

APPLICATION OF COPPER(II) CATALYSIS OF THE OXIDATION OF 2-HYDRAZINO PYRIDINE BY HYDROGEN PEROXIDE: A KINETIC METHOD OF ANALYSIS

F.A. Sunday Fabiyi^{1*}, George O. Adediran¹ and M. Adegboyega Olatunji²

¹Department of Chemistry, Faculty of Science, University of Ilorin, Kwara State, Nigeria

²Department of Chemistry, School of Science, Federal University of Technology, Minna,
Niger State, Nigeria

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ABSTRACT. A sensitive kinetic method of analysis for the determination of trace amounts of Cu^{2+} ion has been developed. The method is based on the catalytic effect of Cu^{2+} ion on the oxidation of 2-hydrazino pyridine. The oxidation product coupled with *m*-phenylenediamine formed a yellow azo dye. The reaction was followed spectrophotometrically at $\lambda_{\text{max}} = 454 \text{ nm}$ and at a fixed temperature of $35 \text{ }^\circ\text{C}$. A fixed time of 11 min was chosen for the quantitative determination of copper(II). Among the ions tested for interference, only Mn^{2+} and Fe^{2+} ions interfered seriously when present in excess of 10 and $8 \mu\text{g mL}^{-1}$, respectively. The method was applied to the determination of copper in some carbonated drinks marketed in Nigeria. The results compared satisfactorily with that of atomic absorption spectrometry. The method is sensitive to Cu^{2+} ion determination in the concentration range of $0.05\text{--}1.5 \mu\text{g mL}^{-1}$.

KEY WORDS: Kinetic method of copper(II) determination, Copper(II) catalysis, Oxidation of 2-hydrazino pyridine, Azo dye of *m*-phenylenediamine, Spectrophotometry, Copper in carbonated drinks

INTRODUCTION

Kinetic methods of analysis are based on monitoring the rate of change in a reactant (or product) concentration [1-4]. In catalytically based methods, the main reaction in which the monitored species participates, written as a stoichiometric and over all reaction, is termed the indicator reaction [3, 5, 6]. The connecting kinetic equations for this type of determination have been established [2, 5, 7, 8]. Similarly, the phenomenon of catalysis has been widely used for kinetic determination of trace amounts of various metal and non-metal ions [9-14].

The oxidations of several organic compounds with hydrogen peroxide in the presence of various catalytic ions have been widely employed for the determination of the individual catalyst [14, 15].

In this paper, a kinetic spectrophotometric method for the ultra micro determination of copper(II) is described based on its catalytic effect on the oxidation of 2-hydrazino pyridine by hydrogen peroxide. The reaction required several hours to go to completion in the absence of the catalyst. However, the reaction took few minutes in the presence of trace amount of copper(II). The reaction product coupled with *m*-phenylenediamine formed a yellow azo dye. The reaction was followed spectrophotometrically. By adjustment of the concentration of the reactants and under controlled experimental conditions (*i.e.* pH and temperature), the method was used for the determination of copper at ultra micro levels.

*Corresponding author.

EXPERIMENTAL

Reagents and solutions. All chemicals used were analytical reagent grade and were used without further purification. Water was purified by distilling (twice) the de-ionized water through an all-glass borosilicate-glass still. Hydrogen peroxide (0.0046 M) solutions were prepared from 30% hydrogen peroxide and standardized daily with 0.0062 M potassium permanganate solution [10]. 2-Hydrazino pyridine solution (0.0036 M) was prepared by dissolving 0.067 g of 2-hydrazino pyridine in 100.00 mL of 5.50×10^{-4} M sulphuric acid solution. *m*-Phenylenediamine solution (0.0065 M) was prepared by dissolving 0.700 g of *m*-phenylenediamine in 1000 mL of distilled deionized water. Acetic acid-sodium acetate buffer solution of pH 5.50 was prepared by adding 8.00 mL of 3.00×10^{-2} M of acetic acid solution to 12.00 mL of 5.00×10^{-2} M of sodium acetate solution. Copper(II) stock solution was prepared by dissolving accurately weighed 1.00 g of anhydrous copper(II) chloride in 50.00 mL of 6.2×10^{-3} M of nitric acid. Ten standard solutions of copper(II) in the range 1.00×10^{-3} - $2.00 \mu\text{g mL}^{-1}$ were prepared from the stock solution using distilled deionized water. For the interference studies, all the cations solutions were similarly prepared from the chloride salts and all anions solutions were prepared from either sodium or potassium salts. Solutions of these salts were prepared in 0.001 M HCl. The concentrations of the cations and anions solutions were in the range of 5.00×10^{-3} - $2.00 \mu\text{g mL}^{-1}$.

Apparatus. All absorbance measurements were taken on an UV-visible spectrophotometer (Jenway 6105 Model) with 10 mm glass cell. The cell compartment of the spectrophotometer was thermostatted with circulating water. The pH of solution was measured with a Crison micro pH meter (Model 200).

Procedure. All the reagent solutions used were submerged in a thermostatted controlled water bath set at a temperature of 35 ± 0.10 °C for at least 30 min before use.

The reaction mixture consisted of 10.00 mL of 0.0046 M H_2O_2 , 8.00 mL of 0.0036 M 2-hydrazino pyridine, 3.5 mL acetic acid-sodium acetate buffer solution of pH 5.50, 15.00 mL of 0.0065 M *m*-phenylenediamine, and 10.00 mL of copper(II) solution. The reactant solutions were added in the order of 2-hydrazino pyridine, buffer solution, *m*-phenylenediamine, and hydrogen peroxide in each run. Appropriate amount of distilled deionized water was added to bring the final volume to 50.00 mL. The mixing was done outside the cells compartment within a few seconds and the reaction solution was immediately transferred to a 10 mm cell and placed in the cell compartments of the spectrophotometer with thermostattedly controlled temperature cell compartment set at 35 ± 0.1 °C. The spectrophotometer chart recorder was set on immediately after adding the H_2O_2 solution. The changes in absorbance of the yellow azo dye formed with time were recorded. All the absorbance measurements were made at wavelength of 454 nm. Fixed time of 11 min was chosen for the quantitative determination of copper(II). To prepare the calibration curves, several runs were made using different concentrations of copper(II). Blank was obtained without copper(II) in the reaction mixture. The effects of reactants concentrations, temperature, and pH on the reaction were studied using similar procedure.

RESULTS AND DISCUSSION

The results obtained from absorbance measurement of the reaction mixtures containing 0.00-1.50 $\mu\text{g mL}^{-1}$ copper(II) at different times are given in Table 1. The reaction was found to be time dependent. The absorbances of the reaction product increased with increase in time of reaction for all the different concentrations of Cu^{2+} in the range of 0.00-1.50 $\mu\text{g mL}^{-1}$ of Cu^{2+} for about 25

min at lower concentrations of Cu^{2+} ion and for about 15 min at higher concentrations of Cu^{2+} ion. A convenient time of 11 min, which fall within the period of absorbance-time linear relationship of the reaction, was chosen for the quantitative determination of copper(II).

Table 1. Absorbance of the product of uncatalysed and catalysed reaction using different concentrations of copper(II) at different times.

Time (min)	Absorbance							
	A	b	c	d	e	f	g	h
0.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
4.0	0.006	0.012	0.041	0.086	0.136	0.134	0.192	0.226
8.0	0.010	0.032	0.086	0.173	0.245	0.296	0.385	0.446
11.0	0.022	0.040	0.132	0.246	0.336	0.424	0.549	0.636
15.0	0.031	0.051	0.164	0.326	0.446	0.576	0.690	0.741
18.0	0.042	0.069	0.204	0.386	0.576	0.714	0.759	0.788
21.0	0.049	0.082	0.244	0.480	0.662	0.782	0.764	0.821
25.0	0.061	0.098	0.276	0.576	0.690	0.793	0.791	0.861

The absorbances of the blank reaction have been subtracted from the respective absorbances reading. Each data is an average of five replicate experimental readings. Concentration ($\mu\text{g mL}^{-1} \times 10^{-3}$) of copper(II): a = 0.00, b = 50.00, c = 100.00, d = 250.00, e = 500.00, f = 1000.00, g = 1250.00, h = 1500.00.

The effect of pH on the reaction is shown in Figure 1. The reaction is found to be critically pH dependent. This is typical of H_2O_2 reaction in acidic medium [17]. Therefore the pH was kept constant to better than ± 0.1 pH unit. The condition was obtained by adding 3.50 mL of the acetic acid-sodium acetate buffer solution of pH = 5.50. The optimum pH was found to be in the range 6.6-6.7.

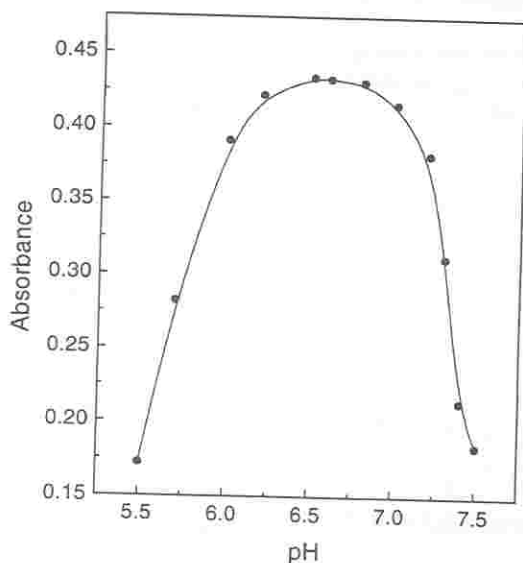


Figure 1. Effect of pH on the reaction ($[\text{H}_2\text{O}_2] = 0.0046 \text{ M}$, $[\text{2-hydrazino pyridine}] = 0.0036 \text{ M}$, $[\text{Cu}^{2+}] = 1.0 \mu\text{g mL}^{-1}$, time = 11 min).

The effects of the reagents concentrations on the system were studied in the concentration range of 0.0004-0.0075 M hydrogen peroxide and 0.001-0.050 M 2-hydrazino pyridine solutions, respectively. Increase in the concentrations of both reactants caused the reaction rates, the sensitivities, and the blanks to increase. These effects are shown in Figures 2 and 3. Both Figures 2 and 3 show that the curves become flat at higher concentrations. This implied that the reaction rates are less affected at higher concentrations of both H_2O_2 and 2-hydrazino pyridine. The concentrations of the reactants ($[\text{H}_2\text{O}_2] = 0.0046 \text{ M}$ and $[2\text{-hydrazino pyridine}] = 0.0036 \text{ M}$) chosen for the determination of copper(II) were a compromise to ensure small blanks.

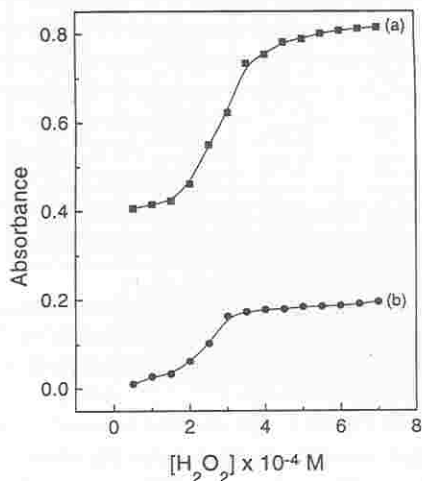


Figure 2. Effect of concentration of H_2O_2 ($[2\text{-hydrazino pyridine}] = 0.0065 \text{ M}$, time = 11 min, pH = 6.60; (a) $[\text{Cu}^{2+}] = 1 \mu\text{g mL}^{-1}$, (b) $[\text{Cu}^{2+}] = 0.00 \mu\text{g mL}^{-1}$).

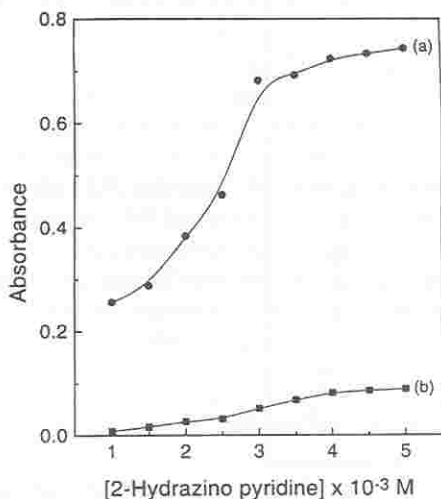


Figure 3. Effect of concentration of 2-hydrazino pyridine ($[\text{H}_2\text{O}_2] = 0.0046 \text{ M}$, time = 11 min, pH = 6.60; (a) $[\text{Cu}^{2+}] = 1 \mu\text{g mL}^{-1}$, (b) $[\text{Cu}^{2+}] = 0.00 \mu\text{g mL}^{-1}$).

The effect of temperature on the reaction was studied in the range 27-40 °C. Linear calibration curves were obtained in the temperature range 30-37 °C. Consequently, temperature of 35 ± 0.10 °C was chosen for all the experiments carried out. To investigate the effects of various ions that might interfere with the determination of copper(II), the measurement step was modified as follows: 0.250 mL of solution containing different concentrations of the ion being examined were added to the reaction solution containing 1.00 µg mL⁻¹ of copper(II). Among the ions tested (Table 2) Fe²⁺ and Mn²⁺ were found to interfere seriously at concentrations over 10.00 and 8.00 µg mL⁻¹, respectively.

Table 2. Effects of diverse ions in the determination of 1.00 µg mL⁻¹ of copper(II).

Ion	Amount permitted (µg mL ⁻¹)	Ion	Amount permitted (µg mL ⁻¹)
Cr ³⁺	30.00	Mn ²⁺	8.00
Co ²⁺	20.00	Mg ²⁺	110.00
Zn ²⁺	80.00	F ⁻	50.00
Fe ²⁺	10.00	I ⁻	100.00
Hg ²⁺	100.00	Cl ⁻	100.00
V ³⁺	90.00	Br ⁻	150.00
Al ³⁺	50.00	NO ₃ ⁻	110.00
Pb ²⁺	40.00	PO ₄ ³⁻	100.00

By using optimum conditions as indicated above, the calibration graphs show a linear range between 5.00 x 10⁻² and 1.50 µg mL⁻¹ Cu²⁺ ion (regression equation: $y = (0.116 \pm 0.043) + (0.46 \pm 0.01) x$, where y = absorbance, x = concentration of Cu²⁺ in µg mL⁻¹, correlation coefficient = 0.9998; standard error of estimate = 0.011). The reaction becomes too fast and non-linear with concentrations of Cu²⁺ ion higher than 1.5 µg mL⁻¹. From regression treatment of the data an average sensitivity of 2.52 x 10⁻³ of the absorbance per 1 µg mL⁻¹ of Cu²⁺ and a limit of detection of 5.00 x 10⁻³ µg mL⁻¹ (based on three times the standard deviation of intercept readings) were calculated from 5 replicates at each concentration. Relative standard deviations (based on five replicates) were about 2%. The calibration graph is shown in Figure 4. The method was applied to the determinations of Cu²⁺ in soft drinks, which are known to contain trace ions. The results obtained (Table 3) compared satisfactorily with that of atomic absorption spectrometry (A.A.S.).

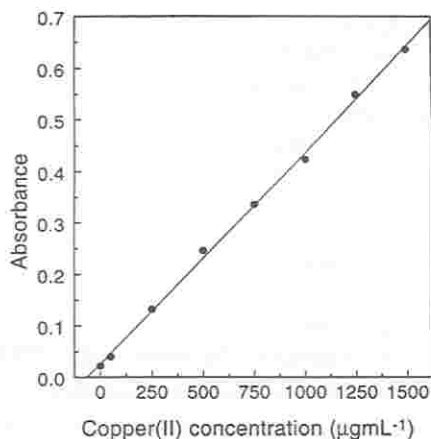


Figure 4. Calibration graph for Cu²⁺ determination (time = 11 min).

Table 3. Copper determination in soft drink using kinetic method and atomic absorption spectrometry.

Brand of soft drink	Concentration of copper(II) ($\mu\text{g mL}^{-1} \times 10^{-2}$)		
	Kinetic method	A.A.S.	Standard deviation
Coca-cola	92.00	90.00	0.12
Fanta (orange)	80.00	81.00	0.04
Fanta (tonic water)	62.00	60.00	0.03
Pepsi-cola	161.00	160.00	0.04
Mirinda	69.00	70.00	0.05
7Up	180.00	179.00	0.03
Fanta (club soda)	208.00	210.00	0.14
Krest (bitter lemon)	58.00	60.00	0.02
Sprite	79.00	80.00	0.13
Dr. Pepper	121.00	120.00	0.03
Fanta (ginger-ale)	62.00	60.00	0.04

CONCLUSION

A method for the determination of trace amounts of copper(II) on the basis of its catalysing H_2O_2 -2-hydrazino pyridine reaction has been developed. Although the application reported here deals with the catalytic determination of copper(II) in soft drinks, the scope of the method is intended to be more general. The basic procedure and general considerations for the determination of copper are given so that the method can be adapted to many specific cases, e.g. natural waters, urine, tissues, bones, blood, etc.

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