Karakalpak Scientific Journal

Volume 3
Issue 2 *Issue 2*

Article 9

June 2020

SPECTROPHOTOMETRIC CHARACTERIZATION OF THE COMPLEXATION OF GOSSYPOL ACETIC ACID WITH COBALT ION

Ugilay Abdurahmanova
Gulistan state University, ugi_lay.912@mail.ru

Habibjon Kushiev
Gulistan State University, kushiev@mail.ru

Maral Askarova
Nukus State Pedagogical Institute, askarovamaral1978@gmail.com

Dilafruz Allanazarova
Gulistan State University, allanazarova_dilafruz@mail.ru

SPECTROPHOTOMETRIC CHARACTERIZATION OF THE COMPLEXATION OF GOSSYPOL ACETIC ACID WITH COBALT ION

ABSTRACT

The authors of the article suggest simple and express method of spectrophotometric determination of cobalt with the help of derivatives of gossypol. Optimal conditions of determining cobalt are found. Under optimal conditions there was created a graded graph, which is more linear in the range for cobalt concentration of 10.0 – 50.0 microgram/25 ml, contents and constants of cobalt complex with gossypol vinegar acid.

Key words: gossypol, gossypol acetic acid (GAA), analytic reagent, cobalt, spectrophotometric method, isomolecular series, graduation table.

Introduction

The presence of functional analytical groups increases the possibility of complex formation of physiologically active compounds; such groups allow natural compounds to be easily coordinated with various intermediate metal ions, resulting in the formation of color complex compounds that are well soluble in water. Gossypol and its derivatives can be included in the list of similar organic reagents.

Among polyphenolic compounds, gossypol is distinguished by its chemical structure and biological activity. Due to the wide range of physiological activity of gossypol and its derivatives, it is now widely used in medicine on the basis of 3% gossypol liniment against viral diseases, 3% megosin ointment against herpes and other drugs [1].

Sometimes it is necessary to obtain pure substances in production laboratories and to determine the ultramicro quantities of certain elements in the samples when applying them in practice. In addition to chemical methods, physico-chemical and physical analysis methods are used to find solutions to such problems. Spectrophotometric methods are now widely used in the detection of heavy metals, especially toxic and potent, because spectrophotometry is of great practical importance due to its sensitivity, simplicity, low cost of measuring equipment and low time for analysis.

Taking into consideration, new selective analytical reagents for spectrophotometric detection and control of heavy and non-ferrous metal ions in various natural samples, industrial sewage, ores and alloys, as well as some biological samples can be developed using new derivatives of polyphenol compounds based on gossypol. This research work is one of the current problems in the field of analytical chemistry.

The aim of the research is to develop a method of spectrophotometric analysis with positive metrological characteristics, such as accuracy, repeatability, selectivity in the qualitative and quantitative study of cobalt metal ions in natural samples based on gossypol.

MATERIALS AND METHODS

Research methods. Distillation, pH metering, spectroscopy (IR-, UV-), spectrophotometry, methods of direct quantitative determination using spectrophotometric measurements (calibration graph method).

Chemical reagents, materials and equipment. For the study, the following reagents, materials and equipment were used: In the work, reagents of the qualification chemically pure and pure for analysis were used.

Reagents and equipment. There were used reagents of chemical cleaning and pure reagents for analyze in the research. Workforce solutions of cobalt were prepared with dissolution of exact band-and-hook hinge salt of $CoCl_2$ (qualifications of chemical cleaning) is removed to the measured flask with the volume of 250 ml in distilled or bi-distilled water and dilute till mark.

The initial solution of GAA was prepared with the solution in ethyl spirit of exact band-and-hook hinge reagent, approximately filtered double recrystallization on water-ethanol solution. Pureness of the reagent was assessed by the method of ascending chromatography on paper.

The organic solutions were used by qualifications of chemical cleaning or approximately filtered by distillation, pureness was controlled on temperature of boiling.

The specters of absorption of solutions of complex Me-R were registered on the spectrophotometer “UV/Vis spectrophotometer Optizen III” (manufactured by

Republic of Korea). Acidity of the solutions were controlled by glass electrode on pH- meter KSL –1100-1.

RESULTS AND DISCUSSIONS

It has been reported in the literature that complex formation reactions of cobalt with many organic reagents have been studied, and it has been noted that in most of the studied methods the analytical students are not fully performed [2].

The polyfunctional structure of the Gossypol molecule provides a wide range of its chemical properties, including the formation of colored complex compounds under certain conditions with non-ferrous and heavy metal ions [3].

One of the most studied derivatives of gossypol is Schiff-based compounds, some of which have also been used in the processes of quantitative analysis and separation of gossypol [4].

The authors proposed a benzoid structure for gossypol amines, compounds with such a structure are characterized by tautomerization properties, as the equilibrium of benzoid-quinoid toutomerization is established as a result of sigmatropic proton migration [5-6].

Gossypol reacts with bimetallic and high-valence metal salts in water-acetone and water-alcohol systems to form corresponding metal gossypolates, which are difficult to dissolve in water.) dissolves well in [4].

The formation of complexes of gossypol azo compounds from monovalent metals with silver in ratios of 1: 1, 1: 2, 2: 1 and 3: 2 and the structure of physicochemical properties and complexes of these compounds is potentiometric, mass spectroscopic (as well as ESI FT-IR as Well as PM5 has been studied using semi-empirical) methods [7-10].

However, the gossypols formed by gossypol and its derivatives with heavy metals, their composition and structure have not been sufficiently studied.

Gossypol acetic acid (GAA) is a light yellow microcrystalline powder with a slightly greenish tint, insoluble in water, well soluble in ether, chloroform, alcohol, benzene, carbon tetrachloride. GAA - 2,2 -bis (1,6,7-trioxy 3-methyl 5-isopropyl 8 aldehydonaphthyl) acetic acid. Liquidus temperature 173-175 ^{0}S. Molecular mass - 578.6; Gross formula: $C_{30}H_{30}O_8 \cdot C_2H_4O_2$, Its structure is showed in Figure -1.

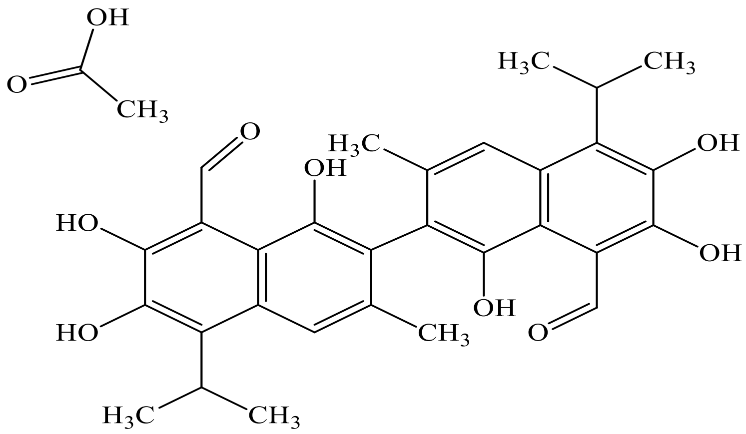

Figure 1. Chemical structure of GAA -2,2-bis(1,6,7-trioxy 3-methyl 5-isopropyl 8 aldehydonaphthyl) acetic acid.

To study the complex formation reaction of cobalt ion with GAA reagent, first of all, the optimal conditions of the analysis were determined.

One of the important conditions for the performance of the spectrophotometric reaction was the use of universal buffer solutions with different pH values in the selection of optimal conditions for the complex combination of cobalt with gossypol, given that the solution is medium.

Light absorption spectra were obtained under the selected optimal conditions of the complex formed by the GAA reagent and the cobalt (II) ion.

Method of determination: 1.0 ml of cobalt (II) ion solution of 40 μg / ml, 5 ml of pH = 10 universal buffer solution, 2.6 ml of 0.05% alcohol solution of GAA to 25 ml of flask to the mark of the flask. diluted with distilled water and stirred. The absorption spectrum of the formed complex compound was measured in an OPTIZEN-III spectrophotometer in a quartzcuvette with a light absorption thickness
l = 1.0 cm relative to the specific solution. The absorption spectrum of the reagent was obtained relative to distilled water (Figure-2). According to the absorption spectrum shown in Figure 2, the maximum absorption area of the GAA reagent complex with cobalt (II) was found to be lkomp = 360 nm, the maximum absorption area of the GAA reagent was observed in the shorter spectral wavelength range of the complex, ie lreagent = 320 nm.

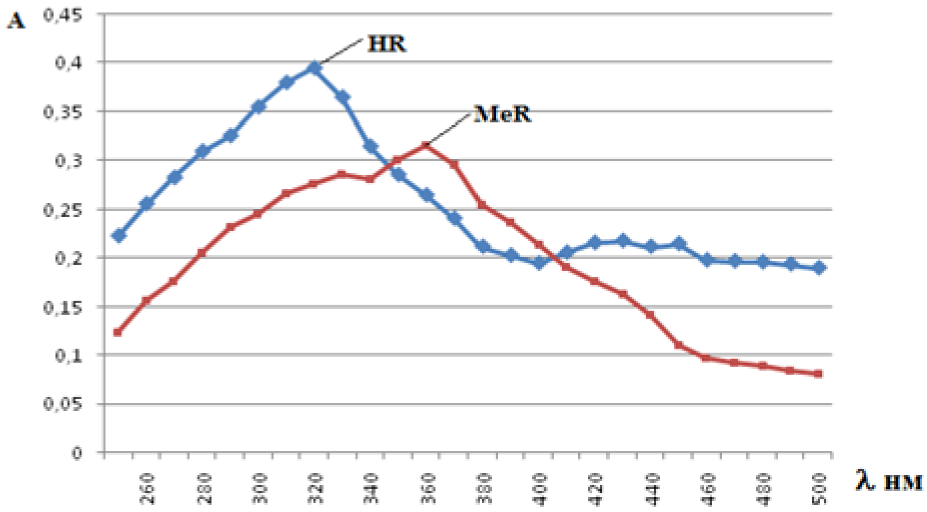

Figure 2. The absorption spectrum of the reagent. Here, HR-Spectrum of reagent solution;MeR– Spectrum of $Co - R_{reagent}$ complex solution .

Buffer solutions of different pH and different compositions were used to find the optimal variant of pH in the analysis. Initially, the optical density value also increased with increasing solution pH i, the maximum light absorption was observed in solutions in the range pH = 10.0–10.25, and pH = 10.11 was chosen as the optimal medium because the optical density in this solution medium has the maximum analytical signal. In subsequent studies, measurements were made in the presence of a buffer solution with a pH of 10.11 (Table 1).

Table 1.

The dependence of the optical density of a complex compound on the solution medium (pH) ($T_{Co}{}^{2+}$ =50 mcg /ml, n=3)

pH	2,02	3,05	4,2	5,01	6,1	7,08	8,26	9,11	10,11	11,25	11,95
Ā	0	0,085	0,107	0,145	0,146	0.146	0.178	0.205	0.26	0.258	0.141

Given that the yield of the spectrophotometric reaction also depends on the order in which the components are poured, the solutions were prepared by the above method and several experiments were performed by changing the order in which the components were poured. The measurement results showed that the value of optical density depends on the flow order of the solutions, the reagent and metal ion concentration, the solution medium and the buffer nature of the solution (Table 2).

Table 2.

Some analytical descriptions of the complex

№	**Analytical descriptions**	$Co - R_{reagent}$
1	0.05 optimal volume of % reagent solution, ml	2,6
2	Optimal volume of 0.05% reagent solution, ml	10,11
4	Sensitivity to Sendel - mkg / $cm^2 \cdot 25ml$	0,0057 mkg / cm^2
5	The maximum absorption coefficient of $Co^{2+} - R$ solution is – λ , nm	360
6	Molar absorption coefficient, ε_{360}^{max}	$1,58 \cdot 10^4$

The dependence of the optical density of the solution on the amount of cobalt ions, ie the obeying of the law of Buger-Lambert-Behr, was studied by the gradual graph method. there is a linear relationship between the optical density of the complex and the actual value of the element being determined, and the law of light absorption was observed to be fulfilled with 3-4% accuracy in the range of 2–40 μg / 25ml of the metal ion (Figure-3).

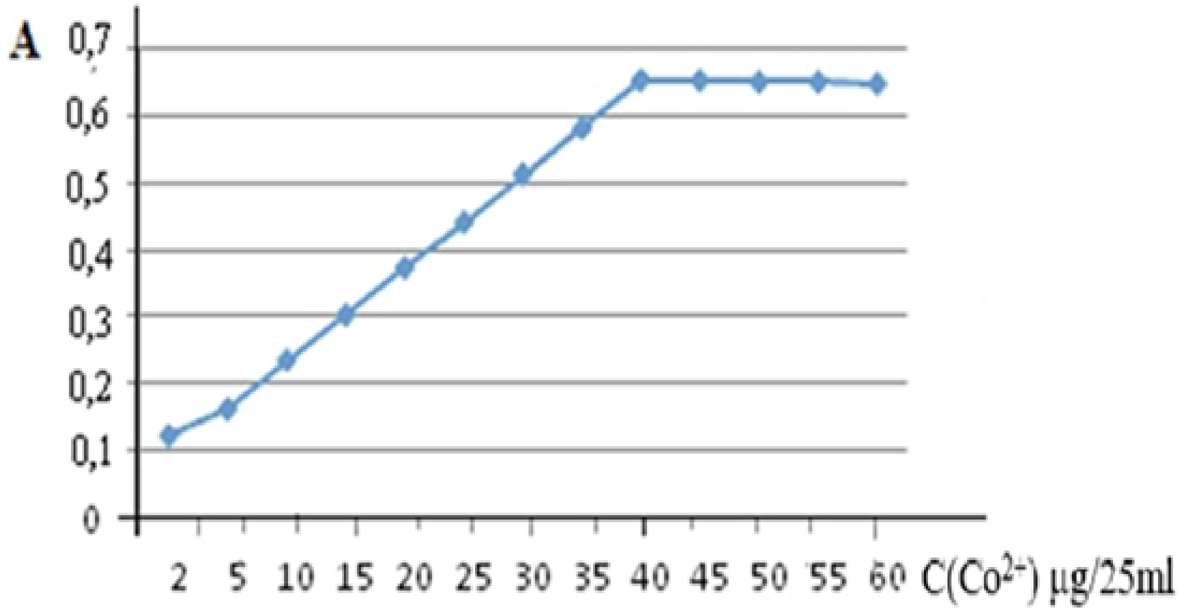

Figure 3. Graphical representation of the complex solution obeying Ber's law

For each concentration of the solutions, 3 parallel measurements were made and the measurement results were recalculated using the mathematical statistical method. The values of the graduated graph and parameters were calculated using the least squares method. Graduated graphic equation based on these results.

The value was determined in detail. The results obtained show that the area of compliance with the law of absorption was observed in the range of 2–40 μg / 25ml. At higher concentrations, however, there was a deviation from the straight-line bond.

The mole ratios of the components in the $Co - R_{reagent}$ complex were determined by isomolar series and Asmus straight line methods (Figure-4).

It can be seen from this graph that the composition of the complex formed by the GSK reagent with the cobalt (II) ion corresponded to a 1: 1 ratio of Me-R moles.

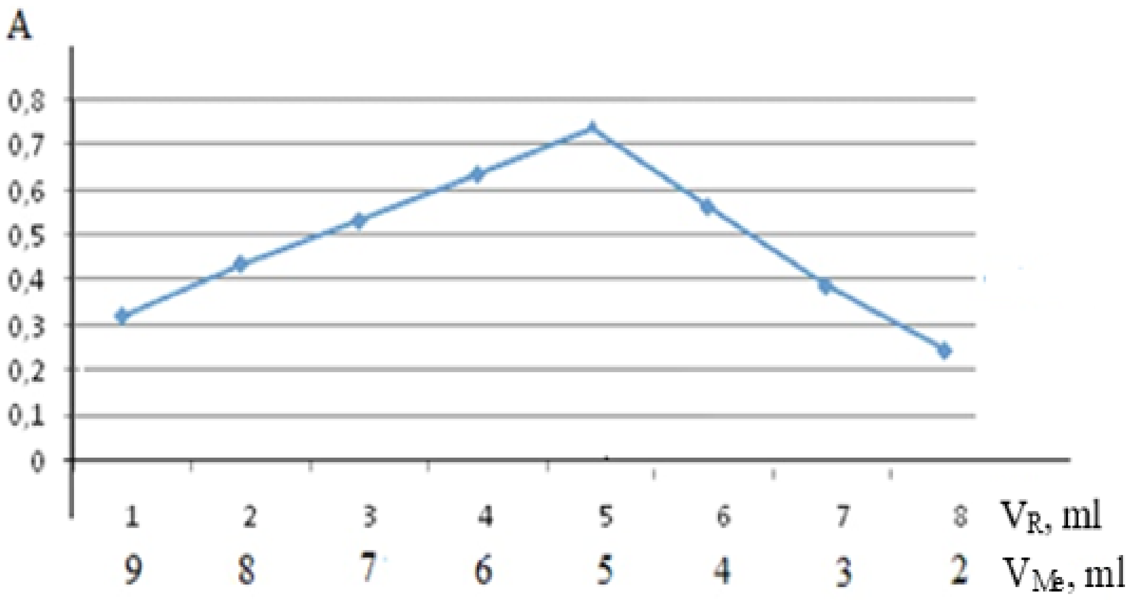

Figure 4. Curve for determining the composition of a complex compound $Co - R_{reagent}$ using the method of isomolar series.

A second method to verify and validate the accuracy of the results of this study was to construct a (1 / V) n = l / A correlation graph to determine the stoichiometric ratios of the interacting components with Asmus " straight line method ".

This relationship only represented that the value of n represents a straight line for the actual value, and that the straight line corresponds to a 1: 1 mole ratio, meaning that both methods confirmed each other and that the Me-R content was found to be 1: 1.

Based on the gradual graph equation (Yi = a + bXi = 0.0498 + 0.0116Xi) for the determination of the complex of cobalt (II) ions formed with GSK reagent, the dependence of the optical density on the concentration of So (II) ions is determined by the optimal The accuracy and recoverability of the method under the conditions were studied, the results obtained show that the accuracy and recoverability of the method of spectrophotometric detection of cobalt (II) ion with GSK reagent. The data show that the amount of cobalt (II) ion obtained corresponds to the amount found, where the relative standard deviation (s_r) did not exceed 0.022.

Conclusions

The optimal conditions for the determination of cobalt metal ion in the form of a color complex formed by gossypol depend on the light filter of the optical density of the complex, the pH of the solution, the nature of the buffer solution, the order of infusion of solutions and reagent concentration and metal ion concentrations. There is also a linear relationship between the optical density of the complex and the actual value of the element being determined, and the basic law of light absorption was observed to be fulfilled in the range of 2–40 μg / 25ml of cobalt in solution. The composition of the complex was found to be in a 1: 1 ratio and the relative standard deviation value did not exceed 0.022.

References:

1. Ziyaev Kh.L., Baram N.I., Khodzhaniyazov B., Kamaev F.G., Bektemirov L, Dzhurabekova A.I., Ismailov A.I., Gossipol, its derivatives and their complexes in solutions.// Chem. Nat. Compd. -1998. V. 1. –P.52.
2. Bingol Haluk, Atalay Tevfik. Issledovanie kinetiki reakcii kompleksoobrazovaniya dvuxvalentnogo kobal`ta s 2-benzoilpiridin-4-fenil-3-tiosemikarbazonom i kinetiko-spektrofotometricheskoe opredeleniya kobal`ta. Acta Ciem.Yndica Chem. 1988, V.42, № 4, p. 241-252. Cit. po RZhXim. 24G10, 2007.
3. U.K.Abdurahmanova, A.N.Abduganiev Determination of cobalt in natural objects Znanstvena misel 2018, №21, 53-56r.
4. Markman A.L., Rzhexin V.P. Gossipol i ego proizvodny`e. -M.: Pishh. prom-t`., -1965. – 250s.
5. Dechary J.M., Brown L.E. Subetituted arylimune derivaties of gossypol // J.Amer. Oil Chem. Soc. -1956. –Vol. 33. –P.76-78.
6. Alley P.W, Shirley D.A. Some new anil derivateis of gossypol // J.Org. chem, 1959 Vol 24 (10). –P.1534-1536.
7. Przybylski P., Brzezinski B. The Complexes Between Schiff Base of Gossypol with L-Phenylalanine Methyl Ester and Some Monovalent Cations Studied

by 1H NMR, ESI MS, FT-IR as Well as PM5 Semi-empirical Methods // J. Mol. Struct. – 2003. -Vol.654.-P.167–176.

8. Przybylski, P., Schroeder G., Brzezinski B. // Complexes of Schiff Base of Gossypol with 5-Hydroxy-3-oxapentylamine and Ca2+, Ba2+ or Pb2+ Cations Studied by NMR, FT-IR, ESI MS as Well as PM5 Semiempirical Methods, Ibid. -2003. -Vol.658. -P.115–124.

9. Przybylski P., Schroeder G., Brzezinski B. // The Schiff Base of Gossypol with 2-(Aminomethyl)-18-crown-6 Complexes and H+, Li+, Na+, K+, Rb+, Cs+ Cations Studied by ESI MS, 1 H NMR, FT-IR and PM5 Semiempirical Methods, Ibid. -2004. Vol.699. –P.65–77.

10. Przybylski P., Schroeder G., Pankiewicz R., Brzezinski B., Bartl F. // Complexes of Schiff Base of Gossypol with nButylamine and Some Monovalent or Bivalent Cations Studied by ESI MS, NMR, FT-IR as Well as PM5 Semi empirical Methods, Ibid.. – 2003. Vol.658. –P.193–205.