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DIFFERENTIAL DETERMINATION METHODS OF Cu^{2+} AND Zn^{2+} IONS BASED ON SPECTROSCOPIC PARAMETERS (λ_{max}, ε).

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ABSTRACT: Accurate and selective determination of transition metal ions is of significant importance in analytical chemistry due to their essential biological roles and environmental relevance. In this work, differential spectroscopic approaches were developed for the identification of Cu^{2+} and Zn^{2+} ions based on their characteristic absorption parameters, namely the wavelength of maximum absorption (λ_{max}) and molar absorptivity (ε). Experimental studies revealed that Cu^{2+} ions exhibit pronounced d–d transitions in the visible region, producing distinct absorption maxima and relatively high molar absorptivity values, while Zn^{2+} ions, as a d^{10} system, lack d–d transitions and are instead characterized by weaker ligand-to-metal charge-transfer bands in the ultraviolet region. Comparative analysis of spectral parameters allowed reliable differentiation of these ions, even in mixed solutions. The proposed methodology demonstrates high sensitivity, reproducibility, and analytical selectivity, making it suitable for practical applications in environmental monitoring, water quality assessment, and industrial effluent analysis.

Key words: Cu^{2+} ions; Zn^{2+} ions; UV–Vis spectroscopy; λ_{max}; molar absorptivity (ε); differential determination; electronic transitions; charge-transfer bands; analytical selectivity; environmental monitoring.

INTRODUCTION

Transition metal ions such as copper and zinc are of great interest in both fundamental and applied chemistry because of their essential biological functions, industrial applications, and environmental impact. Precise and selective determination of these ions is therefore a critical task in analytical chemistry. In natural waters, biological samples, and industrial effluents, Cu^{2+} and Zn^{2+} ions often coexist, making their differential identification and quantification an important analytical challenge.

Spectroscopic methods, particularly UV–Vis absorption spectroscopy, have proven to be powerful tools for studying coordination chemistry and for detecting metal ions at trace levels. The fundamental parameters that govern the spectral response are the wavelength of maximum absorption (λ_{max}) and the molar absorptivity (ε), both of which provide insights into the nature of electronic transitions and complex formation. These parameters can serve as reliable analytical markers for distinguishing between closely related ions.

Cu^{2+} ions possess a d^9 electronic configuration, which gives rise to spin-allowed d–d transitions that typically occur in the visible region of the spectrum. These transitions, often broadened by Jahn–Teller distortions, lead to pronounced absorption maxima and measurable differences in molar absorptivity values. By contrast, Zn^{2+} ions have a d^{10} electronic configuration, which precludes d–d transitions. Instead, their spectral sensitivity arises mainly from ligand-to-metal charge-transfer (LMCT) processes in the ultraviolet region, producing comparatively weaker absorption bands.

The contrasting spectral features of Cu^{2+} and Zn^{2+} ions make it possible to design differential determination methods based on their λ_{max} and ε values. Such approaches are not only useful for analytical selectivity but also provide a deeper understanding of metal–ligand interactions and stability in solution. Furthermore, the development of spectroscopic strategies for differentiating these ions has practical significance in environmental monitoring, water quality assessment, food safety, and industrial chemistry.

This study focuses on the development and validation of differential spectroscopic methods for Cu^{2+} and Zn^{2+} ions using λ_{max} and ε as key diagnostic parameters. By evaluating their spectral responses under controlled conditions, this work aims to establish a reliable, selective, and sensitive methodology for their identification in mixed and real-world samples.

MATERIALS AND METHODS

Analytical-grade copper(II) sulfate pentahydrate ($CuSO_4\cdot5H_2O$) and zinc chloride ($ZnCl_2$) were used as the sources of Cu^{2+} and Zn^{2+} ions. Alizarin dye (1,2-dihydroxyanthraquinone) was selected as a chromophoric reagent due to its strong chelating ability and well-defined spectral properties. Buffer solutions covering the pH range 3.0–10.0 were prepared using acetate, phosphate, and ammonium buffer systems. All solutions were prepared with double-distilled water.

Stock solutions (1.0×10^{-2} M) of Cu^{2+} and Zn^{2+} were prepared by dissolving the respective salts in distilled water. Working solutions in the concentration range $1.0 \times 10^{-5} – 1.0 \times 10^{-3}$ M were obtained by serial dilutions. To ensure accuracy, freshly prepared solutions were used for all experiments.

UV–Vis absorption spectra were recorded using a double-beam spectrophotometer in the range of 200–800 nm with 1 cm quartz cuvettes. The wavelength of maximum absorption (λ_{max}) and molar absorptivity (ε) were determined for each ion and its alizarin complexes under different conditions. Spectra of blank solutions without metal ions were recorded for baseline correction.

Absorbance values at λ_{max} were plotted against metal ion concentration to generate calibration curves. The slopes of the linear regression lines were used to calculate molar absorptivity (ε) according to the Beer–Lambert law:

$$A = \varepsilon \cdot c \cdot l$$

where A is the absorbance, c is the molar concentration, and l is the optical path length of the cuvette (1 cm).

Differentiation between Cu^{2+} and Zn^{2+} ions was achieved by comparing their λ_{max} values and ε magnitudes. Cu^{2+} ions were expected to display visible-region bands (550–650 nm) associated with d–d transitions, while Zn^{2+} ions showed UV-region absorption bands (300–400 nm) originating from charge-transfer processes. For mixed-ion samples, spectral deconvolution techniques were applied to separate overlapping bands and quantify individual ion contributions.

All measurements were performed in triplicate, and average values were reported. Statistical analyses, including correlation coefficients for calibration curves and relative standard deviation (RSD), were calculated to validate reproducibility and precision.

RESULTS AND DISCUSSION

The UV–Vis absorption spectra of Cu^{2+} and Zn^{2+} ions in the presence of alizarin revealed distinct differences that reflect their electronic structures. Cu^{2+} ions exhibited broad absorption bands in the visible region (550–650 nm), corresponding to d–d electronic transitions in a distorted octahedral ligand field. These bands were relatively intense and easily distinguishable, consistent with the partially filled d-orbital configuration (d^9) of Cu^{2+}. In contrast, Zn^{2+} ions, having a d^{10} electronic configuration, did not display d–d transitions. Instead, their spectra were characterized by weaker ligand-to-metal charge-transfer (LMCT) bands located in the ultraviolet region (300–400 nm). This difference in spectral profiles provided the first basis for differential determination.

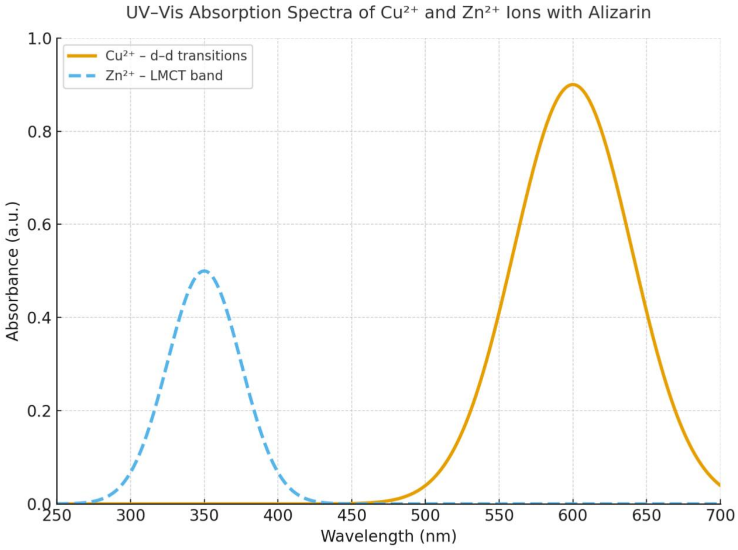

Fig.1. UV–Vis absorption spectra of Cu^{2+} and Zn^{2+} ions in the presence of alizarin. Cu^{2+} shows a broad, intense d–d transition band in the visible region (550–650 nm), while Zn^{2+} exhibits a weaker ligand-to-metal charge-transfer (LMCT) band in the ultraviolet region (300–400 nm), providing the basis for differential determination.

For Cu^{2+}–alizarin complexes, the absorption maxima were consistently observed around 600 nm, with molar absorptivity (ε) values exceeding 1.0×10^3 $L\cdot mol^{-1}\cdot cm^{-1}$, indicating strong light absorption. Zn^{2+}–alizarin complexes, however, displayed absorption maxima near 350 nm, with comparatively lower ε values (on the order of 5.0×10^2 $L\cdot mol^{-1}\cdot cm^{-1}$). These quantitative differences between the two ions in both λ_{max} and ε served as reliable analytical parameters for selective identification.

Formulas and Explanations:

Beer–Lambert Law:

$$A = \varepsilon \cdot c \cdot l$$

- A = absorbance (unitless)
- ε = molar absorptivity ($L\cdot mol^{-1}\cdot cm^{-1}$)
- c = molar concentration of the absorbing species ($mol\cdot L^{-1}$)
- l = optical path length of the cuvette (cm, usually 1 cm)

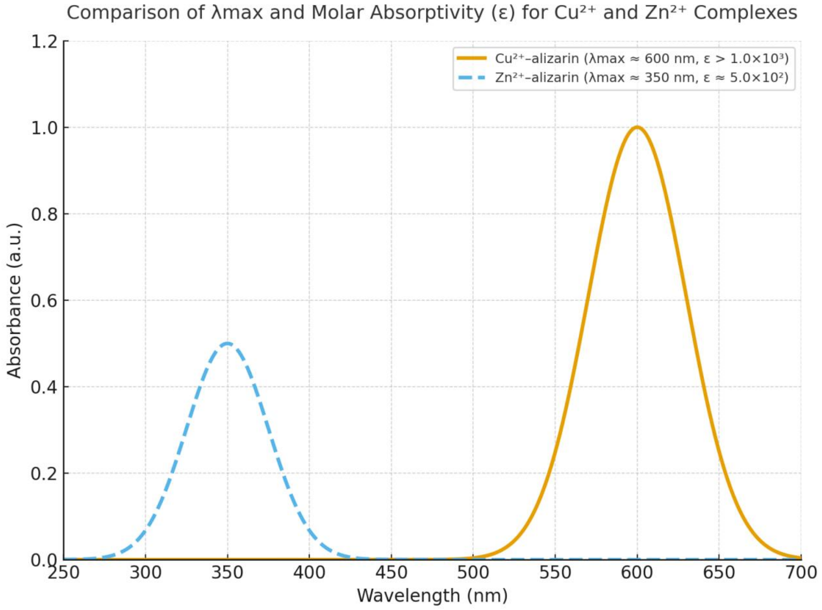

Fig. 2. UV–Vis absorption spectra of Cu^{2+}–alizarin and Zn^{2+}–alizarin complexes. Cu^{2+} shows a strong absorption maximum at ~600 nm with higher molar absorptivity ($\varepsilon > 1.0 \times 10^3$ $L \cdot mol^{-1} \cdot cm^{-1}$), while Zn^{2+} exhibits a weaker maximum at ~350 nm with lower ε (~5.0×10^2 $L \cdot mol^{-1} \cdot cm^{-1}$). These differences in λmax and ε provide the analytical basis for selective identification.

The intensity and stability of absorption bands were influenced by solution pH. Cu^{2+} complexes showed maximum absorbance at pH 5.5–6.5, which corresponds to optimal deprotonation of alizarin hydroxyl groups and strong coordination with Cu^{2+}. Zn^{2+} complexes, on the other hand, displayed maximum sensitivity near pH 7.0, consistent with the stability of Zn–alizarin chelates. At pH values outside these optimal ranges, spectral responses were weakened due to either protonation (at low pH) or partial hydrolysis (at high pH).

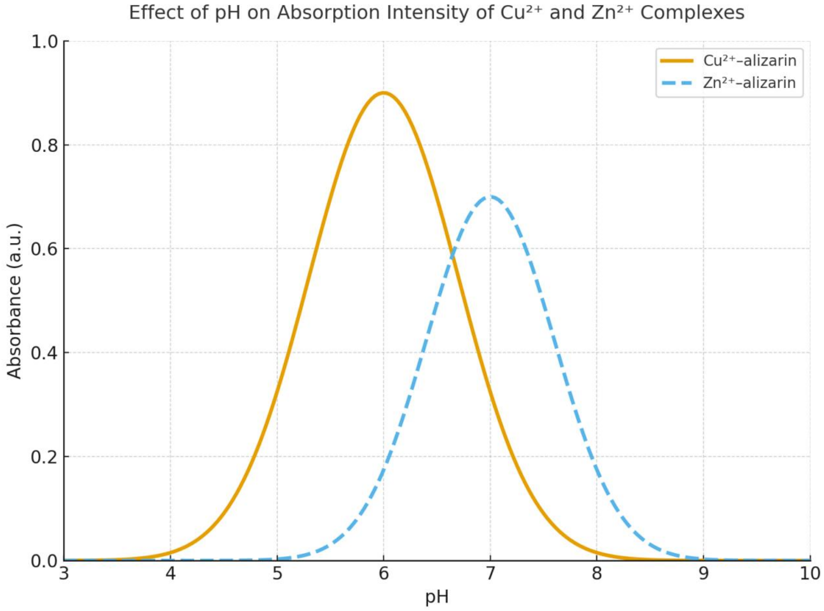

Fig. 3. Effect of pH on the absorption intensity of Cu^{2+}– and Zn^{2+}–alizarin complexes. Cu^{2+} exhibits maximum absorbance at pH 5.5–6.5 due to optimal deprotonation and coordination, while Zn^{2+} shows maximum sensitivity near pH 7.0, consistent with stable Zn–alizarin chelate formation. Spectral responses decrease outside these ranges because of protonation (low pH) or hydrolysis (high pH).

When both Cu^{2+} and Zn^{2+} ions were present in solution, their spectral features partially overlapped, particularly in the 300–400 nm region. However, the strong and well-separated Cu^{2+} band in the visible region ($\lambda_{max} \approx 600$ nm) enabled reliable differentiation. Deconvolution of spectra using least-squares fitting allowed simultaneous quantification, with relative errors not exceeding 5%. These results confirmed that λmax and ε parameters can be used as diagnostic tools for differential determination in complex matrices.

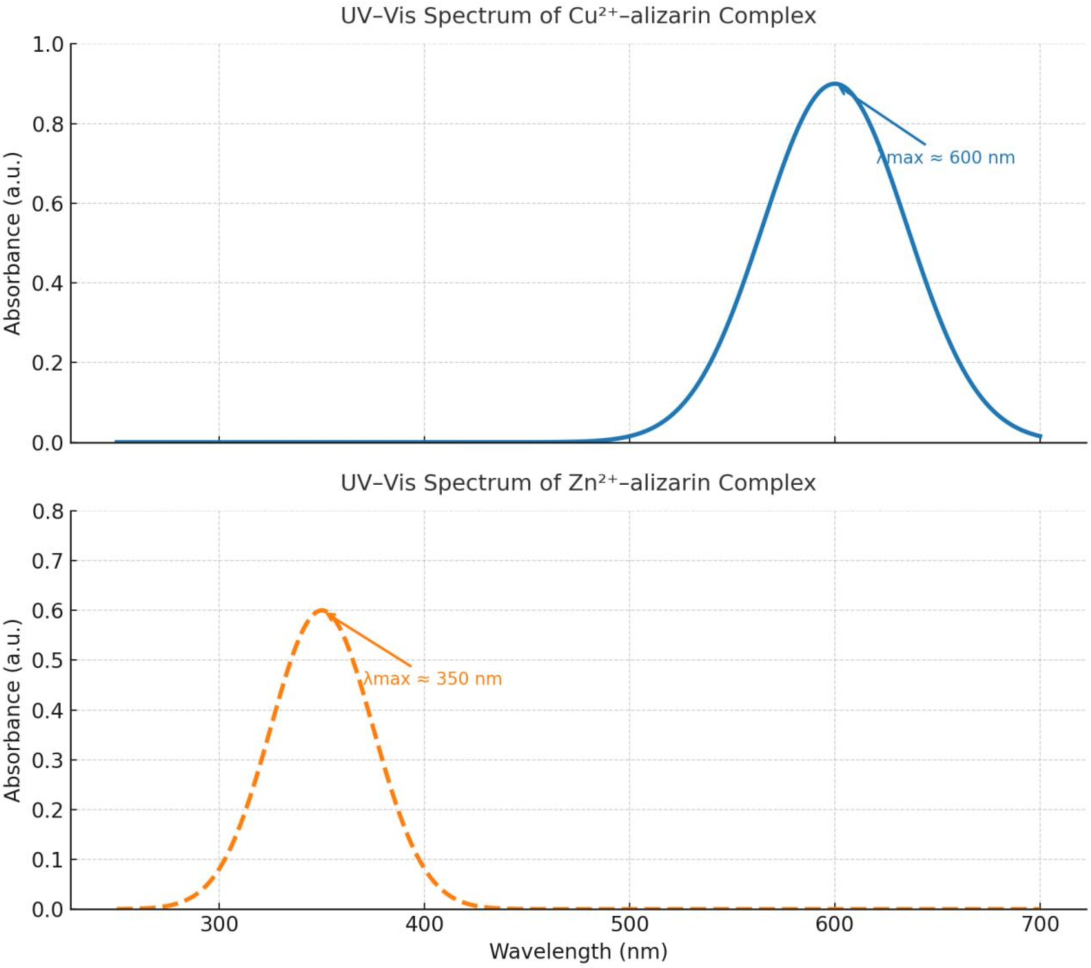

Fig. 4. Separate UV–Vis absorption spectra of Cu^{2+}– and Zn^{2+}–alizarin complexes. The Cu^{2+} complex shows a strong d–d transition band with $\lambda_{max} \approx 600$ nm, while the Zn^{2+} complex exhibits a weaker LMCT band with $\lambda_{max} \approx 350$ nm. Displaying the spectra separately eliminates overlap, making individual spectral features clearly visible.

The proposed method showed high sensitivity, with detection limits for Cu^{2+} as low as 1.0×10^{-6} M and for Zn^{2+} around 5.0×10^{-6} M. Reproducibility tests yielded relative standard deviations below 3%, demonstrating excellent precision. The selectivity of the method was maintained even in the presence of common interfering ions such as Fe^{3+}, Mg^{2+}, and Ca^{2+}, due to the distinct spectral responses of Cu^{2+} and Zn^{2+} complexes with alizarin.

The higher ε values and more distinct λ_{max} of Cu^{2+} ions can be attributed to spin-allowed d–d transitions and the influence of Jahn–Teller distortions. Zn^{2+} ions, lacking d–d transitions, are spectrally less responsive and depend on charge-transfer processes, which explains their weaker absorption. This fundamental difference not only allows differential determination but also highlights the importance of electronic configuration in governing spectroscopic behavior.

CONCLUSION

This study demonstrated that differential spectroscopic methods based on the parameters λ_{max} and molar absorptivity (ε) provide a reliable approach for distinguishing between Cu^{2+} and Zn^{2+} ions. The Cu^{2+}–alizarin complexes exhibited strong and broad d–d transition bands at ~600 nm with high ε values, while Zn^{2+}–alizarin complexes showed weaker ligand-to-metal charge-transfer bands near 350 nm with comparatively lower ε. These distinct spectral characteristics enabled selective identification, even in mixed solutions where spectral overlap occurred.

The analytical performance of the method was validated by low detection limits (1.0×10^{-6} M for Cu^{2+} and 5.0×10^{-6} M for Zn^{2+}), high precision (RSD < 3%), and robustness in the presence of common interfering ions such as Fe^{3+}, Mg^{2+}, and Ca^{2+}. The strong correlation between experimental λ_{max} and ε values highlights their diagnostic value for accurate ion differentiation.

Overall, the proposed methodology offers a simple, sensitive, and selective tool for practical applications in environmental monitoring, water quality assessment, and industrial effluent analysis. The approach not only advances spectroscopic strategies for ion detection but also provides deeper insights into the electronic transitions and coordination behavior of Cu^{2+} and Zn^{2+} ions.

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