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OPTIMAL CONDITIONS FOR SPECTROPHOTOMETRIC DETERMINATION OF CADMIUM(II) ION USING INDIGO

Abstract. Currently, great attention is paid to the development of rapid, sensitive and convenient methods for spectrophotometric determination of heavy and toxic metal ions. At the same time, the selection of environmentally safe reagents and their use in analytical analyzes is also an urgent problem. One of such reagents is indigo. In our study, the optimal conditions for spectrophotometric determination of cadmium(II) ion using indigo reagent were studied, and it was found that the maximum light absorption range of the metallocomplex is: lmax(CdR)=690 nm, the optimal solution environment: pH(CdR)=4.8; the range of compliance with the Bouguer-Lambert-Beer law: C25mg/ml(FeR)=5-45 mg/25ml. In addition, the reproducibility and accuracy of the method and scaled graphs were developed.

Keywords: Indigo, cadmium, metallocomplex, optimal conditions, reagent, buffer solution, pouring procedure, light absorption law, Asmus method, Tolmachyov graph, graded graph, quantum chemical calculations, Isomolar series method, YuQX, etc.

ОПТИМАЛЬНЫЕ УСЛОВИЯ ДЛЯ СПЕКТРОФОТОМЕТРИЧЕСКОГО ОПРЕДЕЛЕНИЯ ИОНОВ КАДМИЯ(II) С ИСПОЛЬЗОВАНИЕМ ИНДИГО

Абстрактный. В настоящее время большое внимание уделяется разработке быстрых, чувствительных и удобных методов спектрофотометрического определения ионов тяжелых и токсичных металлов. При этом актуальным остается вопрос подбора экологически безопасных реагентов и іх использования в аналитических исследованиях. Одним из таких реагентов является индиго. В нашей работе изучены оптимальные условия спектрофотометрического определения ионов кадмия(II) с использованием реактива индиго, максимальная область поглощения металлокомплекса составила: lmax(CdR)=690 нм, оптимальная среда растворения: pH(CdR)=4,8; Установлено, что диапазон соотношений закона Ламберта-Бера-Бера соотносится: C25мкг/мл(FeR)=5-45 мкг/25мл. Кроме того, воспроизводимость и точность метода, а также масштабированные графики.

Ключевые слова: индиго, кадмий, металлокомплекс, оптимальные условия, реагент, буферный раствор, процедура заливки, закон мира, метод Асмуса, график Толмачева, градуированный график, квантово-химические расчеты, метод изомолярных рядов, ЮКХ и др.

Introduction. Cadmium is a heavy metal with the atomic number ^{48}Cd. It is a soft , ductile, bluish-white metal. It occurs in nature as a natural cadmium sulfide ore or has been found to occur in association with zinc [1; 491–502-b].

It is a dangerous heavy metal for biological organisms due to its toxic effects on the gastrointestinal, neurological, reproductive, respiratory and bone systems and its negative effect on plant growth [2; 25-26-b]. Due to its high toxicity, Cd is considered an important pollutant. If the Cd level is between 0.04 and 0.32 mM, the soil is considered uncontaminated. However, if the Cd level exceeds 0.32 mM and rises to 1 mM, the soil is considered moderately contaminated. It has been established that water with a Cd level below 1 ppb is considered drinking water [3; 1815-b].

The main sources of Cd pollution in the environment include smelting and mining, both of which can pollute the air with Cd. Cd compounds can bind to airborne particles and can be transported over long distances, where they have been studied for subsequent deposition to soil with rainfall [4; 326-b].

Incineration of municipal waste, industrial effluents from metal, pigment and battery industries, sewage sludge, runoff from landfills, and chemical fertilizers contaminate soil and water with Cd. Groundwater is known to be contaminated by mining, industrial wastewater discharges, or seepage from hazardous sites. Once Cd enters soil and water, it can easily enter the food chain through plants, a process that has been of great concern [5; 23-41-b].

is a highly toxic metal that negatively affects plant growth and yield. Plants take up Cd through specific transporters such as symplastic and apoplastic proteins . Cd exerts its effects by producing reactive oxygen species and is involved in a number of metabolic and physiological processes [6; 25-39-b]. Studies have shown that it has a detrimental effect on various growth stages of plants, such as germination, vegetative and reproductive stages, by analyzing anatomical, morphological and biochemical changes (changes in photosynthetic machinery and membrane permeability). Plants also respond to Cd toxicity using various enzymatic and non-enzymatic antioxidant systems [7; 529-542-b].

Since cadmium is a heavy and toxic metal, its compounds have negative consequences for the environment and living organisms [8 ; 5-6-b, 9; 60-b]. Several assays have been developed to assess and quantify its effects. One of them is the spectrophotometric determination of Cd (II) with the reagent 2 -hydroxy-4-n-butoxy-5-bromopropiophenone thiosemicarbazone (HBBrPT). The HBBrPT reagent gives a strong yellow color with a solution of Cd (II) in basic media. The maximum absorption was observed at 440 nm in basic solution (pH=10.00) . The molar absorptivity and Sandell sensitivity of the Cd (II)-HBBrPT complex were 4035 mol $^{-1}$ / cm $^{-1}$ and 0.02765 cm $^{-2}$, respectively . The stability constant of the 1:2 Cd(II)-HBBrPT complex is $8.46 \cdot 10^{-6}$ [10; 496-b, 11; 42-43-b].

Cd(II) reacts with 2-hydroxy-4-n-butoxy-5-bromopropiophenone thiosemicarbazone in a buffer solution to give a yellow complex[12; 475-b]. The color reaction of Cd(II) with the reagent occurs instantaneously even at room temperature . The absorption of yellow light at the wavelength corresponding to the maximum absorption, i.e. 440 nm, remains constant for at least one hour . Studies on the effect of pH on absorption have shown that the maximum color is formed in a solution of pH= 10.00. A tenfold excess of the reagent is sufficient for complete color development. Addition of excess reagent does not adversely affect the absorption. The order of addition of different components affects the absorption values. Studies on the effect of cadmium(II)- ion are associated with the presence of a linear relationship between the metal ion concentration [13; 662-b].

and accurate spectrophotometric methods for the determination of cadmium using some thiazole (IV) chromogenic reagents have been developed. Among them, the availability of Triton x-100 and NH_3 /NH_4Cl buffer solutions, optimal conditions for complexation, stoichiometric ratios and stability constants were studied

[14; 163-b]. Obeying Beer's law: occurs in the range of 0.96 and 3.3 mg / ml $^{-1}$ in 10 ml of cadmium solution and the limit of quantitative detection was found to have a variability of 1.9 -3.0%. Molar absorbance and Sandell sensitivity were determined for each reagent . The method was applied to the determination of cadmium in wave samples and plant materials and statistically compared with the AAS method. Extraneous ions were eliminated by preliminary extraction with CCl_4 masking agents. Cadmium(II) 10 0.03-4.4 ml calibrated flasks 2.0 ml 3 10^{-3} M reagent solution, 1.0 ml ethanol, 4.0 ml buffer solution are added and 1.0 ml of 3.0% Triton X-100 solution is added . Then the volume is made up to the mark with double distilled water [15 ; 355-b , 16 ; 120-b]. Then it was mixed well and the solution was left for 3.0 minutes . The absorbance was measured at 616, 653, 670, 648 and 635 nm using reagents I, II, III, IV.

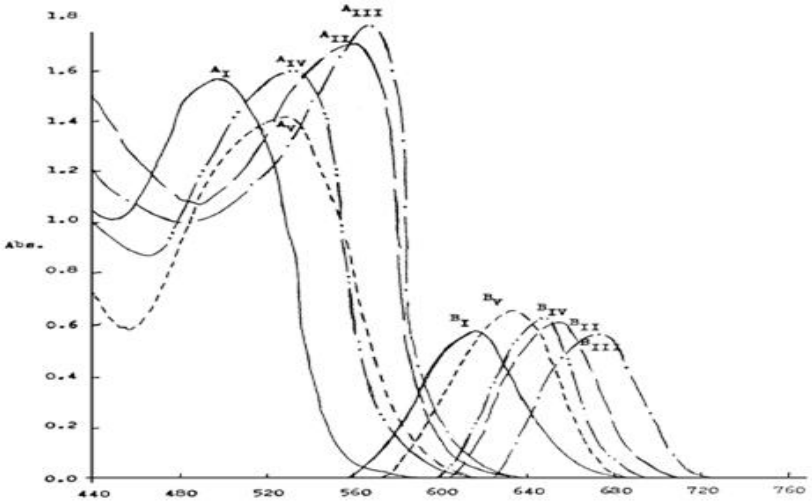


Figure 1. Light absorption spectra of complexes formed by 10 ml of 3 μg Cd^{2+} solution with different concentrations of reagent at the optimal pH [17; 432 -b] .

The experimental part.

To select the optimal light filter for the complexation of cadmium (II) ion with indigo reagent In a 25 ml volumetric flask, add 1.0 ml of a 0.01 % indigo solution and 20 μg/ml of metal ion. Add 1.0 ml of the solution and dilute to the mark on the flask with solvent. The optical density of the resulting complex was measured using a SP-UV 1100 spectrophotometer. The absorption was measured in a cuvette with a thickness of *1.0 cm and* various light filters. A solution of indigo in DMFA was used as a reference solution (Table 1) . and see Figures 2) .

Table 1

Dependence of the optical density of the complex on wavelength

Full sheath length , nm	650	660	670	680	690	700	710	720	730
Optical density	0.028	0.072	0.090	0.095	0.101	0.099	0.096	0.086	0.074

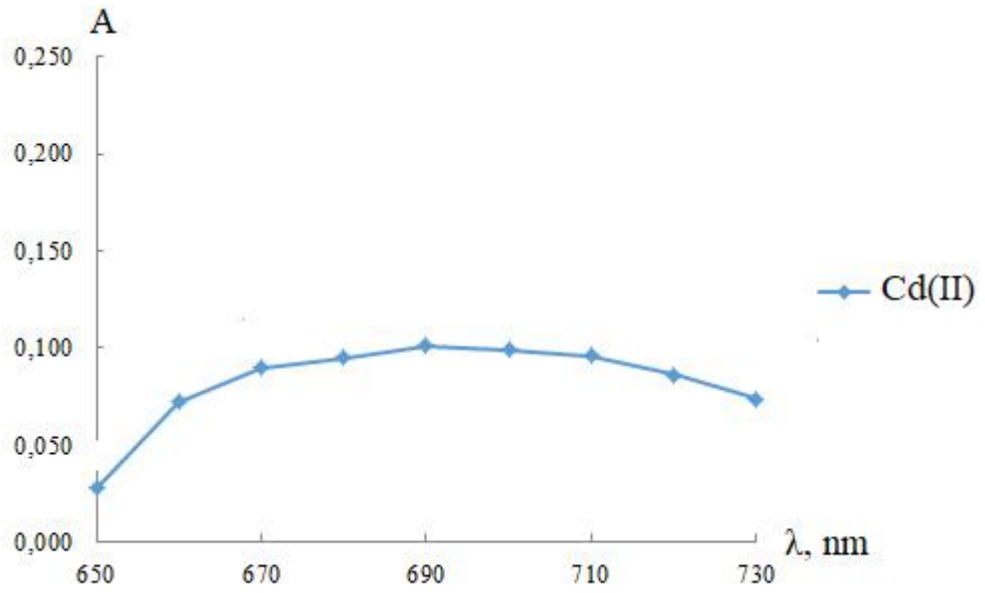


Figure 2. Graph of the dependence of the optical density of the complex formed by indigo with Cd (II) ion on wavelength

Considering that one of the important conditions for the reaction is the solution environment, universal buffer solutions with different pH values were prepared to select optimal conditions for the complex formation of metal ions with the indigo reagent .

Determination method: In a 25 ml volumetric flask, 5.0 ml of universal buffer solution with a pH of 3 to 11, 1.0 ml of 0.01% indigo solution, and 1.0 ml of 20 μg/ml metal ion solution were added to the mark of the flask, and the solvent was poured into the flask. The optical density of the resulting complex was measured using an SP-UV 1100 spectrophotometer and appropriate light filters in a cuvette with a light absorption thickness of l=1.0 cm. A solution of indigo in DMFA was used as a reference solution.

Table 2

of the optical density value of the complex of a metal ion with indigo reagent on the solution medium (pH)

pH	3.0	3.5	4.8	5.6	7.0	8.0	9.0	10.0	11.0
A	0.058	0.121	0.136	0 .113	0.093	0.080	0.072	0.059	0.041

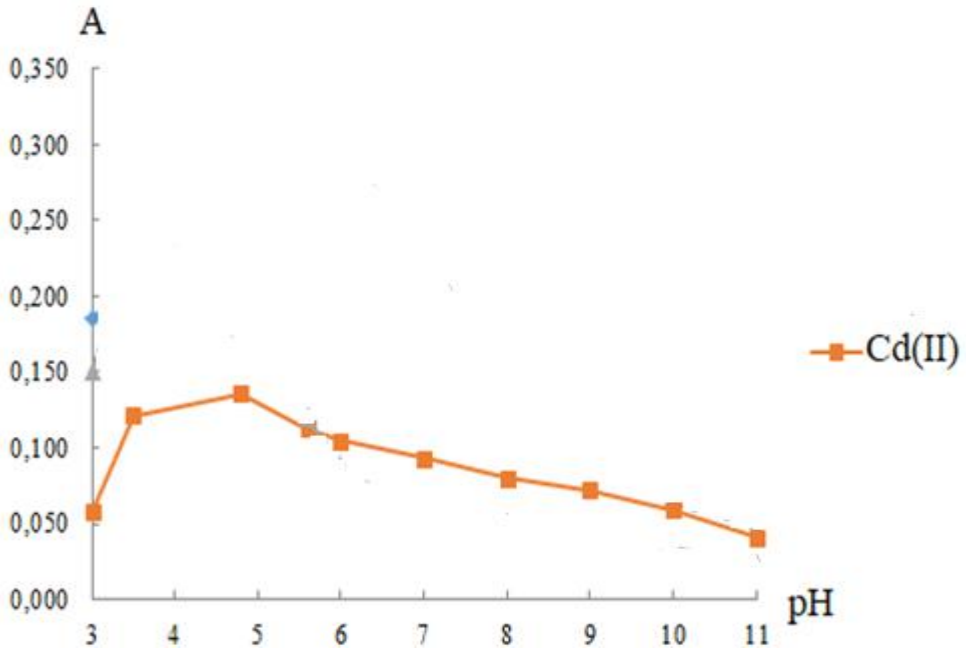


Figure 3. Graph of the dependence of the optical density of the complexes of cadmium(II) ion with indigo on the solution medium .

It was found that the optical density of the resulting complexes has a high index in an acidic environment, and solutions with pH(Fe (III))=5.6, pH(Cd (II))=4.8, and pH(Mn (II))=3.5 were selected. These solutions were used in further analyses.

To study the dependence of the optical density of the complex formed by cadmium (II) ion with indigo on the amount of reagent added, 20 μg/ml of cadmium was added to a 25 ml volumetric flask. (II) ion 1.0 ml of the solution, variable amounts of 0.2-1.4 ml of 0.01 % indigo solution, 5 ml of universal buffer solution with pH=4.8 were added, mixed, and DMF was added to the flask to the mark.

Optical density of the formed complex compounds SP-UV 1100 spectrophotometer The absorption was measured in a cuvette with a working thickness of l= 1.0 cm and in the appropriate light filters. A solution of indigo in DMFA was used as a reference solution . (Table 3) and see pictures 4)

Table 3

Dependence of the optical density of the complex compound on the amount of reagent added

V,ml	0.2	0.4	0.6	0.8	1.0	1.2	1.4
Cd(II)	0.008	0.015	0.065	0.116	0.165	0.165	0.165

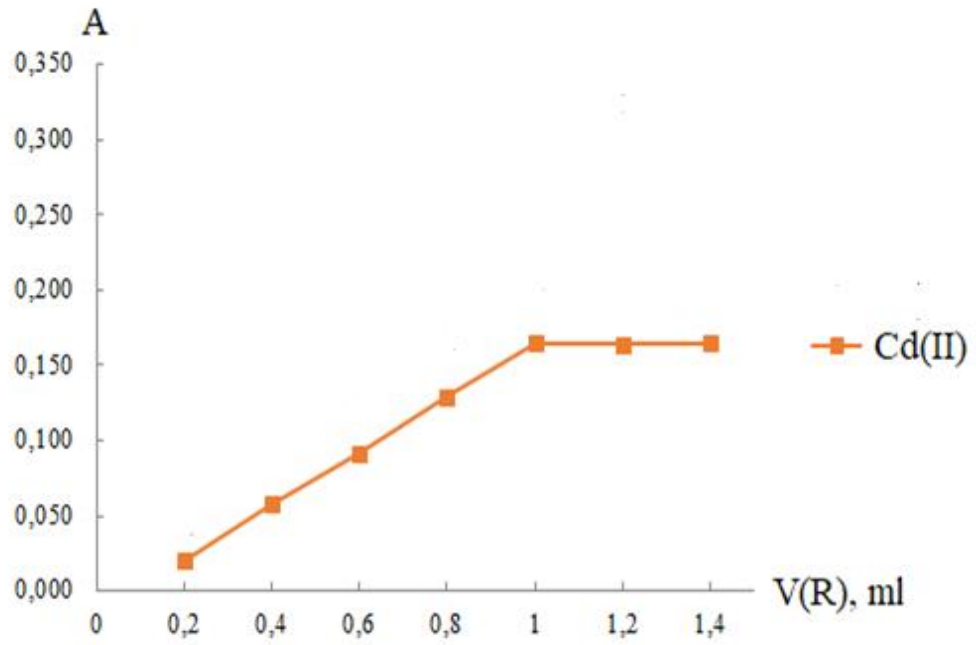


Figure 4. Graph of the optical density of complexes of Cd(II) ions with indigo as a function of the amount of reagent added

1 ml of a 0.01% solution of indigo reagent is required to completely bind 20 µg of Cd (II) ion.

To study the dependence of the complex formed by cadmium (II) ion with indigo on the amount of element, a 25-liter volumetric flask was filled with 50 µg/ml cadmium. (II) ion solution, 1.0 ml of 0.01 % indigo solution and 5 ml of universal buffer solution with pH=4.8 were added and mixed, then DMFA was poured into the flask up to the mark.

the formed complex compounds SP-UV 1100 spectrophotometer The absorption was measured in a cuvette with a working thickness of l= 1.0 cm and the corresponding light filters. A solution of indigo in DMFA was used as a reference solution . (Table 4) and see Figures 5) .

Table 4

dependence of complexes on the amount of elements (Beuer-Lambert-Beer) law

No.	Solution volume , ml	Metal content , mcg	Optical density
			Cd(II)
1	0.1	1	0.005
2	0 , 5	5	0.021
3	1.0	10	0.039
4	1.5	15	0.057
5	2.0	20	0.075
6	2, 5	25	0.093
7	3.0	30	0.111

8	3.5	35	0.129
9	4.0	40	0.147
10	4.5	45	0.165

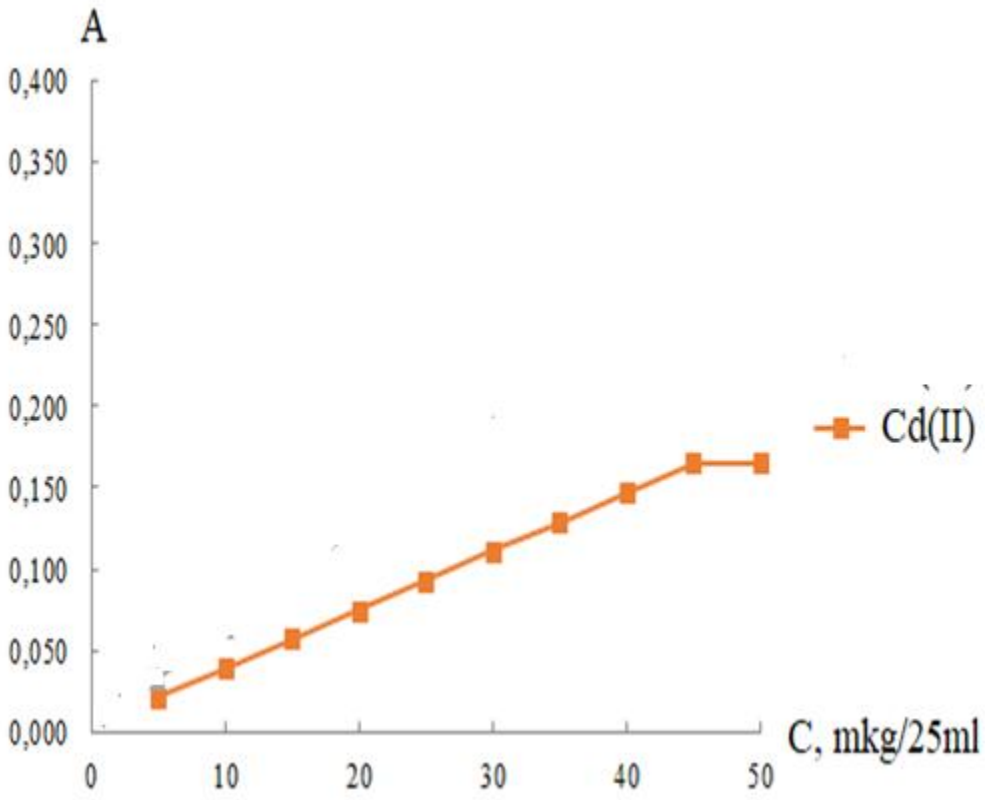


Figure 5. Graph of the compliance of complexes with the Bouguer-Lambert-Beer law

The results show that the complex formed by cadmium(II) ion with indigo obeyed the Beer-Lambert-Boer law in the concentration range of 5-45 µg/ml in a 25 ml solution. At higher concentrations, a deviation from the linear binding occurred [18].

Conclusions:

1. The results of our research show that the optimal conditions studied for the spectrophotometric determination of iron (III) ion using indigo are suitable for conducting analytical analyses.

2. The maximum absorption range of the resulting complex, the solution environment, the amount of reagent added, and the amount of element are examples of this and confirm the possibility of using this method in the future.

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