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Dual-Wavelength Spectrophotometric Determination of Trace Amounts of Copper with Dibromo-*o*-Nitrophenylflurone

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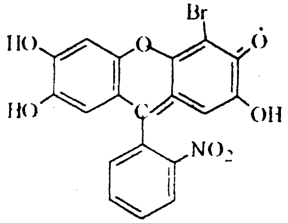
The reaction between copper (Cu^{2+}) and the chromogenic reagent, dibromo-*o*-nitrophenylflurone (DBNPF) was used for the determination of trace amounts of copper by primary-secondary wavelength spectrophotometry (PSWS). It was selective at pH 8 and selective in the presence of fluoride and triethanolamine. The new dual-wavelength spectrophotometry, PSWS, gave more precise and more accurate results than ordinary spectrophotometry because it can utilize simultaneously the peak absorption and the valley absorption of the reacted solution to decrease the influence of excess of ligand. By analyzing several samples, the relative standard deviations were less than 4.7% and the recovery rate of Cu between 92.5 and 107%.

INTRODUCTION

Copper(II) exists widely in ore, wastewater, metal material, etc. Its conventional spectrophotometric determination often involves with the chromogenic agents: 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol[1], di-2-pyridyl-methanone-2-(5-nitropyridyl) hydrazone[2] and so on. The synthesis method of new chromogenic reagent, dibromo-*o*-nitrophenylflurone (DBNPF) with the following structure was reported and ever applied to the analysis of tungsten[3].



In this paper, such a reagent was applied for the determination of copper by primary-secondary wavelength spectrophotometry. The reaction between copper(II) and DBNPF was sensitive at pH between 5 and 10. However, because of

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the wavelength difference only 50 nm between the maximal absorption of complex and that of DBNPF and the influence upon each other, classical spectrophotometry was unsuitable for the determination of Cu(II). The new method, primary-secondary wavelength spectrophotometery used the peak (A_p) and valley (A_s) absorption of the reaction solution so as to increase the analytical precision and accuracy, which was ever used for the determination of some compenents[4, 5], etc. It never usd the classical Lambert-Beer law and it established the following expression: $\lg [A_p + 1)/(A_s + 1)] = \alpha X^\beta$ where X indicates the concentration of the analysed component, both α and β are coefficients and constants if the measurement wavelengths λ_p and λ_s were selected. This expression was often stable with the small variation of the operation condition. Results showed that the detection limit of copper was 0.02 mg/L and the recovery rate between 92.5 and 107% accompanying the relative standard deviation (RSD) less than 4.7%.

EXPERIMENTAL

Visible spectra were recorded with a UV-VIS 265 spectrophotometer in 10 mm glass cells.

Standard Cu(II) solution (1000 mg/L) was prepared by dissolving 1 g of the high-purity metal in nitric acid and diluted to 1000 mL. Standard Cu(II) work solution (10.0 mg/L) must be prepared daily. DBNPF ligand solution (1 mmol/L) was prepared by dissolving 0.2040 g of dibromo-*o*-nitrophenylflurone (DBNPF) in acetone (A.R., Shanghai Chemical), then diluting to 500 mL with non-ionic water. It should be stored in a dark bottle and at 5°C. The buffer solution, pH 8, was prepared with sodium borate (A.R., Shanghai Chemical) for adjusting the pH of the reaction.

Masking reagent was prepared by dissolving 5 g of potassium fluoride and 10 mL of triethanolamine in 100 mL non-ionic water.

Recommended Procedures: A known volume of a sample solution containing less than 20 μg of Cu(II) was taken in a 25 mL volumetic flask. Added 2.5 mL of pH 8 buffer solution, 1 mL of masking reagent and 2 mL of DBNPF solution. Diluted to required volume and mixed well. After 10 min measured absorbances A_s and A_p at 540 and 590 nm against a reagent blank, respectively and calculate the term, $\lg [(A_p + 1)/(A_s + 1)]$.

RESULTS AND DISCUSSION

Absorption Spectra: Fig. 1 showed the absorption spectra of Cu-DBNPF reaction solution. The peak absorption appeared at 590 nm and the valley at 540 nm. Therefore, 590 nm should be selected as primary wavelength (λ_p) and 540 nm as secondary wavelength (λ_s).

Effect of pH: The effect of pH on absorbances and $\lg [(A_p + 1)/(A_s + 1)]$ values of the reaction solution was shown in Figure 2. The absorbances and $\lg [(A_p + 1)/(A_s + 1)]$ values remained constant at pH between 5 and 10. In this study, pH 8 was selected. By comparing curve 2 with 1, the variation of

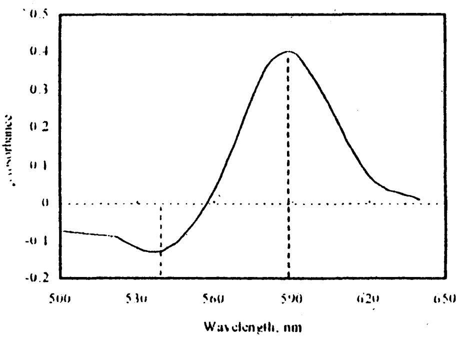

Fig. 1. Absorption spectra of Cu(10 μg)-DBNPF reacted solution at pH 8, against reagent blank

lg [(A_p + 1)/(A_s + 1)] values was more uniform than that of absorbances with the addition of DBNPF solution. Therefore, primary-secondary wavelength spectrophotometry gave out stable coefficients α and β to buffer the effect of the operation conditions' variation on the standard curve.

Effects of Fe-DBNPF Concentration: The effect of the various additions of DBNPF solution on absorbance of Cu(II) complex solution and lg [(A_p + 1)/(A_s + 1)] value is shown in Figure 3. When the addition of 1 mmol/L DBNPF is more than 1.5 mL, the term lg [(A_p + 1)/(A_s + 1)] remains almost constant. In this work, 2 mL of DBNPF solution was used. By comparing curve 2 with 1, the variation of lg [(A_p + 1)/(A_s + 1)] values was more uniform than that of absorbances with the addition of DBNPF solution.

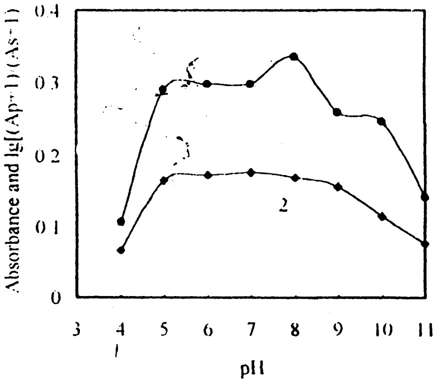

Fig. 2. Effect of pH on absorbance (curve 1 at 590 nm) and lg [(A_p + 1)/(A_s + 1)] (curve 2) of Cu(10 μg)-DBNPF solution

The complex ratio of Cu(II) to DBNPF was determined to be 1 : 2 by using the β-correction spectrophotometry[6].

Effect of Time: Figure 4 shows the effect of the reaction time on lg [(A_p + 1)/(A_s + 1)] values of Cu-DBNPF reaction solution at room temperature (10°C). It was completed in 10 min.

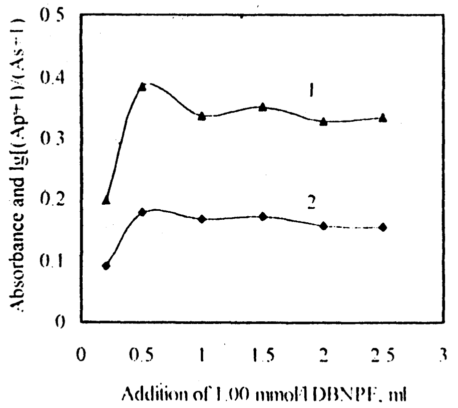

Fig. 3. Effect of 1.00 mmol/L DBNPF addition on absorbance (curve 1 at 590 nm) and lg $[(A_p + 1)/(A_s + 1)]$ (curve 2) of Cu (10 μg) solution

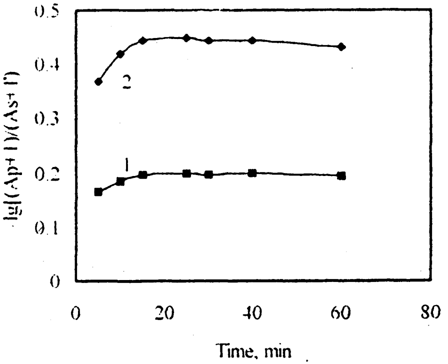

Fig. 4. Effect of color-developed time on absorbance (curve 1 at 590 nm) and lg $[(A_p + 1)/(A_s + 1)]$ (curve 2) or Cu (10 μg) solution

Calibration Graph: A series of standard Cu (0–20 μg/25 mL) solutions were prepared and the absorbance of each was measured and plotted. The lg $[(A_p + 1)/(A_s + 1)]$ value of each solution was calculated. The calibration graph is shown in Figure 5. The following expression was used for the calculation of copper: lg $[(A_p + 1)/(A_s + 1)] = 0.030X^{0.73}$.

Precision, Accuracy and Detection Limit: Eight replicate determinations of standard solution containing 5 μg Cu were carried out. The relative standard deviation (RSD) was 4.9% by PSWS. However, the RSD was 11% by the single wavelength method. The precision of PSWS was therefore higher than that for the ordinary spectrophotometric method.

The equation $L_{min} = kS_b/S$ was used to calculate the detection limit of copper. Results showed that $L_{min} = 0.5$ μg/25 mL (0.02 mg/L).

Effect of Foreign Ions: Once the masking reagent was added, none of the following ions will affect the direct determination of 5 μg of Cu(II) (< 20% error): 1 mg of Cl^-, SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, NO_3^-, NH_4^+, K(I), Na(I), Be(II), Ti(I), Ca(II), Mg(II); 50 μg of Al(III), Fe(III), Fe(II), Sn(II), Pb(II), V(V), Mo(VI), Cr(III), Mn(II), Ag(II) and 10 μg of Co(II), Cd(II), Ni(II), Hg(II).

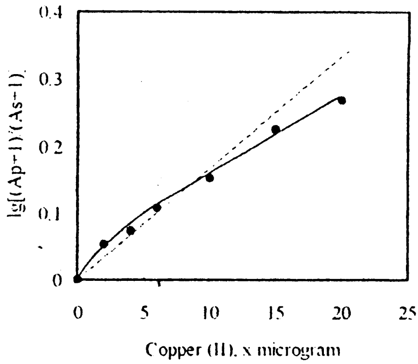

Fig. 5. Calibration graph for the determination of copper

Sample Analyzed: As a test of the method, copper was determined in ore and wastewater. The results were listed in Table 1. The recovery of standard copper (II) was between 90.0 and 105% and the RSD less than 4.7%.

TABLE-1
DETERMINATION OF COPPER IN WATER SAMPLES

Sample	Added	Found	Recovery (%)
Wastewater, mg/L	0	0.214	
		0.203	
		0.221	
		0.199	
		0.205	
		0.195	
		mean. 0.206 ± 0.015	
	0.200	0.419	106.0
		0.403	98.5
		0.421	107
ore, mg/g	0	19.1	
		17.4	
		19.7	
		mean. 18.7 ± 1.3	
	20	38.8	100.0
		38.1	97.0
		37.2	92.5

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