REACTION-RATE DETERMINATION OF Cu(II) BY USE OF A VERY SIMPLE MONITORED THERMOMETRIC TECHNIQUE BASED ON THE ACTION OF THIS CATION ON THE DECOMPOSITION OF HYDROGEN PEROXIDE

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ABSTRACT

A very simple and sensitive kinetic monitored thermometric technique is used for Cu(II) determination in the range 0.02–0.25 ppm. The method is based on the catalytic effect of copper(II) on the decomposition of hydrogen peroxide. The reaction is followed by measuring the rate of increase of temperature. The method suffers little interference.

INTRODUCTION

The measurement of a temperature (heat) change has several advantages over spectrophotometric or spectrofluorimetric procedures of assay (in general terms, the optical methods). The requirement of optically transparent or clear solutions need not be met; the change in temperature of intensely coloured or turbid solutions can be determined. The requirement that the component to be determined has accessible absorption or fluorescence bands, a sine qua non in any spectral method, is of no relevance for calorimetric measurements. Neither does this type of measurement require an interchange of electrons (redox-reaction), which is a necessary condition to be able to apply any electrical method. Thermochemical detection methods can be applied to any reaction which generates or absorbs heat. Since even very low concentrations of catalyst can greatly increase reaction rates, a relatively large amount of heat can be produced by the presence of very low concentrations of catalyst. Thus, catalyst determinations should have improved detection limits in comparison to stoichiometrically limited systems.

In the present paper a kinetic procedure for copper determination is described by monitoring the increase in temperature as a consequence of the catalytic action of this cation on the decomposition of hydrogen peroxide.

The decomposition of hydrogen peroxide

$$2 H_2O_2 \rightarrow 2 H_2O + O_2$$
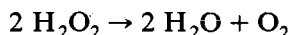
in basic medium is very sensitive to the presence of small concentrations of catalysts such as copper, iron, manganese, palladium, etc. consequently, this reaction was applied to the determination of these ions [1]. The reaction rate was followed either by a measure of the oxygen evolved or by periodic analysis of the solution for its percentage of hydrogen peroxide.

Only two previous kinetic thermometric reaction-rate determinations of copper(II) have been reported; one is based on its catalytic action on the aerial oxidation of 2,2'-dipyridylketone hydrazone [2], and the other on its catalytic action on the aerial oxidation of ascorbic acid [3].

EXPERIMENTAL

Reagents and solutions

Stock solutions include an aqueous solution of hydrogen peroxide 0.1 M prepared and renewed daily, and a copper(II) nitrate solution containing 0.9730 g Cu l^{-1} standardized iodimetrically.

Apparatus and measurement conditions

The temperature-monitoring system consisted of a thermistor miniature type thermometer of rapid response, a Wheatstone bridge and a recorder (Goerz, type Servogor RE 511). The circuit diagram of the thermistor and recorder coupling is shown in Fig. 1. The thermistor was sealed in glass and had a resistance of 100 kΩ at 25 °C. The EMF for the Wheatstone bridge was supplied from a 7.85 V stabilized source. At the sensitivity setting, the thermistor bridge yielded a temperature response of 0.0165 °C mV^{-1} and the full-scale deflection on the recorder was 5 mV (20 cm). This temperature monitoring system is a part of a thermometric titrator which was built according to the design of Lumbiarres et al. [4]. An adiabatic cell (Fig. 1) was also used. The solution in the cell was stirred with a magnetic stirrer.

Procedure for the determination of copper(II)

Two ml of 0.1 M hydrogen peroxide and 5 ml of 0.25 M sodium hydroxide were placed in the cell compartment and enough deionized water was added for a final volume of 25 ml. The recorder was switched on. The chart speed was 3 cm min^{-1}. When the temperature–time curve was horizontal, the necessary volume of cation to ensure a final concentration of copper of between 0.02 and 0.25 ppm were added. From the curve obtained, the rate
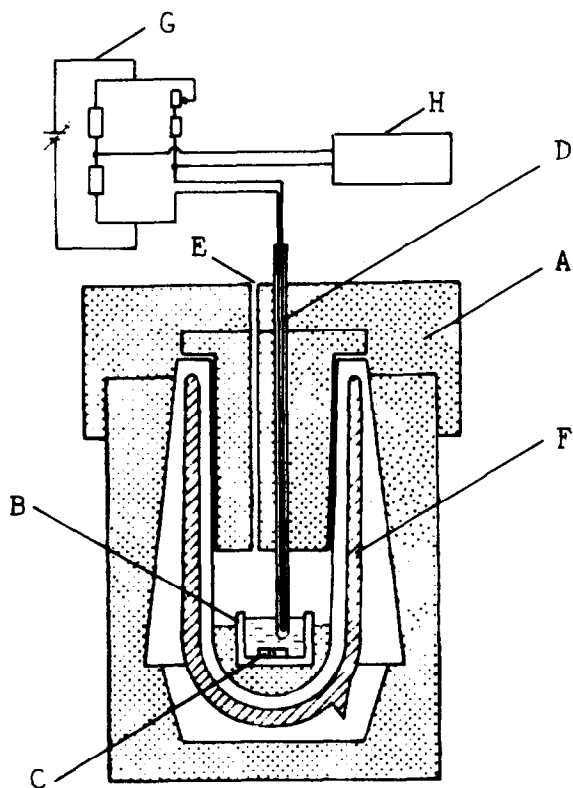
Fig. 1. Diagram of circuitry and apparatus used in reaction-rate thermometric analysis. A, polystyrene insulator; B, plastic beaker; C, magnetic stirrer; D, thermistor; E, pipette's entrance; F, Dewar flask; G, Wheatstone bridge; H. recorder.

of reaction was calculated by the initial rate (tangent) method. All solutions were previously thermostatted at 20°C.

RESULTS AND DISCUSSION

Examples of the temperature–time curves for determination of copper(II) are shown in Fig. 2. The slope of the curve should correspond to the temperature change due to the catalytic reaction. To obtain rapidly stabilized measures (horizontal temperature–time curves) before the addition of the cation, all solutions must be thermostatted at the same temperature and this must coincide with the room temperature, therefore, it is convenient that this is kept constant. When at first a great cooling is produced (great negative slope in the temperature–time curve) due to the heat transmission from the solution to the inner part of the calorimeter, in order to obtain a quick stabilization of the system before performing measurements, it is recommended that the beaker containing the solution is cooled, or the inner part of
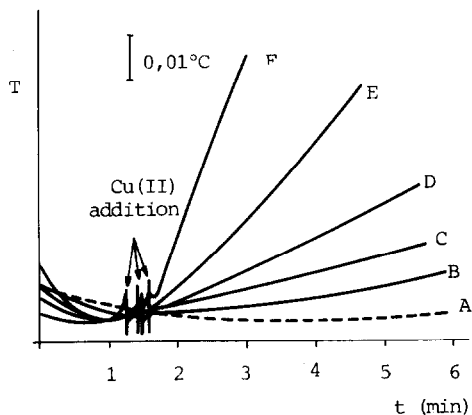
Fig. 2. Temperature–time curves for various copper concentrations (ppm): (B) 0.02; (C) 0.1; (D) 0.15; (E) 0.2; (F) 0.25; (A) reagent blank. The recommended procedure was used.

the calorimeter is heated. If, on the other hand, a heating is produced initially (positive slope in the temperature–time curve) due to heat transmission from the inner walls of the calorimeter to the solution, it is recommended that its interior is cooled or the solution is heated appropriately.

A minimal background is attained in the temperature–time curves with an adequate agitation. Therefore, the precise control of this variable is very important.

Effect of the reaction conditions

For the purpose of finding the optimum conditions for the determination of Cu(II), the influence of sodium hydroxide and hydrogen peroxide concentrations on the reaction rate have been studied. To optimize the concentration of each variable, its initial concentration was varied while the
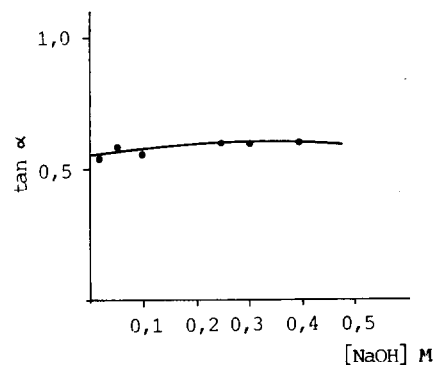

Fig. 3. Effect of concentration of sodium hydroxide on the initial rate: $[H_2O_2] = 4 \times 10^{-2}$ M, $[Cu(II)] = 0.2$ ppm.
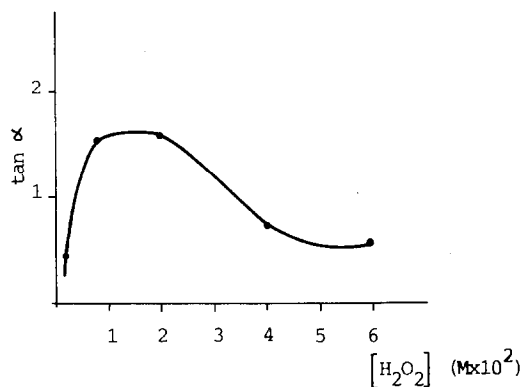
Fig. 4. Effect of concentration of hydrogen peroxide on the initial rate: $[NaOH] = 5 \times 10^{-2}$ M, $[Cu(II)] = 0.2$ ppm.

concentrations of the other components were kept constant, and the initial reaction rate was measured for each concentration (Figs. 3 and 4). The optimum concentrations are those for which the initial rate is maximum and the relative standard deviation of such measurements is as small as possible. This will happen at concentrations where the order of reaction with respect to the variable is as near zero as possible, under which conditions small variations in the concentration of the variable will not affect the initial reaction rate. For this reason a sodium hydroxide concentration of 5×10^{-2} M and a hydrogen peroxide concentration of 8×10^{-3} M are considered to be optimum.

Under these optimum conditions, there was a linear relationship between the logarithm of the initial reaction rate and the logarithm of the copper concentration in the ranges 0.02–0.10 and 0.10–0.25 ppm (Fig. 5) in the final solution.
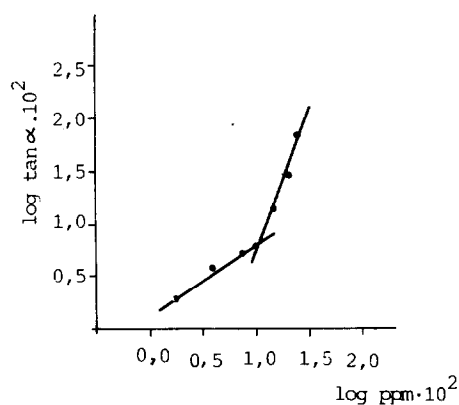

Fig. 5. Calibration graphs for Cu(II), using the recommended procedure.

TABLE 1

Concentration of foreign ions tolerated (error $\leqslant 1.4\%$) for 0.2 ppm copper(II)

Ion added	Amount tolerated (ppm)
Mg(II), Ca(II), Ba(II), Sr(II), Mn(II), Hg(II), Zn(II), Al(III), Pb(II), UO_2^{2+}, Mo(VI), V(V), Cl^-, NO_3^-, SO_4^{2-}	20 [a]
Au(III), Fe(III), Bi(III)	2
Cd(II), Cr(III), Co(II)	0.2
Ni(II)	0.02

[a] Largest amount examined.

Characteristics of the analytical method

The temperature–time curves were recorded for different amounts of Cu(II) (Fig. 2) and for the optimum sodium hydroxide and hydrogen peroxide concentrations. Owing to the shape of these curves, the tangent method was the only one applied for preparing the calibration graph (Fig. 5). The plot was logarithmic because the order of reaction with respect to the cation is not an integer. The relative standard deviation was 7.1% ($n = 11$, $\alpha = 0.05$) for the first interval (0.02–0.1 ppm) and 1.4% ($n = 11$, $\alpha = 0.05$) for the second (0.10–0.25 ppm).

The selectivity of the method has been assayed for studying the effects of foreign ions on the reaction rate under the recommended conditions. The results are shown in Table 1. As can be seen, the method suffers very little interference.

CONCLUSION

The instrumentation used to perform copper determinations proposed in this paper consists of two fundamental parts: the electronic circuit and the cell compartment where the measurements are performed. The electronic part is formed by a stabilized source and a Wheatstone bridge. The temperature-sensitive component is a thermistor which forms part of the Wheatstone bridge and its response is transmitted to a recorder which also forms part of the mentioned bridge. The components that form the electronic part are therefore of common and usual use and consequently easily obtainable. The cell compartment, as a fundamental requirement, allows the measurements to be performed in adiabatic conditions. This can be obtained in different ways with more or less the same standard of precision and with systems varying greatly in complexity and nature, which range from methods surrounding the recipient by a polystyrene insulator to methods using adiabatic

calorimeters equipped with sophisticated electronic circuits to avoid inter-changes of heat. Very simple cells have been reported in the literature [2,3,5], however, in spite of this, keeping in mind a series of precautions and methodology already mentioned, excellent results are obtained with respect to sensitivity. Nevertheless, it is obvious that these results can still be notably improved by using better cells, that would also avoid having to consider certain precautions (e.g., keeping the room of measurement, the solutions and reagents at the same constant temperature). Systems which have a notable background reaction should not be used. Great dilution heats causing too long stabilizing times, i.e. when using hydroalcoholic solutions, should be avoided.

As a consequence of the simplicity and versatility of the equipment used, one of the first advantages of this technique is its easy adaptation to automatized processes.

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