakında reaktivlə təyini daha yüksək seçiciliyə malikdir. İşlənilmiş metodika Azərbaycan Respublikası Kəlbəcər rayonu ərazisindən götürülmüş Kiçik Qafqazın vulkanik dağ süxurlarında dəmirin təyini üçün tətbiq edilmişdir.

Açar sözlər: *dəmir(III), 1,2-bis((4-oksopentan-2-iliden)amin)etan, 1,10-fenantrolin, müxtəlifliqandlı kompleks, vulkanik dağ süxuru*

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ЖЕЛЕЗА(III) С 1,2-БИС ((4-ОКСОПЕНТАН-2-ИЛИДЕН)АМИН)ЭТАНОМ

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Спектрофотометрическим методом исследовано комплексообразование железа(III) с 1,2-бис((4-оксопентан-2-илиден)амин)этаном в присутствии третьего компонента – 1,10-фенантролина, 4-аминоантипирина и додецилсульфат натрия и разработана высокоселективная методика определения его в природных объектах. Установлено, что в присутствии третьих компонентов железа(III) с реагентом образуются разнолигандные комплексы, при этом наблюдаются батохромные сдвиги в спектре поглощения, и максимальный выход сдвигается в кислую среду по сравнению с бинарным комплексом. Изучено влияние реагирующих компонентов, времени и температуры на образование разнолигандных комплексов и определена их стехиометрия различными методами. Показано, что определение железа(III) с 1,2-бис((4-оксопентан-2-илиден)амин)этаном в присутствии 1,10-фенантролина высокоизбирательна. Разработанная методика применена для определения железа в вулканогенных породах Малого Кавказа Кельбаджарского района Азербайджанской Республики.

Ключевые слова: *железо(III), 1,2-бис((4-оксопентан-2-илиден)амин)этан, 1,10-фенантролин, разнолигандный комплекс, вулканогенные породы*