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2-HYDROXY-2-CARBOXY-5-SULFOPHARMAZYL BENZENE AND ITS PHYSICOCHEMICAL CHARACTERISTICS

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Abstract. This article investigates the infrared (IR) and ultraviolet (UV) spectroscopic properties of the organic reagent zincon. During the research, the main vibrational frequencies corresponding to the functional groups of the zincon molecule were determined using IR spectroscopy, and their role in the molecular structure was analyzed. The optical and colorimetric characteristics of zincon – the sodium salt of 2-hydroxy-2-carboxy-5-sulfoformazyl benzene – were studied in aqueous solutions at pH 4–10 and an ionic strength of 0.5-1. The ionic strength of the sodium salt of 2-hydroxy-2-carboxy-5-sulfoformazyl benzene was reduced to zero and compared with literature data. IR spectra of zincon in powder form were also obtained. It is shown that the IR spectra of the zincon reagent are crucial for identifying its constituent functional groups, highlighting the relative affordability and advantages of spectrophotometry.

Keywords: Zincon, universal buffer, IR spectrum, UV-Vis spectroscopy, colorimetric characteristics, ionic strength.

Аннотация. В настоящей статье исследуются инфракрасные (ИК) и ультрафиолетовые (УФ) спектроскопические свойства органического реагента цинкон. В ходе исследования с помощью ИК-спектроскопии были определены основные колебательные частоты, соответствующие функциональным группам молекулы цинкона, и проанализирована их роль в молекулярной структуре. Оптические и колориметрические характеристики цинкона – натриевой соли 2-гидрокси-2-карбокси-5-сульфоформазилбензола – изучались в водных растворах при pH 4–10 и ионной силе 0,5–1. Ионная сила раствора натриевой соли 2-гидрокси-2-карбокси-5-сульфоформазилбензола была снижена до нуля и сопоставлена с литературными данными. Также получены ИК-спектры цинкона в виде порошка. Показано, что ИК-спектры реагента цинкон имеют решающее

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значение для идентификации его функциональных групп, подчеркивая относительную доступность и преимущества спектрофотометрии.

Ключевые слова: цинкон, универсальный буфер, ИК-спектр, УФ-видимая спектроскопия, колориметрические характеристики, ионная сила.

Annotatsiya. Ushbu maqolada sinkon (sincon) organik reagentining infraqizil (IQ) va ultrabinafsha (UV) spektroskopik xususiyatlari o‘rganildi. Tadqiqot davomida sinkon molekulasining funksional guruhlariga tegishli asosiy tebranish chastotalari IQ spektroskopiyasi yordamida aniqlanib, ularning molekulyar tuzilmadagi o‘rni tahlil qilindi.Sinkon – 2-gidroksi-2-karboksi-5-sulfofarmazilbenzol natriyli tuzining optik va kolorimetrik xarakteristikalari pH 4–10 da, 0,5-1 ion kuchida suvli eritmalarda o‘rganildi. Sinkon – 2-gidroksi-2-karboksi-5-sulfofarmazilbenzol natriyli tuzining ion kuchi nolga tushirildi va adabiyot ma’lumotlari bilan taqqoslandi.Kukun holatdagi Sinkonning IQ spektrlari xam olindi.Sinkon reagentining IQ spektorlari uning tarkibidagi funksional guruhlarini identifikatsiya qilishda muhim ahamiyatga ega ekanligi va spektrofotometriyaning nisbatan arzon va afzalliklari ko‘rsatib berilgan.

Kalit so‘zlar: Sinkon, universal buffer, IQ spektr, UV-vis spektroskopiyasi, kalorometrik xarakteristika, ion kuchi.

Introduction.

Zincon (2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene) has recently attracted attention as a colorimetric reagent for zinc and copper. One of the most common classical reagents is zincon (the sodium salt of 2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene). It was first used in 1952 by Yoe and Rush for the detection of Zn^{2+} and Cu^{2+} [1,2]. This ligand has also been used for the spectroscopic detection of Co^{2+}, Cd^{2+}, Hg^{2+}, and Ni^{2+} [3–5]. Its ability to bind some metal ions demonstrates rather low selectivity. However, from an analytical perspective, the various physicochemical properties of metal ion complexes with zincon are very useful for developing methods to simultaneously determine metal ions in mixtures [6]. For example, Cu^{2+} and Zn^{2+} ions can be determined sequentially in a flow-through process based on changes in the stability of their zincon complexes at different pH values [7]. Zincon – the sodium salt of 2-hydroxy-2-carboxy-5-sulfoformazylbenzene – is widely used in analytical chemistry as its water-soluble analogue. Nevertheless, data on the optical characteristics of its various ionic forms are scarce and often inconsistent, as they were determined at different temperatures, different ionic strengths, and in different ionic media. The aim of this work is to study the optical and colorimetric characteristics of zincon – the sodium salt of 2-hydroxy-2-carboxy-5-sulfoformazyl benzene – in the pH range of 4–10. Among the suitable techniques for determining metal content, methods for ions in metalloproteins, inductively coupled plasma mass spectrometry, and atomic

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absorption and emission spectroscopy are the most widely used [8]. However, although these methods are reliable and sensitive, they are limited by being relatively expensive (considering instrument purchase and maintenance), time-consuming (in terms of sample preparation), and not always available [9,10]. Thus, simple spectrophotometric (or spectrofluorometric) methods could serve as an alternative to more expensive, labor-intensive methods requiring more complex instrumentation. The detection of heavy metals using visible ultraviolet (UV-Vis) spectroscopy typically relies on changes in the absorption spectrum of a chromophoric chelator that binds the target metal ion [11]. Among analytical methods, UV-Vis spectroscopy is the most common technique for detecting metal ions due to its speed and simplicity [12–14]. Molecular absorption spectrometry (or spectrophotometry) in the UV-Vis region is an effective method for developing simple, fast, and inexpensive analytical procedures for various analytes [15, 16]. This method is based on the property of light absorption at a specific wavelength by colored solutions containing the analyte [17]. Therefore, we decided to first study the properties of the reagent itself, namely Zincon (2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene), using these convenient methods.

Experimental Section

Reagents and Solutions: Reagents with analytical grade purity or higher were used. Zincon (2-carboxy-2'-hydroxy-5'-sulfoformazylbenzol) was purchased from MACLIN, China (CAS: 62625-22-3).

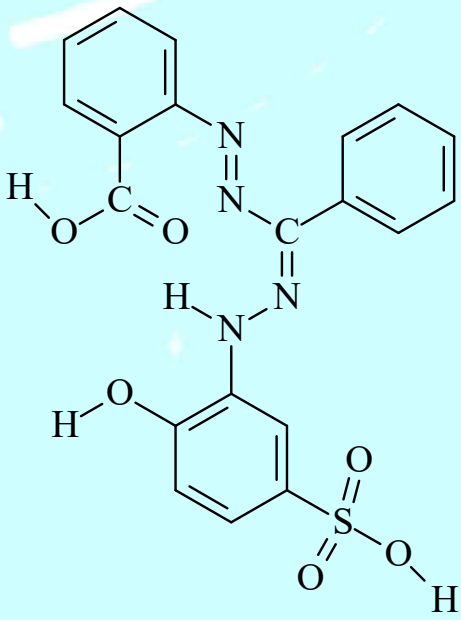


Figure 1. Provides a graphical representation of Zincon, the sodium salt of 2-hydroxy-2-carboxy-5-sulfoformazylbenzene.

Universal Buffer: The buffer was prepared as a mixture of H_3PO_4, CH_3COOH, and H_3BO_3 (each 0.04 M), with the pH adjusted using 0.2 M NaOH [13]. A 1 M KCl solution was used to maintain the ionic strength.

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Instrumentation: All experiments were conducted using high-precision equipment. Reagents were weighed on an AS 220.R2 Plus analytical balance manufactured in Poland. Deionized water required for solution preparation was obtained using an EASYpure RoDI system manufactured in the USA. The pH values of the solutions were measured with a Five Easy F20 pH meter (Mettler-Toledo GmbH, Switzerland). The wavelength and optical density of the reagent were determined using SPECORD 50 and UV-1900i spectrophotometers, manufactured in Germany. IR spectra were acquired using a LabSolutions IR system (Shimadzu, 2018, Shimadzu Corporation).

Results and Discussion A 1×10^{-4} mol/L solution of Zincon was prepared by dissolving 0.00462 g of the reagent in a 100 mL volumetric flask with water, mixed with 1 mL of 5% NaOH, resulting in a dark red color. The universal buffer solution was prepared as follows: a mixture of H_3PO_4, CH_3COOH, and H_3BO_3 (each 0.04 M), with pH adjustment using a 0.2 N sodium hydroxide solution. Solutions were prepared according to the following Table 1, using a 1 M KCl solution to adjust the ionic strength.

Table 1

Universal buffer solutions prepared at different pH values.

№	Final Solution Volume (mL)	pH Value	Universal Buffer (mL)	1 M KCl (mL)	Remarks
1	10	4.51	1	1	Low pH – Acidic environment
2	10	5.66	1	1	Slightly acidic environment
3	10	6.11	1	1	Near-neutral environment
4	10	7.59	1	1	Near-neutral environment
5	0	8.61	1	1	Slightly alkaline environment
6	10	9.30	1	1	Alkaline environment
7	10	10.03	1	1	Highly alkaline environment
8	10	0.00	1	1	Control solution (pH not specified)

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Calculation of Ionic Strength for KCl Solutions at 0.5 M and 1 M Concentrations:

$M=1/2(C_1*Z_1+C_2*Z_2+\ldots\ldots)$

$M=1/2(0,5*1^2+0,5*1^2) = 0,5$ (1)

$M=1/2(1*1^2+1*1^2) =1$ (2)

Based on this table, the colorimetric characteristics of the prepared solutions were measured using a Shimadzu UV-Vis Spectrophotometer (path length l = 0.5 cm).

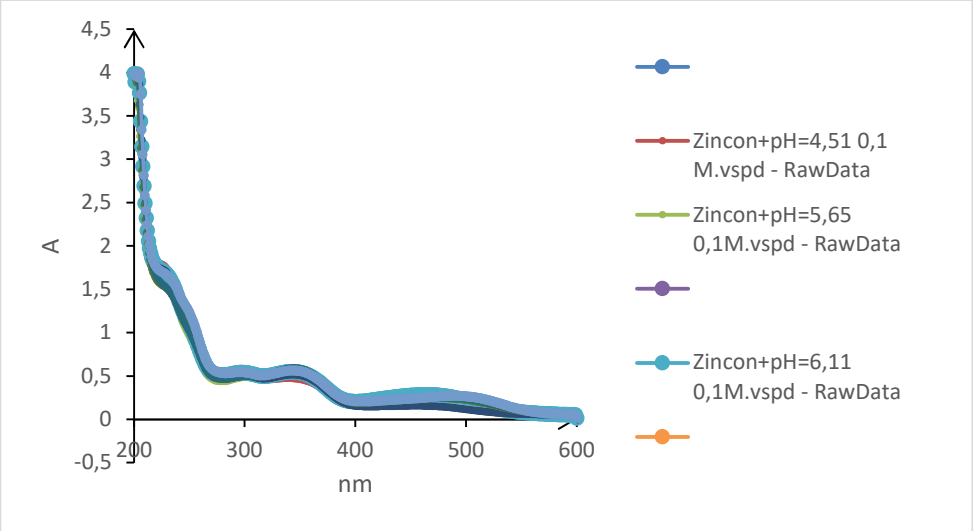


Figure 2. UV-Vis spectra of Zincon under different pH conditions.

The UV-Vis spectra of the Zincon reagent were recorded in the 200–600 nm range under different pH conditions (pH 4.51–10.03) at a constant ionic strength of 0.1 M (Figure 1). The general profile of the spectra indicates that in all cases, the primary absorption maximum is observed in the short-wavelength region (200–230 nm), with the absorbance value approaching 4. This intense absorption is associated with $\pi\rightarrow\pi^*$ electronic transitions of the aromatic systems within the Zincon molecule. As the pH value increases, the absorption intensity in the 230–250 nm range decreases slightly. The relatively weak absorption signals observed in the 320–360 nm and 420–460 nm regions are characteristic of $n\rightarrow\pi^*$ transitions in the Zincon molecule and appear to be sensitive to protonation and deprotonation processes. In low pH environments (pH 4.51–5.65), the absorption intensity is higher due to the predominance of protonated forms. Conversely, in high pH environments (pH 8.61–10.03), deprotonation of the molecule leads to a redistribution of electron density, resulting in a decrease in spectral intensity.

Maintaining a constant ionic strength of 1 M stabilized the ionic environment in the solution and resulted in significantly smoother spectral lines. These results demonstrate the pH sensitivity of the Zincon reagent and its distinct spectral properties in different protonation states. Thus, the Zincon molecule not only shows potential for use as a pH indicator in the UV-Vis region but also holds significant

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analytical importance for studying complex formation processes with metal ions. The IR spectra of a 1×10^{-4} M Zincon solution are presented in the following figure.

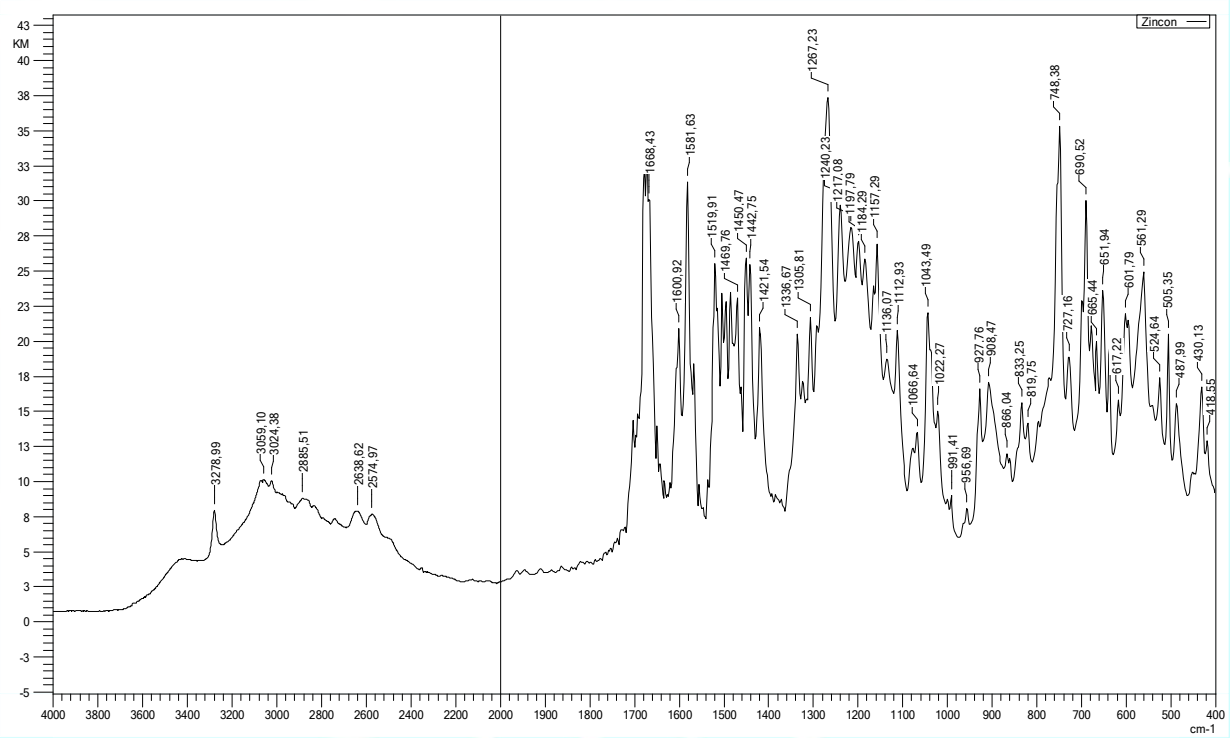


Figure 3. IR spectra of Zincon.

Analysis of the results indicates the following group absorption regions: The absorption spectrum in the 3200-3500 cm^{-1} range is attributed to the aromatic ring-bound -OH group. The absorption band observed at 3278.99 cm^{-1} in Zincon's IR spectrum confirms the presence of the -OH group. The absorption bands for the -N=N- group typically fall within 1600-1400 cm^{-1}. The absorption spectrum of the reagent in the 1581.63-1421.54 cm^{-1} range indicates the presence of the aromatic ring-bound -N=N- bond. The absorption spectrum in the 1700-1680 cm^{-1} region is characteristic of the aromatic ring-bound COO^- group. The absorption band at 1668.43 cm^{-1} in Zincon's IR spectrum signifies the presence of the COO^- group in the Zincon salt. Absorption bands in the 1250-1220 cm^{-1} region are specific for the asymmetric -SO2-O-R- group, while those in the 1050-1030 cm^{-1} region are characteristic of the symmetric -SO2-O-R- group. The IR spectrum of the reagent shows bands at 1240.23 cm^{-1} for the asymmetric -SO2-O-R- group and at 1043.49 cm^{-1} for the symmetric -SO2-O-R- group, confirming their presence. The region 600-400 cm^{-1} is assigned to the -O-Na group; the reagent exhibited peaks at 561.29-418.55 cm^{-1}, proving the existence of the -O-Na group [14].

Conclusion: This research investigated the spectral properties of the sodium salt of 2-hydroxy-2-carboxy-5-sulfoformazylbenzene — the Zincon reagent — in the infrared (IR) and ultraviolet-visible (UV-Vis) regions under varying conditions of pH and ionic strength. The results of the IR spectral analysis enabled the reliable

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identification of the main functional groups present in Zincon: –OH, –N=N–, symmetric and asymmetric $–COO^-$, $–SO_2–O–R$, and –O–Na. UV-Vis spectra were measured in the 200–600 nm range, and the results demonstrated the high sensitivity of the reagent molecule to the pH environment. At low pH values (4.5–5.6), the absorption intensity was higher due to the dominance of protonated forms, whereas at high pH values (8.6–10.0), the absorption decreased due to deprotonation. These changes are linked to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions within the molecule, demonstrating their sensitivity to the protonation state.

The study results confirm that the optical and colorimetric properties of the Zincon reagent are sensitive to pH and ionic strength. This expands the potential for its analytical application as a pH indicator, as well as in studying complex formation reactions with heavy metal ions. Furthermore, the UV-Vis and IR spectroscopic methods employed are distinguished by their simplicity, cost-effectiveness, and reliability, making them suitable and recommendable options for practical application in analytical chemistry, particularly for environmental and biological samples.

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