THE USE OF PHYSIOLOGICALLY ACTIVE SUBSTANCES IN THE BIOSORPTION OF IRON (III) ION

ПРИМЕНЕНИЕ ФИЗИОЛОГИЧЕСКИ АКТИВНЫХ ВЕЩЕСТВ ПРИ БИОСОРБЦИИ ИОНОВ ЖЕЛЕЗА (III)

ТЕМИР (III) ИОНЛАРИНИНГ БИОСОРБЦИЯСИДА ФИЗИОЛОГИК ФАОЛ МОДДАЛАРНИНГ ҚЎЛЛАНИЛИШИ

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Abstract. This article proposes a simple and rapid method for the spectrophotometric determination of iron (III) using a physiologically active compound - the mono ammonium salt of glycyrrhizic acid (MASGA). The spectral characteristics of the *MASGK-Fe (III)* complex - absorption maxima (λmax = 440nm) and the actual molar extinction coefficient ($\varepsilon = 3,425 \times 10^2$) were determined.

The experimental results showed that when using a universal buffer solution, the complex compound had the maximum optical density. Therefore, in subsequent studies, a universal buffer solution with pH = 5 was used. The experimental results showed that the optical density of the complex compound practically did not change within 2 hours, and after 2 hours a slight decrease was observed. The optimal conditions for the determination of iron (III) in the range of its concentrations of 2,0–45,0 µg / 25 ml of solution have been established.

The developed technique was applied to determine iron in model solutions of algae. To establish the possibility of spectrophotometric determination of iron (III) for the analysis of real objects, model mixtures were compiled, the results of which were verified by the "introduced-found" method. The s_r value in all cases did not exceed 0.022.

Keywords: monoammonium salt of glycyrrhizic acid, iron(III), spectrophotometric determination, graduation table, absorption maxima, optical density.

Аннотация. В данной статье предложена простая и экспрессная методика спектрофотометрического определения железа (III) с помощью физиологическое активное соединение - моноаммониевой солью глицирризиновой кислоты *(МАСГК)*. Определены спектральные характеристики комплекса *МАСГК-Fe (III)* максимумы поглощения (λ_{max}=440нм) и фактический молярный коэффициент экстинкции (ε=3,425·10^2). Результаты экспериментов показали, что при использовании универсального буферного раствора комплексное соединение имеет максимальную оптическую плотность. Поэтому в последующих исследованиях использовали универсальный буферный раствор с pH = 5. Полученные результаты показали, что оптическая плотность комплексного соединения практически не изменилась в течение 2 часов, а через 2 часа наблюдалось небольшое снижение. Установлены оптимальные условия определения железа (III) в диапазоне его концентраций 2,0–45,0 мкг/25мл раствора.

Разработанная методика применена для определения железа в модельных растворах водорослей. Для установления возможности спектрофотометрического определения железа (III) для анализа реальных объектов были составлены модельные смеси, результаты которых проверены методом «введено-найдено». Значение s_r во всех случаях не превышало 0,022.

Annotatsiya. Ushbu maqolada temir (III) ionini fiziologik faol birikma - glitsirrizin kislotasi monoammoniy tuzi (GKMAT) bilan spektrofotometrik usulda aniqlashning sodda va ekspres usuli taqdim qilindi. GKMAT - Fe (III) kompleksining spektral xarakteristikalari, maksimal nur yutish sohasi (λ_{max}=440нм) va haqiqiy molyar so'nish koeffitsienti (ε=3,425·10^2) aniqlanadi. Tajriba natijalari shuni ko'rsatdiki, universal bufer eritmasidan foydalanganda kompleks birikma maksimal optik zichlikka ega bo'ladi. Shuning uchun keyingi o'lchashlar pH q 5ga teng bo'lgan bufer eritma ishtirokida olib borildi. Olingan natijalar ko'rsatishicha, murakkab birikmaning optik zichligi amalda 2 soat ichida o'zgarmadi va 2 soatdan keyin biroz pasayishi kuzatildi. 2,0-45,0 mkg G' 25 ml eritma kontsentratsiyalari oralig'ida temirni (III) ionini aniqlashning optimal sharoiti belgilandi.

Ishlab chiqilgan usul yordamida suv o'tlarining model eritmalari namunalaridan temirni aniqlashda qo'llanildi. Usulni real ob'ektlardan temirni (III) ionini spektrofotometrik aniqlash uchun model eritmalar namunalari tayyorlanib, natijalari "kiritildi-topildi" usul bilan tekshirildi. s_r qiymati barcha holatlarda 0,022 dan oshmadi.

Kalit so'zlar: glisirrizin kislotasining monoammoniy tuzi, temir (III), spektrofotometrik aniqlash, graduirovkali grafik, nur yutish maksimumi, optik zichlik.

Introduction

The intensification of industrial production and the introduction of new technological lines inevitably affects the quality of the environment, in particular, the increasing pollution of waste and surface waters with ecotoxicants. In this regard, the search for effective engineering and environmental solutions aimed at improving the living environment is an urgent task. These may include sorption technologies that allow concentration of substances from a large volume of solutions on a compact sorbent without introducing additional pollutants, which most fully corresponds to the principles of "green chemistry" [1-2].

Today all over the world there is an increased interest in sorption technologies using microorganisms and plant materials intended for concentration and extraction of heavy metal ions, radionuclide, organic and other ecotoxicants from waste and surface waters [2-4]. At the same time, the use of expensive synthetic sorption materials for the extraction of heavy metals in low concentrations is not always economically feasible.

It should be noted that the development of biosorption technologies contributes to the enrichment of analytical methods of preliminary concentration, which is especially necessary for the determination of ultra-micro and trace concentrations of ecotoxicants [2,4-5]. Thus, the use of renewable raw materials to create effective biosorbents for analytical purposes is of particular importance.

Licorice (*Glycyrrhiza*) grows in the territory of Uzbekistan, the roots of which are rich in glycyrrhizic acid and its salts [6-8]. Studies carried out by a number of scientists on the chemistry of glycyrrhizic acid [9-10] have shown the possibility of its use in analytical practice.

The aim of the study is to develop a sensitive, selective and express method for the spectrophotometric determination of iron (III) ions using monoammonic salt of glycyrrhizic acid as an analytical reagent.

The interest shown by ecologists and analytical chemists to the Fe (III) ion is also due to the fact that its content in drinking and industrial-technical waters determines their color, which is also strictly regulated by IST.

Several spectrophotometric methods have been developed for the analysis of iron in minerals and natural samples using analytical reagents, but these methods do not fully meet the requirements of

the analysis, one of the existing methods is less sensitive, and the other does not have sufficient selectivity.

Objects and methods

To determine the content of iron (III) ions in artificial mixtures of algae, its standard solution was prepared from salt $Fe_2(SO_4)_3 \cdot 6H_2O$. Also used are ammonia, acetate and universal buffer mixtures, freshly distilled organic solvents (ethyl alcohol, chloroform, benzene, acetone, and toluene), solutions of sulfuric, hydrochloric and nitric acids and alkaline solutions. The monoammonium salt of glycyrrhizic acid (MASGA) was used as a reagent and its freshly prepared solution was used in each measurement. The solutions were monitored on a KSL-1100-1 pH meter. Quantitative analysis of the metal ion associated with the reagent in the test solution (UV/VisOptizen III - spectrophotometer (South Korea)).

The light absorption coefficients of the solutions were measured on a UV/VisOptizen III spectrophotometer in cuvettes 1 cm thick ($l = 1cm$).

Identification Method: One of the most convenient methods for studying the chemistry of metal complex formation reactions is the spectrophotometric method. To determine the optimal conditions for the complex formation reaction of trivalent metal ions with MASGA, the initial absorption spectrum of the MASGA-Fe (III) complex, the molar absorption coefficient, and the reaction sensitivity were studied.

Results and their discussion

GA forms water-soluble salts with some ions of heavy and non-ferrous metals (manganese, cobalt, nickel, copper I, II), the main chemical changes in the molecule are associated with the structure of the aglycone fragment of glycyrrhizic acid. For example, the belonging of glycyrrhizic acid to the class of triterpenes has been proven by the dehydration of this acid. Fig. 1 shows the structure of this fragment.
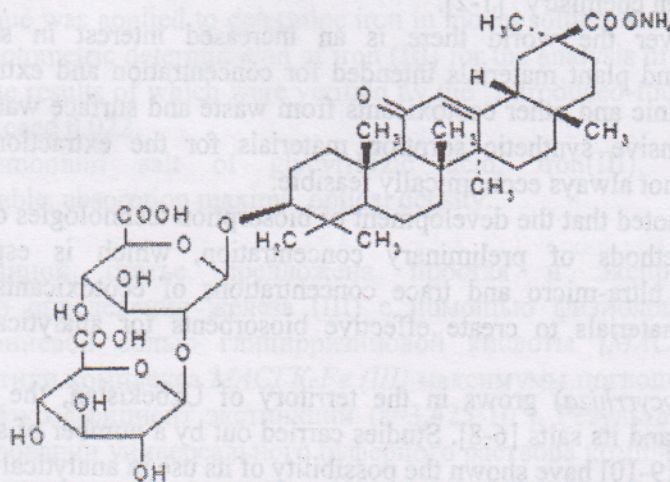
Fig. 1. Structural formulae of monoammonium salt of glycyrrhizic acid

Analysis of the structure of the reaction products shows that the main substance is { 3-0-(β-0-β-D glucuronopyronosyl) - λ - 0 - glucuronopyronoside-3- β -hydroxy-11-oxo-12-yen- β H, 20 β-olean-30- acid. The molecular structure of glycyrrhizic acid consists of two parts: the first part is aglycone-triterpene, i.e. the hydrophobic part, and the second part is hydrophilic, that is, sugar-glucuronic acid. Since glycyrrhizic acid is a complex tribasic acid, it forms three interchangeable salts

Fig. 2. Hydrophobic and hydrophilic part of the structure of glycyrrhizic acid
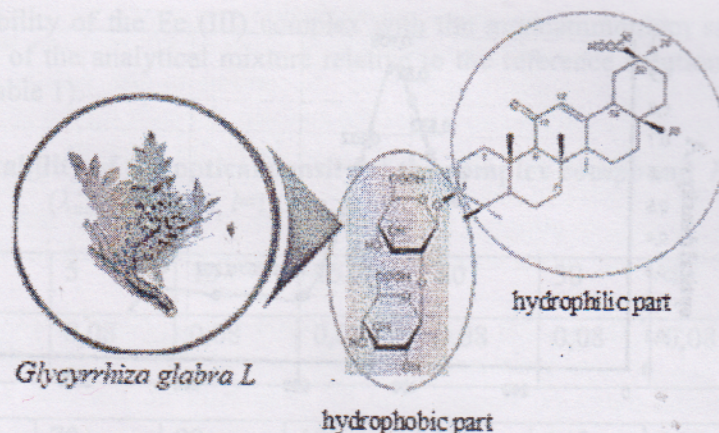
Its salts of lithium, sodium, potassium and ammonium were obtained [9,11]. In their production, mainly a solution of technical glycyrrhizic acid in acetone or alcohol is obtained by the interaction of these metals with an alcoholic solution of hydroxides and ammonia. The resulting salts dissolve in glacial acetic acid to form a monosubstituted salt, in which case the carboxyl group in the carbohydrate moiety changes from the salt state to the acid state.

Spectrophotometric study of GA and similar derivatives and complexes formed in solutions with manganese, cobalt, nickel, copper I, II [10] makes it possible to study the reactivity of MASGA to iron (III) ions by methods of physicochemical analysis.

For a complete characterization of the complex compound, it is necessary to obtain information on the chemistry of formation and the composition of the complex; to determine the stability constant of the complex compound, the molar coefficient of light absorption of the complex and the pH value of the solution at which the highest degree of its formation is achieved. Before determining the composition and other characteristics of the complexes, the optimal conditions for the formation of metal complexes with MASGA were determined.

So, when a 0.1% solution of iron is exposed to the monoammonium salt of glycyrrhizic acid in the presence of a universal buffer solution, the solution turns yellow, such a change in the color of the solution indicates the formation of a complex that allows quantitative determination of iron by the spectrophotometric method. Initially, the wavelength of the maximum absorption of the analytical solution was determined, the light absorption of the complex in the solution was investigated on an Optizen-III spectrophotometer.

The results obtained showed that the wavelength of the absorbing light of the solution of the complex compound showed the highest optical density at λ_{max}=440 nm; therefore, subsequent measurements were carried out at λ_{max}=440 nm (Fig. 2).

After studying the optimal pH of the solution, there was studied the dependence of the optical density of the complex compound on the composition of the buffer solution. The solution was diluted to 25 ml by adding 6.0 ml of various buffer solutions with pH = 2÷2.0 ml of an alcohol solution of monoammonium salt (0.0001 M) MASGA, 2.0 ml of Fe (III) solution with a concentration of 10 mg/ml.

The optical densities of the prepared analytical mixture were measured in a cuvette λ=1.0 cm relative to the reference solution. The experimental results showed that when using a universal buffer solution, the complex compound had the maximum optical density. Therefore, in subsequent studies, a universal buffer solution with pH = 5 was used.

Thus prepared method for the determination of iron in medicinal plants, its speed, convenience, and ease of analysis make it possible to use them in the practice of laboratories when detecting iron (III) ions in various objects.

the analysis, one of the ... methods is less sensitive and the others do not have sufficient selectivity.

To determine the ... of ... a standard solution was prepared from salt ... freshly distilled ... (region ..., benzene, acetone, and toluene), solution of sulfuric, hydrochloric, and nitric acids were used. The mono-ammonium salt glycyrrhizic acid (MASGA) ... was used ... The prepared solution was used in measurement. The solution ... were measured ... Quantitative analysis of metal ion associated with the reagent in ... solution ... spectrophotometer (South Korea).
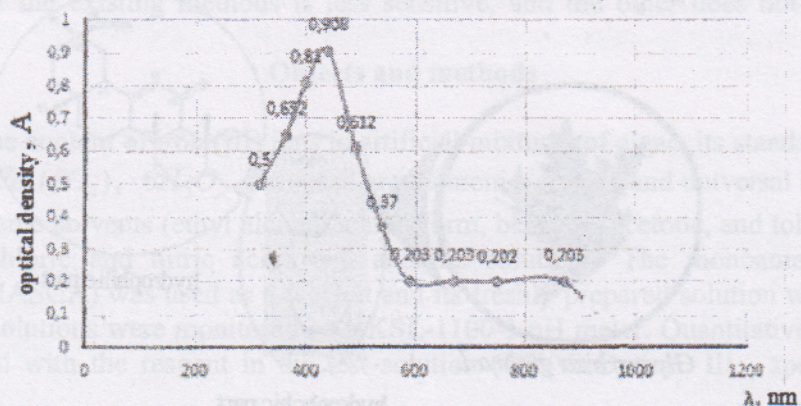
Fig. 3. The dependence of optical density of the complex solution MASGA-Fe (III) on the wavelength of the absorbed light.

When studying the dependence of the optical density of the complex compound on the solution medium (pH), the complex compound was observed in the medium with the highest optical density, pH = 5.
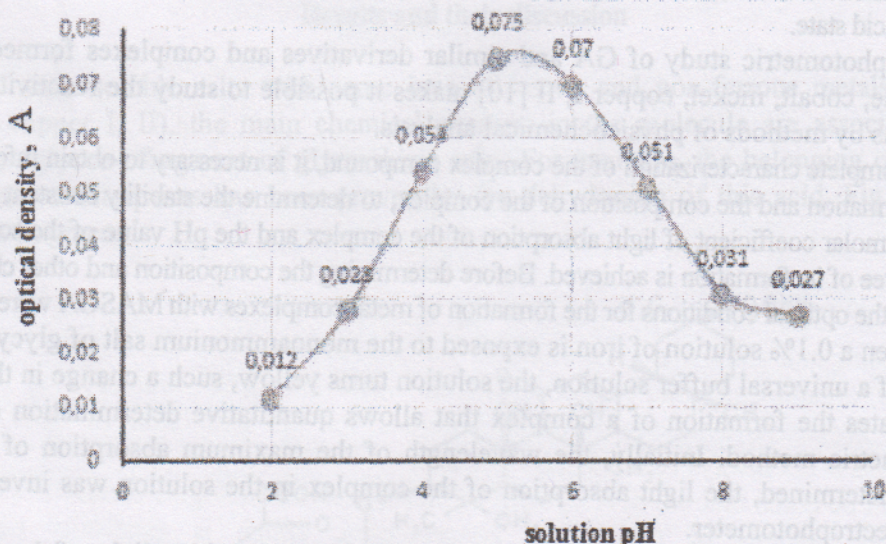
Fig. 4. Graph of the dependence of the optical density of the MASGA-Fe (III) complex on the solution medium

After studying the optimal pH of the solution, there was studied the dependence of the optical density of the complex compound on the composition of the buffer solution. The solution was diluted to 25 ml by adding 5.0 ml of various buffer solutions with pH = 5, 2.0 ml of an alcohol solution of monoammonium salt (0.0001 M) MASGA, 2.0 ml of Fe (III) solution with a concentration of 10 mkg/ml.

The optical densities of the prepared analytical mixture were measured in a cuvette $l=1.0$ cm relative to the reference solution. The experimental results showed that when using a universal buffer solution, the complex compound had the maximum optical density. Therefore, in subsequent studies, a universal buffer solution with pH = 5 was used.

To study the stability of the Fe (III) complex with the monoammonium salt of glycyrrhizic acid, the optical density of the analytical mixture relative to the reference solution was measured at certain time intervals (Table 1).

Table 1

Time stability of the optical density of the complex compound $Fe^{3+} - R$
(λ_{Max}=440 nm, l=1,0cm, n=3)

T_{minute}	1	5	10	15	20	30	40	50
$\bar{A}_{medium}$	0,08	0,08	0,08	0,08	0,08	0,08	0,08	0,08

T_{minute}	60	70	90	100	120	140	160	180
$\bar{A}_{medium}$	0,085	0,081	0,081	0,080	0,080	0,080	0,079	0,079

The experimental results showed that the optical density of the complex compound practically did not change within 2 hours, and after 2 hours a slight decrease was observed. It can be concluded that this time interval is sufficient to complete the analysis.

It is known that spectrophotometric reactions also depend on the order of mixing of the components of the complex compound; therefore, the optical density of the solution was measured by pouring the components in order to form a complex in solution, and several experiments were carried out with changing the order of mixing of the components. In subsequent studies, a specific order of mixing the solutions was also chosen.

While the optical density of a complex compound depends on the amount of added reagent, in practical studies, an excess amount of reagent is usually obtained in order to completely bind the metal to the complex. For this, photometric solutions were prepared in 25 ml measuring tubes to study the dependence of the optical density of the complex compound on the amount of added reagent, and the measurement results showed that 2.0 ml of 0.1 M reagent is optimal (sufficient) for complete binding at 50 mkg/ml iron (III).

Solutions of iron complexes with MASGA obey Beer's law in the range of 2–48 mkg/25 ml.

The developed technique was applied to determine iron in model solutions of algae. To establish the possibility of spectrophotometric determination of iron (III) for the analysis of real objects, model mixtures were compiled, the results of which were verified by the "introduced-found" method. The s_r value in all cases did not exceed 0.022 (Table 2).

Table 2

Results of verification of the procedure for the determination of iron (III) in model solutions
(n = 3, P = 0.95)

Introduced iron, mg/l	Obtained iron, mg/l	s	s_r
2,0	1,91		
	2,08	0,046	0,022
	2,17		

Note: n is the number of parallel determinations, P is the confidence level, s is the standard deviation, s_r is the relative standard deviation.

Thus, the proposed method for the determination of iron (III) ions, high selectivity, fast performance, and ease of analysis make it possible to use them in the practice of chemical analysis when detecting iron (III) ions in various objects.

Conclusion

The conditions for the spectrophotometric reaction of the iron ion with the monoammonium salt of glycyrrhizic acid have been optimized. According to the results of the study, it can be concluded that the accuracy and sensitivity of the analysis depends on the structure and amount of the reagent, as well as on the nature and concentration of the buffer solution.

The absorption spectra of the reagent and its complex with the iron (III) ion were obtained under the selected optimal conditions. Spectral characteristics were determined - absorption maxima (l_{max}=440 nm) and the actual molar extinction coefficient of the complex (ε =3,425·10^{2}).

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