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DETERMINATION OF IRON IN MUSHROOMS WITH 3-ACETYL-4,6-DIPHENYLHEXANEDIONE-2,6 AND HYDROPHOBIC AMINES**A.Y. Abiyeva***Baku State University**Z. Khalilov, str. 23, AZ 1148 Baku, Azerbaijan; e-mail: arzu.abiyeva.82@inbox.ru*

Methods of spectrophotometric determination of iron (III) with 3-acetyl-4,6-diphenylhexanedione-2,6 and hydrophobic amines - 1,10-phenanthroline and diantipyrylmethane were developed. The complex-forming of the iron (III) with reagent were examined to discover that in the presence of hydrophobic amines there are formed mixed-ligand complexes accompanied by bathochromic shift which is observed in the absorption spectra and the optimal pH formation shifts move toward more acidic environment. Effect of concentration of reagents, time and temperature on formation of mixed-ligand complexes has been investigated and their stoichiometry determined with different methods. High-selective technique of spectrophotometric determination of micro-amounts of iron (III) in the mushrooms "Champignon" picked from the settlement of Zira, Baku, was developed.

Keywords: iron (III), 3-acetyl-4,6-diphenylhexanedione-2,6, 1,10-phenanthroline, diantipyrylmethane, mushrooms.

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INTRODUCTION

For spectrophotometric determination of iron (III) organic reagents containing various donor atoms as well as oxygen are used [1-3]. There are a lot of well-known methods for the determination of iron (III) with oxygen-containing organic reagents in natural and industrial objects in the form of binary and mixed ligand complexes [1-5]. Earlier [6-8], were offered some methods for the determination of iron (III) in natural

objects by oxygen-containing organic reagents in the form of mixed-ligand complexes.

The purpose of the work is to develop a high-selective method for the spectrophotometric determination of iron (III) in mushrooms using a new organic reagent based on acetylacetone-3-acetyl-4,6-diphenylhexanedione-2,6, hydrophobic amines - 1,10-phenanthroline and diantipyrylmethane.

EXPERIMENTAL PART

Reagents. A standard $1,0 \cdot 10^{-1}$ M iron (III) solution was prepared by dissolving the calculated metallic iron sample according to the procedure [9]. $2,0 \cdot 10^{-3}$ M solutions were obtained by diluting the stock solution with distilled water before use.

$2,0 \cdot 10^{-3}$ M solutions of 3-acetyl-4,6-diphenylhexanedione-2,6 (R) and hydrophobic amines - 1,10-phenanthroline (Phen) and diantipyrylmethane (DAM) which were prepared by dissolving the corresponding weights in ethanol, were used. All the used

reagents were of analytical grade. Acetic-ammonium buffer solutions (pH = 3-11) and HCl (pH = 0-2) were used to create the necessary acidity.

Equipment. Spectrophotometric measurements in the UV and visible regions were carried out on a Lambda-40 spectrophotometer with computer software (Perkin Elmer), in cuvettes of 1 cm of light part. The pH of the solutions was measured using a pH-meter pH-121 with a glass electrode.

RESULTS AND DISCUSSION

Investigation of the complexation of iron (III) with a reagent. The absorption spectra of the reagent in various acidities of the solution were studied to find that its absorption is maximum at 293 nm in a medium pH 0-5 and 326 nm at pH 6-11, due to the presence of keto-enol tautomerism. In the course of interaction with the reagent iron (III) forms a colored complex compound in an acidic medium at pH 0-7.0. The absorption spectra of the reagent and its complex with

iron (III) are shown in Fig.1. The maximum absorption of the Fe (III) -R complex is observed at 383 nm (curve 2). The dependence of optical density on the pH of the solution showed that the output of the complex is maximum at pH 4.5-5.0 (Fig. 2, curve 1). For the complete binding of iron(III) ions into the complex, a $2.0 \cdot 10^{-4}$ M reagent solution and its 2.5-8.0-fold molar excesses that do not affect the optical density of the complex, are necessary.

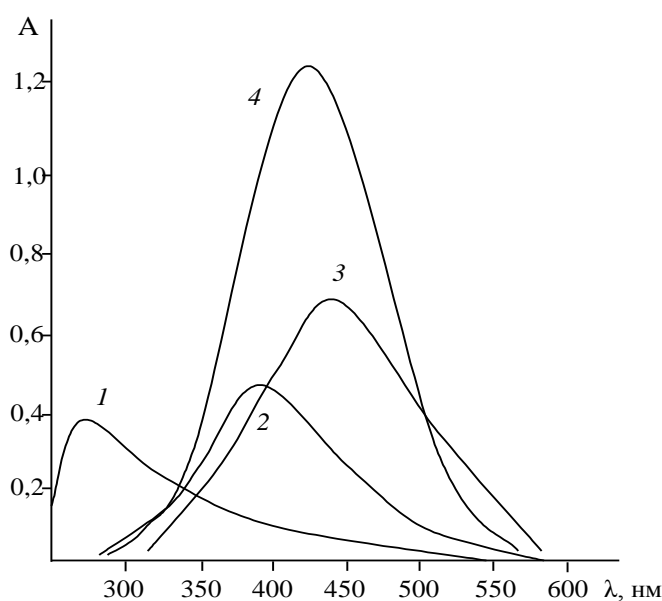


Fig.1. Absorption spectra of iron (III) complexes at optimal pH value.

1 - R, 2 - Fe(III)-R, 3 - Fe(III)-R-Phen, 4-Fe(III)-R-DAM.
 $C_{Fe}=8.0 \cdot 10^{-5}M$, $C_R=2.0 \cdot 10^{-4}M$, $C_{Phen(DAM)}=1.6 \cdot 10^{-4}M$,
 λ_{40} , $l=1.0$ sm

Effect of hydrophobic amines on chemical and analytical properties of Fe(III)-R complex. In the presence of hydrophobic amines - 1,10-phenanthroline and diantirylmethane mixed-ligand complexes Fe(III)-R-Phen and Fe(III)-R-DAM are formed, while the bathochromic shifts in the absorption spectrum are observed, and their maximum output goes to more acidic environment compared to the binary complex Fe(III)-R. The light absorption of Fe(III)-R-Phen and Fe(III)-R-DAM complexes are

maximum at 428 and 421 nm (Fig. 1, curves 3 and 4). Optimal values of pH (pH_{opt}) for complexes Fe(III)-R-Phen and Fe(III)-R-DAM are equal to 1.5-2.0 and 1.0-1.5, respectively (Fig. 2, curves 2 and 3).

To select the optimal conditions, effect of the concentration of reacting substances on the formation of mixed-ligand complexes was studied. The output of mixed-ligand complexes are maximum at $2.0 \cdot 10^{-4}$ M concentration of reagent and $1.6 \cdot 10^{-4}$ M of hydrophobic amines. The optical density of

solutions of complexes remains to be constant at 2.5-10.0-fold molar excess of reagent and

The effect of time and temperature.

All complexes of iron (III) are formed immediately after mixing the solutions of the components and differ in stability. So, if the binary complex Fe(III)-R is stable for 2 hours

2.0-10.0-fold molar excess of hydrophobic amines.

and when heated to 60° C, then the mixed-ligand complexes Fe(III)-R-Phen and Fe(III)-R-DAM are stable for more than a day and when heated to 80° C.

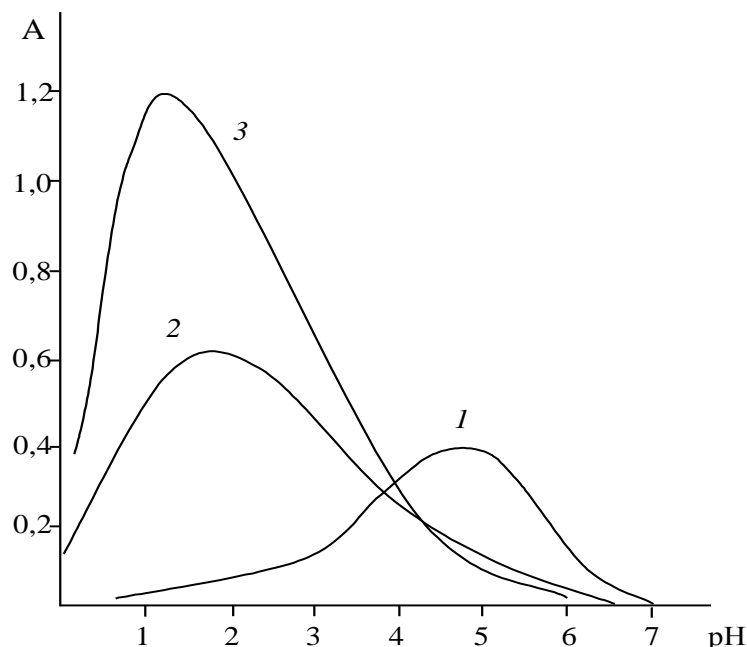


Fig.2. Effect of pH on light absorption of iron (III) complexes at λ_{opt} . 1 - Fe(III)-R, 2 - Fe(III)-R-Phen, 3 - Fe(III)-R-DAM
 $C_{Fe}=8.0 \cdot 10^{-5}M$, $C_R=2.0 \cdot 10^{-4}M$, $C_{Phen(DAM)}=1.6 \cdot 10^{-4}M$,
 $\Lambda=40$, $l=1.0sm$

Stoichiometry and stability constants.

The ratios of the components in the resulting complexes were established by the methods of isomolar series, the Starik-Barbanel's relative yield and the equilibrium shift [10]. All the methods showed that the ratios of the components in the binary complex were 1:2,

and 1:1:1 in mixed-ligand complexes. The number of protons displaced during complexation was determined by the Astakhov's method, and the pointed ratio of the components in the complexes was confirmed [11].

Table 1. Chemical and analytical properties of iron(III) complexes with 3-acetyl-4,6-diphenylhexadione-2,6 in the presence of hydrophobic amines

Complex	pH _{opt}	λ_{max} , nm	$\Delta\lambda$, nm	$\epsilon \cdot 10^4$ (at λ_{max})	C_R/C_{Fe}	$C_{Phen(DAM)}/C_{Fe}$	Lg β	Stoichiometry of components	Linearity range of calibration curvemg/ml
Fe-R	4.5-5.0	383	90	0.35±0.01	2.5-8.0		7.94±0.18	1:2	1.12-13.44
Fe-R-Phen	1.5-2.0	428	135	0.72±0.02	2.5-10	2.0-10	11.79±0.15	1:1:1	0.56-5.60
Fe-R-DAM	1.0-1.5	421	128	1.50±0.02	2.5-10	2.0-10	12.45±0.21	1:1:1	0.22-4.48

The stoichiometry and the conditional stability constant of the binary complex Fe(III)-R were determined by the method of curves intersection. The results obtained by these methods are confirmed in determining of stoichiometry and it was found that $\lg\beta = 7.94 \pm 0.18$. Considering the molar ratio of the

The interval of linearity in the calibration curve. The calibration curve is linear in the range of iron (III) concentration of 1,12-13,44 mg/ml for the complex Fe(III)-R, 0.56-5.60 mg/ml - Fe(III)-R-Phen and 0.22-0.45 mg/ml for Fe(III)-R-DAM, respectively. Molar absorption coefficients, as well as other chemical and analytical characteristics of the complexes are listed in Table 1. It can be seen that in the presence of 1,10-phenanthroline and diantipyrylmethane the molar coefficient of light absorption significantly increases.

The influence of foreign ions. The study of the influence of foreign ions on the spectrophotometric determination of iron has shown that in the presence of hydrophobic amines the selectivity of the reaction is significantly increased. The determination of iron (III) in the form of mixed-ligand complexes of Fe(III)-R-Phen and Fe(III)-R-DAM does not interfere with more than 4500-fold amount of alkaline, alkaline-earth and rare-earth elements; 2000-fold of Zn(II), Mg(II), Mn(II), Ni(II), Co(II), Cd(II), Cr(III), Th(IV), U(VI); 1000-fold of Cu(II), Sn(II), Ga(III), In(III), Al(III), Bi(III), Sb(V); 500-fold -Zr(IV), Hf(IV), Mo(VI), W(VI), F-, $C_2O_4^{2-}$.

A method developed for the spectrophotometric determination of iron (III) in the form of a mixed-ligand complex Fe

components in mixed-ligand complexes their conditional stability constants were determined, and it was found that in the presence of hydrophobic amines the stability of the complexes increased by about four orders of magnitude: $\lg\beta(\text{Fe-R-Phen}) = 11,79 \pm 0,15$; $\lg\beta(\text{Fe-R-DAM}) = 12,45 \pm 0,21$.

(III)-R-DAM is applied for determination of its microamounts in the "Champignon" mushrooms picked from the settlement of Zira, Baku.

Determination of iron in mushrooms.

A sample of mushrooms weighing 200g after drying, was placed in a graphite cup burned in a muffle furnace at 500-650° C until complete decomposition of organic substances. The resulting ash was dissolved in a mixture of 15 ml of HCl and 5 ml of HNO₃ in a glassy carbon cup and treated three times with 4-5 ml of HCl at 50-60° C until complete removal of nitrogen oxides. Next, the mixture was dissolved in distilled water, filtered in a flask with capacity of 100 ml and diluted to the mark. An aliquot of the solution was transferred to a 25 ml flask, 2,5 ml of $2,0 \cdot 10^{-3}$ M reagent solution, 2,0 ml of $2,0 \cdot 10^{-3}$ M solution of antiantipyrylmethane were added and the volume adjusted to the mark with 0,1 M HCl (pH 1.0). The optical density of the solution was measured on a Lambda-40 instrument at $\lambda = 421$ nm against a background of water in a cuvette with a thickness of light absorbing layer $l = 1$ cm. The iron content was found on a pre-built calibration curve. The obtained results are presented in Table 2 compared with the analyzed data on the atomic absorption method (AAS).

Table 2. The results of the determination of iron in mushrooms (n = 5, P = 0.95)

Mushroom samples	Found Fe, mg/kg		S _r	
	R-DAM	AAS	R-DAM	AAS
I	1.072±0.049	1.069±0.057	0.040	0.046
II	1.045±0.045	1.050±0.053	0.037	0.044

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**3-ASETİL-4,6-DİFENİLHEKSANDİON-2,6 VƏ HİDROFOB AMİNLƏRLƏ
DƏMİRİN GÖBƏLƏKDƏ TƏYİNİ**

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3-Asetil-4,6-difenilheksandion-2,6 və hidrofob aminlər – 1,10-fenantrolin və diantipirilmətdən istifadə etməklə dəmirin(III) spektrofotometrik təyini metodikaları işlənmişdir. Dəmirin(III) reaktivlə kompleks əmələ gətirməsi tədqiq edilmiş və hidrofob aminlər iştirakında müxtəlifliqandlı komplekslərin əmələ gəldiyi müəyyən edilmişdir. Bunun da nəticəsində udma spektrlərində batoxrom sürüşmələr və optimal kompleks əmələgəlmə pH-nın daha turş mühitə sürüşməsi müşahidə olunur. Müxtəlifliqandlı komplekslərin əmələ gəlməsinə komponentlərin qatılığının, vaxt və temperaturun təsiri öyrənilmiş, stexiometrik tərkibi müxtəlif metodlarla təyin edilmişdir. Bakı

şəhəri, Zirə qəsəbəsindən götürülmüş "Şampinyon" göbələyində dəmirin(III) mikromiqdarının spektrofotometrik təyini üçün yüksək seçiciliyə malik metodika işlənmişdir.

Açar sözlər: dəmir(III), 3-asetil-4,6-difenilheksandion-2,6, 1,10-fenantrolin, diantipirilmetan, göbələk.

ОПРЕДЕЛЕНИЕ ЖЕЛЕЗА В ГРИБАХ С 3-АЦЕТИЛ-4,6-ДИФЕНИЛГЕКСАНДИОНОМ-2,6 И ГИДРОФОБНЫМИ АМИНАМИ

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Разработаны методики спектрофотометрического определения железа(III) с 3-ацетил-4,6-дифенилгексадионом-2,6 и гидрофобными аминами - 1,10-фенантролином и диантипирилметаном. Исследовано комплексообразование железа(III) с реагентом и установлено, что в присутствии гидрофобных аминов образуются разнолигандные комплексы, при этом наблюдается bathochromный сдвиг в спектрах поглощения и оптимальные рН образования сдвигаются в более кислую среду. Исследовано влияние концентрации реагентов, времени и температуры на образование разнолигандных комплексов и определена их стехиометрия различными методами. Разработана высокоселективная методика спектрофотометрического определения микроколичества железа(III) в грибах «Шампиньоны», взятых из поселка Зире, города Баку.

Ключевые слова: *железо(III), 3-ацетил-4,6-дифенилгексадион-2,6, 1,10-фенантролин, диантипирилметан.*