Thermochimica Acta, 117 (1987) 89–95
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

A SENSITIVE KINETIC–THERMOMETRIC METHOD FOR Co(II) DETERMINATION BASED ON THE TIRON–HYDROGEN PEROXIDE REACTION

R.M. MARCÉ, M. CALULL and F. BORRULL *

Departament de Química, Facultat de Química de Tarragona, Universitat de Barcelona, 43005 Tarragona (Spain)

V. CERDÀ

Departament de Química, Facultat de Ciències, Universitat de les Illes Balears, 07071 Palma de Mallorca (Spain)

(Received 1 January 1987)

ABSTRACT

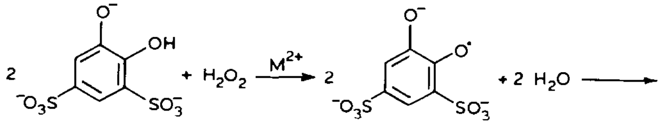
A new kinetic–thermometric method for Co(II) determination at ppb levels has been developed based on its catalytic effect on the tiron–hydrogen peroxide reaction in basic media.

The different reaction rates have been measured by means of the temperature–time curves. The application range lies between 3 and 120 ppb and the r.s.d. is 2.1% for 8 ppb of Co(II). Only Ni(II) ($\geqslant$ 3 ppm) and Mn(II) ($\geqslant$ 80 ppb) interfere.

The proposed method has been applied to determine cyanocobalamine (vitamin B_{12}) in a collyrium.

INTRODUCTION

The tiron (pyrocatechol-3,5-disulfonic acid disodium salt (monohydrate))–hydrogen peroxide reaction is catalyzed by metallic traces in basic media.



Several studies have been carried out to determine different metals, such as Co(II) [1,2], Ni(II) [3] and Mn(II) [4] based on its reaction. More recently

---

* Author for correspondence.

0040-6031/87/$03.50

[5], a spectrophotometric study was performed with the aim of clarifying the kinetic action of Co(II), Mn(II), Ni(II) and Cu(II) using mathematical models.

As thermometry possesses an advantage in that coloured compounds and precipitates do not interfere in the analytical procedures, we have developed a new kinetic–thermometric method for cobalt ultratrace determination and have applied it to samples of practical interest.

EXPERIMENTAL

Apparatus

Kinetic measurements were carried out using a thermometric system described elsewhere [6,7], and comprising an adiabatic nylon cell, a 100 kΩ (25 °C) thermistor, a conventional stirrer, a stable voltage source and a register.

Reagents

All reagents were of analytical grade. Tiron (pyrocatechol-3,5-disulfonic acid disodium salt (monohydrate)) (Merck (art. 1922)) was purified by precipitation from a water/ethanol mixture. Hydrogen peroxide (Panreak) concentration was determined with potassium permanganate. A Co(II) 1000 ppm standard solution (Merck) and a $NaHCO_3$–NaOH buffer solution (pH 10.5) were used. All solutions were prepared using deionized and bidistilled water.

PROCEDURE

10 ml of 0.0978 M solution of tiron, the appropriate volume of sample, 40 ml of buffer (pH 10.5) and the appropriate quantity of bidistilled water to a final volume of 60 ml was placed in the thermometric cell. Once the mixture was thermometrically stabilized 1 ml of hydrogen peroxide (15%) was injected and the thermometric curve was measured.

RESULTS

For this method to be quantitatively applicable for Co(II) determination, a number of experimental conditions must be met. There must be a proportional relationship between the reaction rate and that of the concentration of the catalyst, and the reaction rate without the catalyst must be significantly small.

Several assays were carried out to determine the best reproducibility and precision. Since tiron–hydrogen peroxide mixtures react slowly, even in the absence of catalyst (probably due to the presence of impurities in the reagents), the same procedure used elsewhere [8,9] could not be applied. The best results were obtained by placing the required quantity of tiron solution, the catalyst, the buffer and sufficient bidistilled water to a final volume of 60 ml in the thermometric cell. Once this mixture had thermometrically stabilized, a quantity of hydrogen peroxide was added. Another method, adding the tiron solution to a mixture of hydrogen peroxide, catalyst and buffer was studied. In this case erroneous results were obtained due to the instability of the hydrogen peroxide solutions.

Another study was performed in order to determine maximum concentration with minimum temperature increments of the blanks. The best conditions found for the blank are those stated in the procedure described in the experimental section. As can be seen in Fig. 1, the tangent value of the thermometric curve was modified considerably by a small quantity of the catalyst (8.1 ppb).

To determine the influence of pH, a carbonate solution was used instead of the borate solution recommended by Bognar [1], as borate complexes with the metal and diminishes its catalytic effect [5]. This study of pH was performed by preparing several solutions of 10 ml of 0.0978 M tiron, 0.5 ml of 1 ppm Co(II) and 40 ml of buffer solution with different pH values. All these solutions were diluted to 60 ml with bidistilled water. Once thermometrically stabilized, 1 ml of 15% hydrogen peroxide was added. Results are

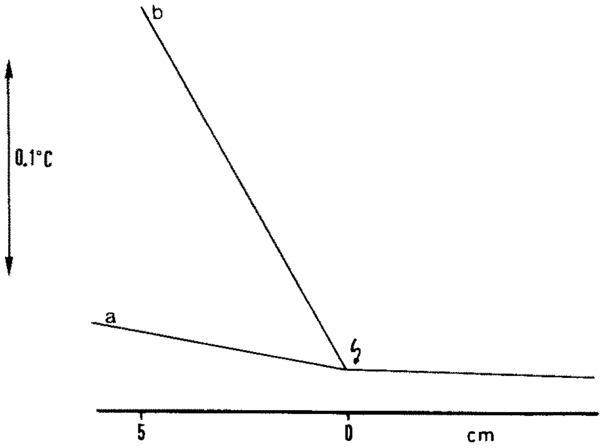


Fig. 1. Thermometric curves: (a) blank (tg $\alpha = 0.17$); (b) 8.1 ppm of Co(II) (tg $\alpha = 1.64$). [Tiron] = 0.0163 M, pH = 9.5, $V_0 = 60$ ml, $S = 50$ mV, $v = 3$ cm min^{-1}, 1 ml H_2O_2 15% injected.

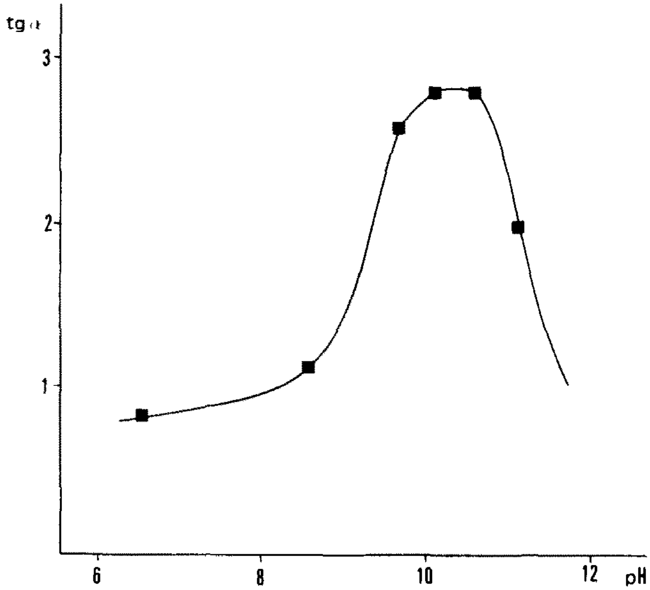


Fig. 2. pH influence on the catalytic reaction. [Tiron] = 0.0163 M, V_0 = 60 ml, S = 50 mV, v = 3 cm min^{-1}, [Co(II)] = 8.1 ppb, 1 ml H_2O_2 15% injected.

given in Fig. 2. Maximum response was obtained in the pH range 10.5–11.0. A pH value of 10.5 was selected for further work, since with this the blank values are practically unmodified.

With the aim of determining the reproducibility of this method, the

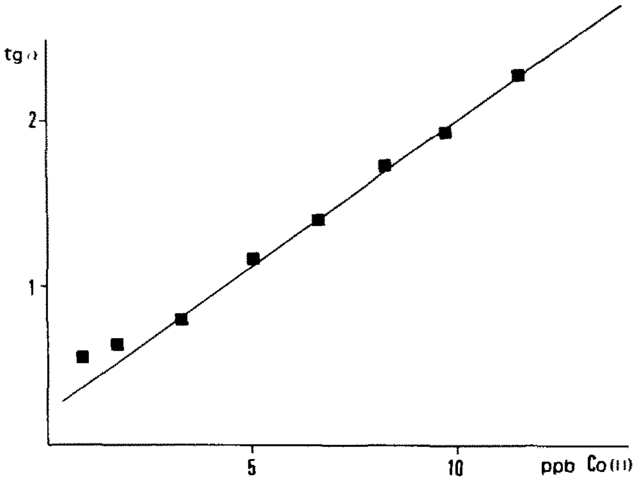


Fig. 3. Calibration curve. [Tiron] = 0.0163 M, pH = 10.5, V_0 = 60 ml, S = 50 mV, v = 3 cm min^{-1}, 1 ml H_2O_2 15% injected.

TABLE 1

Application range for Co(II) determination using the proposed method

S (mV)	Straight line equation (ppb)	r	Range (ppb)
50	tg $\alpha = 0.208 + 0.178\ C$	0.997	3- 12
200	tg $\alpha = 0.112 + 0.041\ C$	0.997	5- 54
500	tg $\alpha = 0.115 + 0.015\ C$	0.999	8-120

relative standard deviation ($n = 8$) was calculated using 8.1 ppb of Co(II). The value obtained was 2.1%.

The calibration curve was obtained by preparing several solutions with different quantities of Co(II), 10 ml of tiron (0.0978 M), 40 ml of buffer (pH 10.5) and diluting the mixture to a final volume of 60 ml. Results are presented in Fig. 3.

The application interval of the method lies between 3 and 120 ppb of Co(II), depending on the sensitivity of the bridge chosen (Table 1).

INTERFERENCE

Potential interference in cobalt determinations was studied by adding 100 ppm of the following cations to a solution containing 8.1 ppb of Co(II): 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). As expected from the literature, only Cu(II), Ni(II) and Mn(II) interfered in the spectrophotometric method.

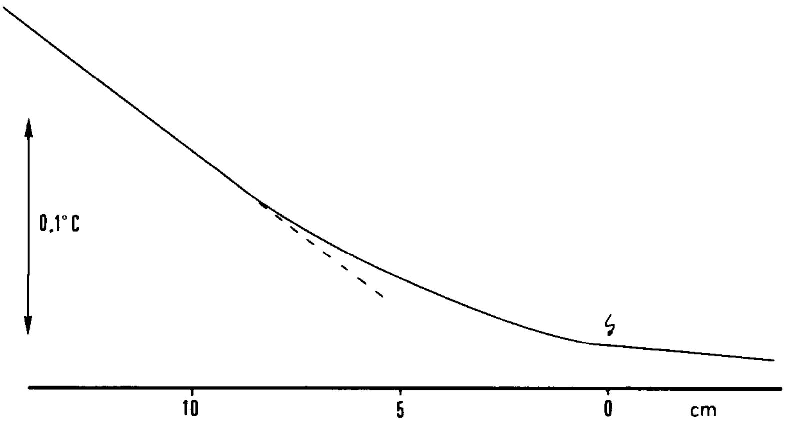


Fig. 4. Mn(II) catalyzed reaction. [Tiron] = 0.0163 M, pH = 10.5, $V_0 = 60$ ml, $S = 50$ mV, $v = 3$ cm min^{-1}, [Mn(II)] = 81.3 ppb, 1 ml H_2O_2 15% injected.

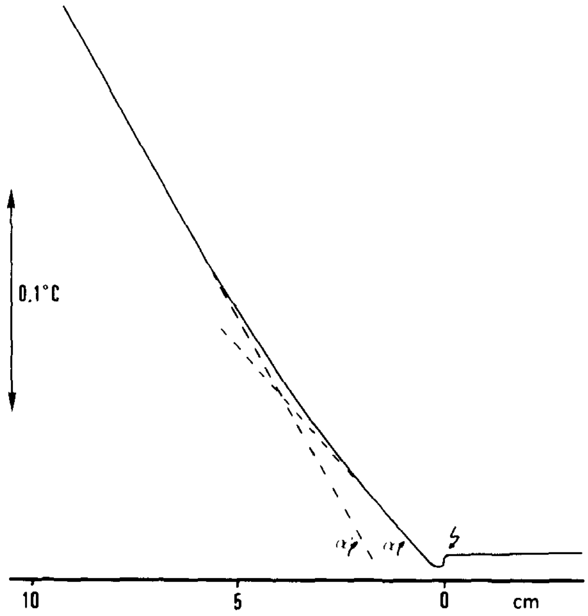


Fig. 5. Thermometric curve obtained in the simultaneous presence of Co(II) and Mn(II). [Tiron] = 0.0163 M, pH = 10.5, $V_0 = 60$ ml, $S = 50$ mV, $v = 3$ cm min^{-1}, 1 ml H_2O_2 15% injected. [Co(II)] = 3.22 ppb, tg $\alpha = 0.76$; [Mn(II)] = 0.16 ppm, tg $\alpha = 0.95$; Σtg $\alpha = 1.81$ (expected = 1.71).

We must point out however that the catalytic action of Mn(II), which is produced after an induction period (Fig. 4), only takes place in the presence of activators [4], such as 1,10-phenanthroline or 2,2′-bipyridine. As already stated in this paper, the catalytic action of Ni(II) and Cu(II) is produced when tiron and hydrogen peroxide concentrations are very high. The maximum interference tolerance levels for these cations are 80 ppb for Mn(II) and 3 ppm for Ni(II). Although Ni(II) interference is not very important, Mn(II) presents more problems, with an additive effect on the cobalt catalysis (Fig. 5). After several tests we were unable to eliminate this interference.

APPLICATIONS

We have used this method to determine vitamin B12 (cyanocobalamine), which contains a cobalt atom in its structure. The selected sample was a collyrium which contained 500 μg ml^{-1} of vitamin B12.

Since the direct determination of the sample gave no thermometric signal, it was necessary to carry out previous mineralization of the sample to eliminate the excipient and break down the cyanocobalamine molecule. The following procedure was used: different quantities of the samples were placed in a crucible, 0.5 ml of HNO_3 (1 M) were added and the mixture heated to dryness in a sand bath. The mineralized samples were dissolved in water and analyzed using the proposed thermometric method.

Using a calibration curve obtained with a register sensitivity of 200 mV, a value of 22.5 ± 0.1 ppm Co(II) was obtained, which agrees with the supposed value of 21.7 ppm for the collyrium (with 3.3% error).

ACKNOWLEDGEMENT

We acknowledge EMP Tarragona and CAICYT (Grant GR85-0050) for financial support granted for this work.

REFERENCES

1 J. Bognar and O. Jellinek, Acta Chim. Hung., 29 (1961) 21.
2 R. Kucharkowsky and H. Döge, Z. Anal. Chem., 238 (1968) 241.
3 I.F. Dolmanova, G.A. Zolotova, T.P. Kabanova and V.M. Peshkova, Vestn. Mosk. Univ., 6 (1968) 96.
4 L.D. Tiginyanu, Koord. Khim., 2 (1976) 809.
5 M. Otto and G. Werner, Anal. Chim. Acta, 147 (1983) 255.
6 F. Borrull, V. Cerdà, J. Guasch and J. Torres, Thermochim. Acta, 98 (1986) 1; 98 (1986).
7 F. Borrull, V. Cerdà, P. Rodriguez and J. Torres, Thermochim. Acta, 104 (1986) 247.
8 F. Borrull and V. Cerdà, Thermochim. Acta, 112 (1987) 335.
9 F. Borrull, V. Cerdà, P. Rodriguez and J. Torres, Analyst (London), in press.
10 R. Feys, J. Devynck and B. Tremillon, Talanta, 22 (1975) 17.