Spectrophotometric Determination of Trace Amount of Copper(II) Ion Based on Complexation with an Anthraquinone Derivative

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

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Introduction

Cu(II) ion is widely distributed in foods of plant tissue and animal organs. It is an essential trace element, but is also toxic in the environment. The determination of traces 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 the determination of copper, various methods, including inductively coupled plasma-mass spectrometry,¹⁻⁴ ion chromatography,⁵⁻⁷ anodic stripping analysis⁸⁻¹² and atomic absorption spectrophotometry¹³⁻¹⁶ have been used. Many of these methods are either time-consuming or require complicated and expensive instruments.

Although numerous organic reagents, such as PAN,¹⁷ zincon,¹⁸ PAR¹⁹ and DDTC²⁰ 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 metals.²¹

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 solution. 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. Deionized water was used throughout all experiments. An acetic acid-sodium acetate buffer solution (pH 5.0) was used. An Alizarin Red S solution (4.0×10^{-3} mol dm⁻³) was prepared by dissolving 0.1457 g of the reagent (Merck) in 100.0 cm³ of water. A stock standard solution of copper ion (1.3×10^{-3} mol dm⁻³) was prepared by dissolving 0.0332 g of CuSO₄·5H₂O (Merck) in 100.0 cm³ 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-cm³ volume of buffer solution, 5.0 cm³ of stock Alizarin Red S solution and an appropriate volume of Cu(II) were added to a 25.0 cm³ volumetric flask and made up to the mark with deionized water. The solution was left for 5 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 sample

After 0.58 g of copper wire sample was dissolved in mixture of 15 cm³ HNO₃ and 1 cm³ H₂SO₄, the solution was heated to drive off the oxides of nitrogen and then cooled, neutralized and diluted to 1000 cm³. Then 2.5 cm³ of this solution were taken and, using the recommended procedure, analyzed for Cu(II).

Also, 10.0 cm³ 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

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

Fig. 2 pH effect on the change in the absorbance of the Cu(II)-ARS complex ($\text{Cu(II)} = 4.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $\text{ARS} = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$).

Fig. 3 Effect of the reagent concentration on the absorbance of the Cu(II)-ARS system at pH 5.0.

the system are discussed below.

Spectral characteristics

The absorption spectra of the Cu(II)-ARS complex and ARS show a maximum absorption at 510 and 420 nm, respectively (Fig. 1), and the absorbance of the complex showed the maximum values for pH values in the 4.8–5.2 range (Fig. 2). In more acidic or more alkaline solutions, the absorbance decreased because of incomplete complex formation and

Table 1 Tolerance limit of foreign ions ($\mu\text{g cm}^{-3}$)

Cation	Conc.	Anion	Conc.
Na^+ , K^+	1000	F^- , Cl^- , Br^-	1000
Mn^{2+} , Zn^{2+} , Mg^{2+} , Ba^{2+} , Ca^{2+} , Cd^{2+}	1000	SCN^-	500
Ni^{2+}	550	NO_3^-	700
Pb^{2+} , Co^{2+}	500	Acetate	2000
Fe^{3+} , Cr^{3+}	500	Citrate	200
Sn^{4+}	1000	Oxalate	1000

Table 2 Determination of Cu(II) in real samples ($\mu\text{g cm}^{-3}$)

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

a. Mean of five-determination $\pm$ relative standard deviation.

Table 3 Determination of Cu(II) added to a water sample ($\mu\text{g cm}^{-3}$)

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

a. The sample contained no detectable Cu(II).

hydrolysis of the complex. A 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 method.²² This method showed that the composition of the complex is 1:2 (Fig. 3).

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 mmol dm^{-3} at 510 nm. The molar absorptivity and correlation coefficient were calculated to be $9.37 \times 10^3 \text{ dm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$ and 0.9997, respectively. The precision of the present method was evaluated by the determining concentration Cu(II) at the 20 $\mu\text{g cm}^{-3}$ 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 the standard deviation of the blank)²³ for Cu(II) was found to be 0.038 $\mu\text{g cm}^{-3}$.

Interferences

To assess the usefulness of this method, the effects of foreign ions, which often interfere with the determination of Cu(II) were studied. The tolerance limits given in Table 1 are the concentrations that cause an error of less than $\pm 5.0\%$ in the

absorbance of a 30 $\mu\text{g cm}^{-3}$ Cu(II) solution. Some interfering ions may be masked using proper masking agents.²⁴ The tested results were as follows: 1 cm^3 of 1000 $\mu\text{g cm}^{-3}$ tartarate could mask 500 μg of Co(II) and (III), Mn^{2+} and Fe^{3+} . 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)²⁵ and is very quantitative.

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 the determination of industrial copper products and real samples.

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