COPPER(II) DETERMINATION BY MEANS OF A THERMOMETRIC METHOD BASED ON ITS CATALYTIC EFFECT ON THE HYDRAZINE–HYDROGEN PEROXIDE REACTION

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ABSTRACT

A new catalytic–thermometric method for Cu(II) determination at ppb levels has been established based on the hydrazine–hydrogen peroxide redox reaction. The reaction rate is obtained from the temperature–time curve and shows two linear response zones, between 15–200 ppb and 0.1–0.9 ppm, with a relative standard deviation of 2.0% and 2.2%, respectively. Only 20 ppm of Pb(II) and Fe(III), 1 ppm of Mn(II) and 5 ppb of Co(II) interfere. Interferences of Pb(II) and Fe(III) can be eliminated by the use of maskings. The proposed method can be applied to determine Cu(II) in several samples. In the present paper, this method has been applied to determine Cu(II) in wine.

1. INTRODUCTION

A great many reactions, mainly redox, are catalysed by metallic traces. Hydrogen peroxide is one of the most widely used oxidants. The catalytic effect of Cu(II) on the hydrazine–hydrogen peroxide system [1] is similar to the Cu(II)-2,2'-bipyridyl complex [2,3]. From hydrogen peroxide decomposition studies, one can deduce that these catalysts are only active if the copper coordination sphere is not saturated by the ligand [4]. Although it has been demonstrated that ternary complexes (copper–peroxo–ligand) are involved, other studies showed that this reaction is also catalysed by hydrated copper ion [3]. Nevertheless, in this case the catalytic action is limited within the pH range where copper remains unprecipitated.

The main overall reactions that take place are:

$$2H_2O_2 \rightarrow O_2 + 2H_2O$$
$$2H_2O_2 + NH_2NH_2 \rightarrow N_2 + 4H_2O$$

The Cu(II) catalytic effect was used by Weisz and Pantel [1] to detect the final point in its determination with EDTA.

In the present work we have studied the hydrazine oxidation by hydrogen peroxide, monitoring the reaction by means of thermometric techniques.

EXPERIMENTAL

Apparatus

The thermometric system has been described elsewhere [5,6], and consisted by a nylon adiabatic cell, a conventional stirrer, a quick response thermistor (of the thermometric type, with a nominal value of 100 kΩ at 25°C), a syringe for rapid addition of the reagent into the thermometric cell, a stabilized voltage source and a register.

Reagents

Solutions were prepared of H_2O_2 15% (w/v) and N_2H_5OH 0.4794 M. A Cu(II) stock solution was prepared of 1000 ppm; more dilute solutions were prepared daily from this stock solution.

Procedure

The normal procedure, used in previous works [7,8], could not be followed in this case, as there was a positive reaction between hydrazine and hydrogen peroxide, even in the absence of the catalyst. Thus, the mixture of hydrazine and copper was placed in the thermometric cell and the hydrogen peroxide was added by means of a syringe once the system had been thermometrically stabilized.

RESULTS AND DISCUSSION

Optimization of variables

The response variation, according to the hydrazine and hydrogen peroxide quantities present in the solution, was first studied in absence of catalyst. In order to determine the influence of the hydrogen peroxide, different quantities of the 15% solution were added by means of a syringe into the cell containing 60 ml of hydrazine (0.0799 M). The $tg\alpha$ values obtained, deduced from the line base and the exothermic reaction curve, are represented in Fig. 1. Similarly, the influence of the hydrazine concentration was studied by introducing different quantities of this compound and then
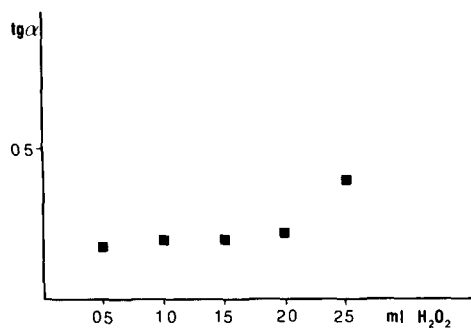
Fig. 1. Influence of the hydrogen peroxide concentration in the kinetic–thermometric reaction. $S = 50$ mV; $V_0 = 60$ ml; $|N_2H_5OH| = 0.0799$ M.
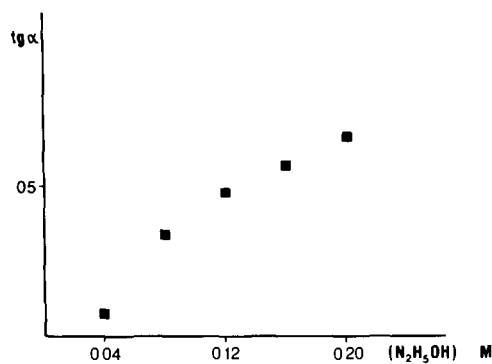

Fig. 2. Influence of the hydrazine concentration in the kinetic–thermometric reaction. $S = 50$ mV; $V_0 = 60$ ml; 2 ml of hydrogen peroxide 15% (w/v) were injected.
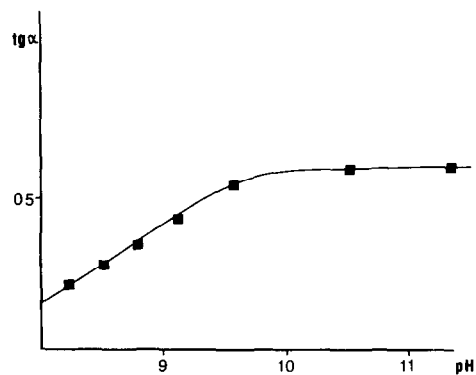

Fig. 3. Effect of pH on the initial rate. $S = 50$ mV; $V_0 = 60$ ml; $|N_2H_5OH| = 0.0799$ M; $|Cu| = 33$ ppb; 2 ml H_2O_2 were injected.

adding water to a final volume of 60 ml. Hydrogen peroxide (2 ml) was injected once the system was thermometrically stabilized (Fig. 2).

The influence of the pH value on the reaction was also studied. Hydrazine (60 ml, 0.0799 M) and Cu(II) solution (0.2 ml, 10 ppm) were placed in the adiabatic cell and the pH value was adjusted with HCl (0.1 M) or NaOH (0.1 M). When the solution was thermometrically stabilized, 2 ml of hydrogen peroxide were injected. The results are represented in Fig. 3.

Calibration curve

In order to determine the linear response zone within the calibration curve, 2 ml of hydrogen peroxide were injected into a 60 ml hydrazine 0.0799 M solution which contained different quantities of copper at pH 9.5. Figure 4 is the thermometric curve obtained by injecting 2 ml of hydrogen peroxide into 60 ml of hydrazine 0.0799 M with 33 ppb of copper solution. Two different linear zones can be appreciated, which agree with the results obtained by other techniques described in the literature.

The first interval of the thermometric curve was studied with a register sensitivity of 50 mV. The relative standard deviation for 7 measurements was 2.0%, with a good linearity between 15–200 ppb of copper (Fig. 5). The
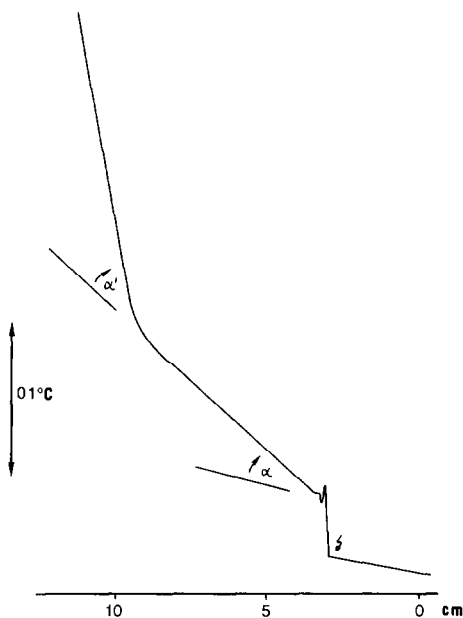

Fig. 4. Thermometric curve of the hydrazine–hydrogen peroxide reaction catalysed by Cu(II). $S = 50$ mV; $V_0 = 60$ ml; $|N_2H_5OH| = 0.0799$ M; $|Cu(II)| = 33$ ppb; 2 ml of H_2O_2 15%; ($\leadsto$) addition.
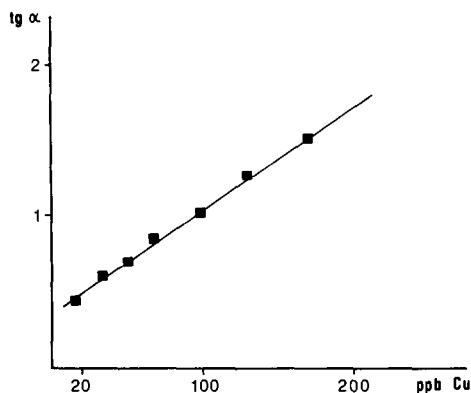
Fig. 5. Response linearity of the first zone of the thermometric curve. $S = 50$ mV; $V_0 = 60$ ml; $|N_2H_5OH| = 0.0799$ M; 2 ml of H_2O_2 15%.

second interval, a lot more exothermic than the first, was studied with a register sensitivity of 0.2 V and gave a relative standard deviation of 2.2% with a linear interval between 0.1–0.9 ppm (Fig. 6). Concentrations greater than 1 ppm showed non-linear thermometric curves (Fig. 7).

Interferences

The effect of several potential interferences was studied using 100 ppb Cu(II) solutions: Hg(II), Ag(I), Cd(II), Bi(III), As(III), Sb(III), Sn(IV), Ni(II), Al(III), Zn(II), Ca(II), Ba(II), K(I), Mg(II), Mo(VI) and Ti(IV) did
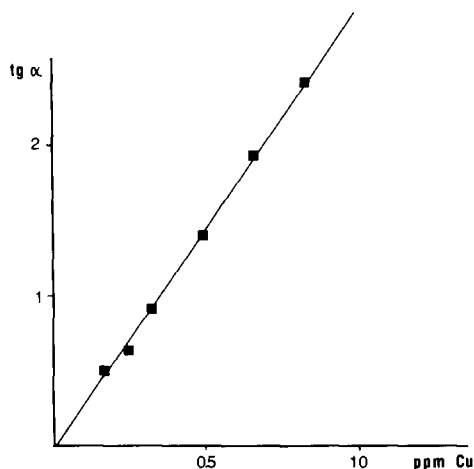

Fig. 6. Response linearity of the second zone of the thermometric curve. $S = 0.2$ V; $V_0 = 60$ ml; $|N_2H_5OH| = 0.0799$ M; 2 ml of H_2O_2 15%.
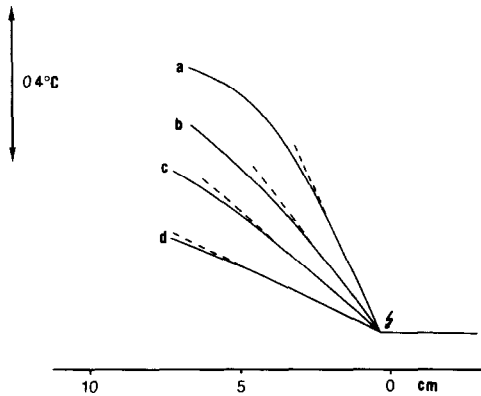
Fig. 7. Effect of the copper concentration on the shape of the second interval of the thermometric curve. $S = 0.2$ V; $V_0 = 60$ ml; $|N_2H_5OH| = 0.0799$ M; 2 ml of H_2O_2 15%; ($\rightarrow$) addition. (a) 0.83 ppm; (b) 0.50 ppm; (c) 0.33 ppm; (d) 0.17 ppm.

not interfere at 2000 ppm levels, maximum tested quantities. Only 20 ppm of Pb(II) and Fe(III), 1 ppm of Mn(II) and 5 ppb of Co(II) interfere. We achieved elimination of Pb(II) and Fe(III) interferences by means of Cl^- (NaCl) and F^- (NaF) addition.

Application

To test the applicability of the proposed method, it was applied to the determination of Cu(II) in wine. Cu(II) was determined after mineralization of the sample. A previous destruction of organic matter is required because it interferes in the determination. The sample was evaporated to dryness, after addition of hydrogen peroxide and nitric acid, on a hot plate. The cooled residue was dissolved in a minimum of 1M hydrochloric acid and diluted with water. The value obtained was 1.7 ppm of Cu(II), close to the result obtained by atomic absorption spectrometry, 1.4 ppm.

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