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Cu(II) TRACE DETERMINATION BY MEANS OF A CATALYTIC THERMOMETRIC METHOD BASED ON THE HYDROXYLAMINE–HYDROGEN PEROXIDE REACTION

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ABSTRACT

A new thermometric method for Cu(II) determination at ppb levels has been developed, based on its catalytic effect on the hydroxylamine–hydrogen peroxide reaction.

This method allows Cu(II) determination in the 5–500 ppb range, with a relative standard deviation of 2.3% ($n = 8$, 50 ppb Cu(II)). Fe(III), Co(II) and Ni(II) interfere.

The new method has been applied for copper determination in plasma.

INTRODUCTION

Different papers dealing with the catalytic effect of several metals on the redox reactions between hydrogen peroxide and a number of reducers, such as hydrazine, hydroxylamine, etc., have been published [1–4].

Since the metal levels required to perform the catalysis lie in the ppb range, these kinetic methods are very appropriate for metallic trace determination.

The hydroxylamine reaction with hydrogen peroxide is catalyzed by Cu(II) traces or by some of its own complexes, e.g. Cu(II)–2, 2′-bipyridyl [1]. Likewise, nitrogen is obtained as a main subproduct, nevertheless several authors do not exclude the possible presence of N_2O, NO_2^- and NO_3^- [5–8].

In this reaction, and, in general, others of this type, the catalyst agent is the Cu(II)–ligand–H_2O_2 system when bipyridyl is added as an activator.

Previous kinetic studies on the Cu(II)–ethylenediamine–H_2O_2 reaction, which we are going to consider in this paper, show that the catalysis takes place via a binuclear complex [9], whereas in the case of the phosphate buffer Cu(II)–histamine–H_2O_2 system, the reaction takes place via a monomeric complex [10].

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Although all the cited papers are related with the kinetic–spectrophotometric study of this catalyzed reaction, it can also be applied to determine the Cu(II) concentration.

In previous papers [11–13], we have demonstrated the advantages when using kinetic catalytic–thermometric techniques, i.e. very low determination limits, cheap and simple instrumentation and non-interference of precipitates and coloured compounds.

In the present paper we have optimized the different variables that affect the catalytic action of Cu(II) on the hydroxylamine–hydrogen peroxide reaction in order to establish a new sensitive quantitative method for such determination.

EXPERIMENTAL

Apparatus

The thermometric system has been described elsewhere [11–13] and it consists of a nylon adiabatic cell, a 100 kΩ thermistor (25 °C), a Wheatstone bridge, a conventional stirrer, a stabilized voltage source and a register.

Reagents

All reagents were of analytical grade and prepared with deionized bidistilled water: (1) Standardized solution of 2 M hydroxylamine chlorhydrate. More diluted solutions were prepared daily by mixing the appropriate quantity of the stock solution and a pH = 7 buffer. (2) Standardized solution of hydrogen peroxide 15%. (3) pH 7 buffer solution (NaH_2PO_4–Na_2HPO_4). The sodium salts were purified by recrystallization in water. (4) Standard Cu(II) stock solution (1000 ppm), Titrisol Merck.

Procedure

Place in the thermometric cell, 5 ml of the hydroxylamine 0.4 M solution, 40 ml of the pH = 7 buffer, an appropriate quantity of sample and bidistilled water for a final volume of 60 ml. Once the thermal stability of the cell solution is achieved, add with a syringe 1 ml of hydrogen peroxide 15%.

RESULTS

As in previous papers, we have optimized several variables in order to achieve maximum sensitivity and a wide application range. Thus, not only did we find the maximum hydroxylamine and hydrogen peroxide concentra-

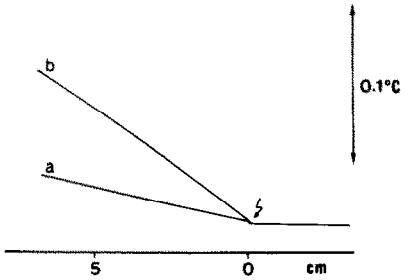

Fig. 1. (a) Thermometric curve of the blank; (b) thermometric curve in presence of 33 ppb of Cu(II): 5 ml hydroxylamine 0.4 M, 40 ml pH = 7 buffer, $V_0 = 60$ ml, $S = 50$ mV (0.02° C cm^{-1}), 1 ml H_2O_2 15% addition.

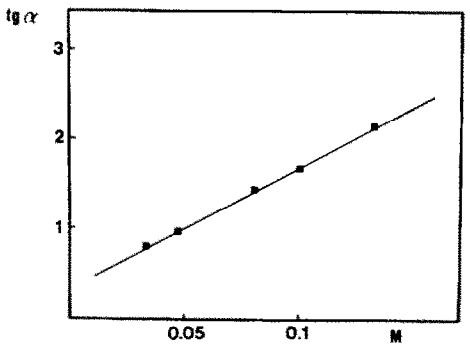

Fig. 2. Concentration effect of hydroxylamine.

TABLE 1

Interval of application for the kinetic thermometric method

S (mV)	Equation (ppb Cu)	r	Interval (ppb)
50	tg $\alpha = 0.1642 + 0.0165C$	0.9998	5–200
200	tg $\alpha = 0.1187 + 0.0032C$	0.9968	50–500

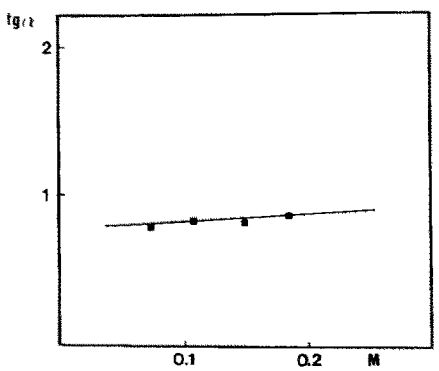

Fig. 3. Influence of the $[H_2O_2]$ on the thermometric cell.

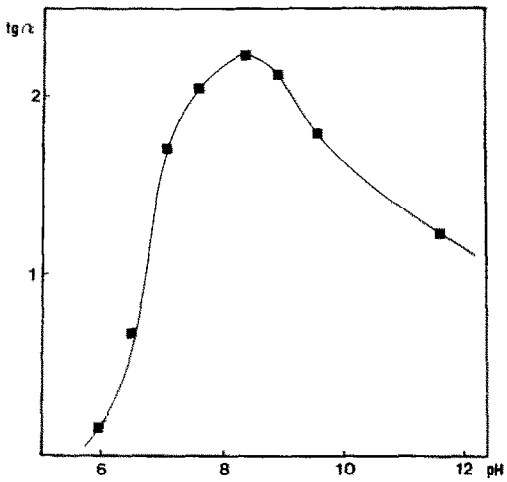

Fig. 4. pH influence on the thermometric curve.

tions allowed for a minimum register signal of the blank (Fig. 1), but the more appropriate reagents addition order.

As can be seen in Fig. 2, there is a good linearity between the tg α value and the hydroxylamine concentration, whereas this relationship is not so clear in the hydrogen peroxide case, Fig. 3.

In the pH study (Fig. 4), there is a clear influence of the protic concentration on the tg α values within the 6–8 pH range. From pH 8–8.5 the signal decrease is probably due to a secondary reaction between the copper and the OH^- ions of the media. Therefore, a 7.5 pH buffer (phosphate) was selected for further work.

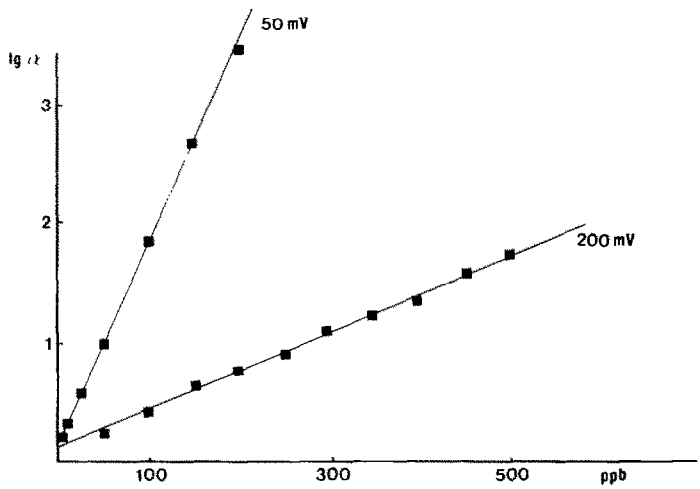

Fig. 5. Calibration curves for two register sensitivities.

The analytical procedure was established, with a 2.3% relative standard deviation for 50 ppb of copper ($n = 8$).

The application ranges are summarized in Table 1 and Fig. 5 for different register sensitivities.

With the aim to increase these sensitivities we added 2, 2′-bipyridyl to the solution, which has already been used as an activator by different researchers [1,14,15] in some catalytic reactions. However, no positive results were obtained since this reagent inhibited the reaction.

Interferences

In order to know the potential analytical interferences in the proposed method, we have applied the described procedure to a solution with 50 ppb of Cu(II) in presence of up to 100 ppm of different metals: Ag(I), Cd(II), Bi(III), As(III), Sb(III), Sn(IV), Ni(II), Al(III), Zn(II), Ca(II), Ba(II), Sr(II), K(I), Mg(II), Mo(VI), Ti(IV), Pb(II), Fe(III), Fe(II), Cu(II) and Mn(II).

Only Fe(III) and Co(II) interfered at the 1 ppm level, and Ni(II) at the 10 ppm level.

Whereas Co(II) presents an additive effect on the Cu(II) catalytic action, Fe(III) and Ni(II) inhibited the reaction, probably due to a complex formation between these cations and hydroxylamine.

It was not possible to avoid the effect of these cations by means of complexants and these interferences could only be removed by ionic exchangers. However, due to the different sensitivity levels of the interferences (ppm levels) in front of Cu(II) (ppb levels) it was not necessary to apply this separating procedure, for most samples.

Applications

The new method has been applied to determine Cu(II) in plasma of adult, male Wistar mice with a weight of 150 g.

Cu(II) concentration control in plasma is important in order to forsee or detect possible illnesses caused by a defect of this metal, which forms part of the structure of various molecules and participates in a great number of reactions, usually of the redox type.

The proposed method can be applied to determine Cu(II) in plasma, since (besides the major metals (Na, K, Ca and Mg)) only Zn(II) and Fe(III) are present in a concentration of 103 ppm. Cu(II) has an average concentration of 0.5–1.5 ppm, although it is usually present between 0.8 and 1.2 ppm [16].

Procedure

The plasma sample has to be previously mineralized in order to remove the organic matter, which would interfere in the determination.

Different quantities of samples (between 0.5 and 3 ml) were treated with 13 M HNO_3 under pressure in a Teflon vessel placed in a sand bath to total mineralization (twelve hours at 120 °C). The sample was then heated to near dryness and diluted with 2 ml of bidistilled water containing a small quantity of 2 M nitric acid.

RESULTS

The plasma samples were analysed by using two independent methods: atomic absorption spectrophotometry (AA) and the proposed thermometric method.

The obtained results were 1.2 ± 0.07 ppm by AA and 1.1 ± 0.1 ppm by thermometry.

CONCLUSION

Thermometry is simple and cheap, and with an appropriate design of the thermometric cell it can be applied to very small quantities of samples, due to the great sensitivity of the method, which is of great importance when biological samples are investigated. The obtained results agree with those of AA.

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