

Spectrophotometric determination of trace amount of copper(II) ion based on the complexation with an anthraquinone derivative

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Abstract : The spectrophotometric determination of Cu^{II} with an anthraquinone derivative (Alizarin Red S) has been investigated. Experimental conditions such as the pH of the sample and concentration of ligand were optimized. This method is a simple and sensitive method for determination of Cu^{II} ion. The interfering effects of diverse ions were investigated. Copper ion was determined by measuring the absorbance of Cu^{II} -ARS complex at 510 nm. Beer's law is obeyed over the concentration range of 0.011–0.320 mM and the detection limit ($S/N = 3$) is 0.038 ppm. The relative standard deviation at the 20 ppm is 1.02% ($N = 5$). The method was applied for the real samples.

Keywords : Copper(II), spectrophotometry, Alizarin Red S.

Cu^{II} ion is widely distributed in foods of plant tissue and animal organ. It is an essential trace element but is also toxic in the environment. The determination of trace of copper has received considerable attention in the battle against environmental pollution. In order to assess its accumulation or deficiency in biological and environmental samples, sensitive and accurate analytical methods are required.

In determination of copper, various methods, including inductively coupled plasma-mass spectrometry¹, ion chromatography², anodic stripping analysis³ and atomic absorption spectrophotometry⁴ have been used. Many of these methods are either time-consuming or require complicated and expensive instruments.

Although numerous organic reagents, such as PAN⁵, zincon⁶, PAR⁷ and DDTC⁸ have been proposed for the spectrophotometric determination of copper, none of the methods presently available are completely satisfactory.

In analytical chemistry, anthraquinone derivatives have been widely used, mainly as strong chelating agents and chromophores. These chelates are then used in selective and sensitive determination of metals⁹.

Therefore, an attractive alternative method that could determine trace amount of copper, rapidly and conveniently, by using Alizarin Red S (ARS) chelating agent, was researched. In this study, ARS was used to react with Cu^{II} , forming a colored, water-soluble complex. The reaction is very fast and the sensitivity of the reagent has been made selective by controlling the pH of the solu-

tion. Therefore, in this investigation, an effort was made to develop a simple, selective, reproducible and sensitive method for the determination of Cu^{II} in a wide range of materials.

Experimental

Reagents : All chemicals used in this experiment were of analytical grade. The deionized water was used throughout all experiments. An acetic acid-sodium acetate buffer solution (pH = 5.0) was used. Alizarin Red S solution (4.0×10^{-3} M) was prepared by dissolving 0.1457 g of the reagent (Merck) in 100.0 mL water. A stock standard solution of copper ion (1.3×10^{-3} M) was prepared by dissolving 0.0332 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Merck) in 100.0 mL water.

Apparatus : All absorbance measurements were made with a Shimadzu UV 2100 spectrophotometer using 1-cm quartz cells. All pH measurements were made with a Metrohm 691 pH-meter. For reference method measurements, a Philips PU 9100X atomic absorption spectrometer at 324.7 nm was used for comparing the results.

General procedure : A 5.0 mL volume of buffer solution, 5.0 mL of a stock Alizarin Red S solution and an appropriate volume of Cu^{II} were added to a 25.0 mL volumetric flask and made up to the mark with deionized water, the solution was left for five min and then the absorbance was measured. These spectra were recorded over the 380–660 nm wavelength range. The absorbance was measured against the blank solution.

Determination of Cu^{II} in real samples : 0.58 g of copper wire sample was dissolved in mixture of 15 mL HNO₃ and 1 mL H₂SO₄. The solution was heated to drive off the oxides of nitrogen and then cooled, neutralized and diluted to 1000 ml. 2.5 mL of this solution were taken and, using the recommended procedure, analyzed for Cu^{II}.

Also 10.0 mL of water samples were analyzed by using the recommended general procedure.

Results and discussion

Cu^{II} reacts with Alizarin Red S giving a intensive red color in acidic solution. The spectral characteristic, effect of variables and foreign ions on Cu^{II}-ARS absorbance and applications of the system are discussed below.

Spectral characteristics : The absorption spectra of the Cu^{II}-ARS complex and ARS show a maximum ab-

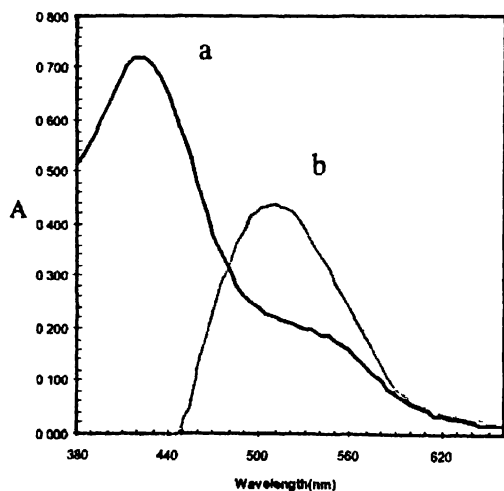


Fig. 1. Absorption spectra of (a) ARS against deionized water, (b) Cu^{II}-ARS complex against reagent blank, both at pH = 5.0.

sorption at 510 and 420 nm, respectively (Fig. 1), and the absorbance of the complex showed the maximum values at pH of the rang 4.8–5.2 (Fig. 2). In more acidic or more alkaline solutions, the absorbance decreased because of incomplete complex formation and hydrolysis of the complex. Buffer solution of acetic acid-acetate solution (pH = 5.0) was chosen for subsequent studies.

The stoichiometric composition of the complex was studied under the established experimental conditions by the molar-ratio method¹⁰. This method showed that the composition of the complex is 1 : 2 (Fig. 3).

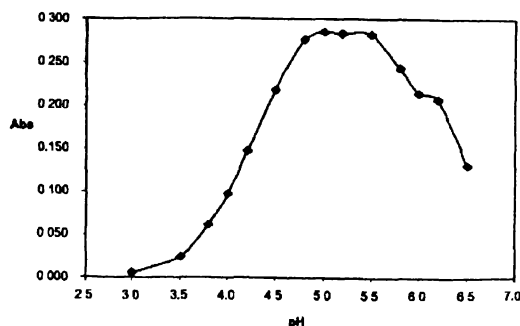


Fig. 2. pH effect on the change in the absorbance of Cu^{II}-ARS complex (Cu^{II} = 4.0 × 10⁻³ M and ARS = 8.0 × 10⁻³ M).

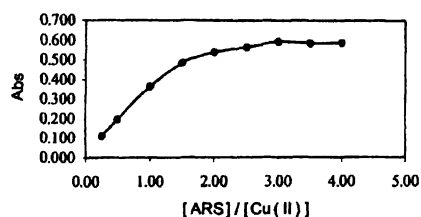


Fig. 3. Effect of the reagent concentration on absorbance of Cu^{II}-ARS system at pH = 5.0.

Effect of time : The complexation reaction is very fast. A constant maximum absorbance was obtained just after dilution to volume and remained unaltered for 24 h.

Calibration graph, precision and detection limit : Beer's law is obeyed over the concentration range of 0.011–0.320 mM at 510 nm. The molar absorptivity and correlation coefficient were calculated to be 9.37 × 10³ mol⁻¹ cm⁻¹ L and 0.9997 respectively. The precision of the present method was evaluated by determining concentration Cu^{II} at the 20 ppm level (analyzed at least five times). The relative standard deviation (*n* = 5) was 1.02%, indicating that this method is highly precise and reproducible. The detection limit (3 times of the standard deviation of blank)¹¹ for Cu^{II} was found to be 0.038 ppm.

Interferences : To assess the usefulness of this method, the effects of foreign ions which often interfere the determination of Cu^{II} were studied. The tolerance limits given in Table 1 are the concentrations that cause error of less than ±5.0% in the absorbance of 30 ppm Cu^{II} solution. Some interfering ions may be masked using proper masking agents¹². The tested results were as follows : 1 cm³ of 1000 ppm tartarate could mask 500 µg of Co^{II,III}, Mn²⁺ and Fe³⁺. For this reason, the selectivity of the proposed method is greatly improved.

Applications to real samples : To evaluate the analytical applicability and to check the accuracy of the proposed method, we applied it to the determination of Cu^{II} in two electric copper wire samples and tap water and river water spiked with Cu^{II}. The obtained results are summarized in Tables 2 and 3 respectively. This method is in good agreement and comparable in accuracy and precision with reference method (atomic absorption spectrometry)¹³ and is very quantitative.

Table 1. Tolerance limits of foreign ions (ppm)

Cation	Concn.	Anion	Concn.
Mn ²⁺	1000	F ⁻	1000
Co ²⁺	500	Br ⁻	1000
Ni ²⁺	550	Cl ⁻	1000
Zn ²⁺	1000	Nitrate	700
Mg ²⁺	1000	Acetate	2000
Ba ²⁺	1000	Citrate	200
Ca ²⁺	1000	Oxalate	1000
Fe ³⁺	500	SCN ⁻	500
Na ⁺	1000		
K ⁺	1000		
Pb ²⁺	500		
Cd ²⁺	1000		
Cr ³⁺	500		
Sn ⁴⁺	1000		

Table 2. Determination of Cu^{II} in real samples (ppm)

Sample	Reference method	Proposed method ^a
1	57.17	56.28 ± 0.08
2	51.75	51.62 ± 0.05

^aMean of five-determination ± relative standard deviation.

Table 3. Determination of Cu^{II} added to water sample (ppm)

Sample	Spiked	Measured	Recovery (%)
Tap water ^a	10	9.8	98.0
	20	20.1	100.5
	40	40.8	102.0
River water ^a	10	10.3	103.0
	20	20.4	102.0
	40	40.7	101.8

^aThe sample contained no detectable Cu^{II}.

Conclusion :

Alizarin Red S is a good spectrophotometer reagent for the determination of Cu^{II}. The method is very simple, sensitive and more selective than most reported methods. The results obtained by the recommended method are in excellent agreement with those determined by FAAS. The procedure is suitable for determination of industrial copper products and real samples.

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