

## COBALT(II) DETERMINATION AT PPB LEVELS BASED ON ITS CATALYTIC EFFECT ON THE HYDRAZINE–HYDROGEN PEROXIDE REACTION. STUDY BY THERMOMETRIC METHOD

M. CALULL, R.M. MARCÉ, N. HOMS, P. RAMIREZ DE LA PISCINA and F. BORRULL  
*Dep. de Química, Facultat de Ciències Químiques de Tarragona, Universitat de Barcelona, 43005 Tarragona (Spain)*

(Received 28 October 1987)

### ABSTRACT

A new thermometric method to determine cobalt(II) at ppb levels based on its catalytic effect on the hydrazine–hydrogen peroxide redox reaction is reported.

The linear response range lies between 2 and 1500 ppb, with a relative standard deviation of 2.2% for 20 ppb of Co(II). The method interferences are Mn(II) and Fe(III) ( $\geq 1$  ppm), Pb(II) ( $\geq 20$  ppm) and Cu(II) at a similar level to that of Co(II). The Fe(II) interference has been eliminated by tartrate addition. The new method has been applied to determine cobalt in a catalyst prepared from  $\text{Co}_2(\text{CO})_8$  supported in acid-modified  $\gamma$ -alumina.

### INTRODUCTION

In the hydrazine–hydrogen peroxide reaction, the catalytic effect of Cu(II) has been that most extensively studied by different authors [1,2]. Nevertheless, the catalytic action of other metallic ions or complexes is also known [3]. Thus, several multivalent metallic ions catalyse the redox reaction between hydrazine and hydrogen peroxide



These metallic ions also catalyze, specially in basic medium, the reaction



In previous reports we have established new catalytic–thermometric methods for Cu(II) and Mn(II) determination at ppb levels based on the hydrazine–hydrogen peroxide reaction [4,5]. These reports showed that cobalt traces also catalyze the hydrazine oxidation by hydrogen peroxide with a sensitivity limit that could allow us to establish a new thermometric method for cobalt determination at ppb levels.

In the work reported here, the study of different variables that affect the catalytic cobalt action on the hydrazine–hydrogen peroxide reaction has

been carried out. We have also determined, under the experimental conditions, the relative importance of reactions (1) and (2) in the catalytic oxidation of hydrazine. Finally, we report here a new kinetic-thermometric method for determination of Co at ppb levels, based on its catalytic effect on the oxidation of hydrazine by hydrogen peroxide.

## EXPERIMENTAL

### *Apparatus*

The thermometric system has been described elsewhere [4]. It consists of a nylon adiabatic cell, with a conventional stirrer, a quick response thermistor (of thermometer type, with a nominal resistance of 100 k $\Omega$  at 25°C), a Wheatstone bridge fed with 9.45 V from a stabilized source and a recorder.

### *Reagents*

Hydrazine (N<sub>2</sub>H<sub>5</sub>OH) 24% (w/v) solution was prepared by dilution of a concentrated solution (R.A., Merck). Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) Standard 15% (w/v) solution was prepared by dilution of a H<sub>2</sub>O<sub>2</sub> solution (33% R.A., Panreac). A standard Co(II) solution of 1000  $\mu\text{g ml}^{-1}$  (titrisol Merck) was used. More dilute solutions were prepared from this stock solution. More dilute standardized solutions of HNO<sub>3</sub> were prepared from HNO<sub>3</sub> (13N Panreac).

Oxygen puriss. 99.999% (Abelló - Oxígeno Linde), and argon puriss. 99.999% (Abelló - Oxígeno Linde) were used.

### *Procedure*

The mixture of hydrazine and Co(II) was placed in the thermometric cell, and hydrogen peroxide solution was added by means of a syringe once the system had been thermometrically stabilized. During addition the thermometric curve was registered.

In order to obtain the most wide range of application and following the conclusions of Feys and coworkers [6], several attempts were made to determine the experimental conditions for obtaining a maximum method sensitivity (high reagent concentrations) with a minimum temperature increment of the blanks.

Experimental conditions finally used were: a mixture of 0.9988 N hydrazine solution (20 ml), the catalyst, and bidistilled water to a final volume of 60 ml (pH of solution = 9.2) was placed in the adiabatic cell. After thermic equilibrium was achieved, 1 ml of a hydrogen peroxide solution (15%) was added by means of a syringe.

In the thermometric titrations carried out under argon or oxygen, the gas was bubbled through the solution before hydrogen peroxide addition, and either oxygen or argon atmospheres were kept in the cell during the reaction.

## RESULTS AND DISCUSSION

The variation of response according to the hydrazine and hydrogen peroxide concentrations in solution was studied in the absence of a catalyst. The results were similar to those reported previously [4]. The curve obtained in absence of a catalyst and the characteristic thermometric curves for different quantities of Co(II) are shown in Fig. 1. Different linear zones as a function of Co(II) concentration can be seen. At low Co(II) concentrations only one linear zone is present, which decreases when Co(II) concentration is increased; simultaneously another less exothermic linear fragment appears and increases progressively. Finally, at a Co(II) concentration of 1000 ppm the thermometric curve is distorted and a new non-linear zone appears, probably due to a heat loss at this sensitivity.

A study of the variation in response as a function of pH was carried out; 20 ml of 0.9988 N hydrazine solution, 1 ml of 1 ppm Co(II) solution, and 30 ml of bidistilled water were placed in the thermometric cell, and the solution pH was adjusted with different volumes of either NaOH (0.1 N) or HCl (0.1 N) solutions, adding bidistilled water to a final volume of 60 ml. The results are shown in Fig. 2. The maximum response is obtained at pH = 9.5, which will be used for all determinations.

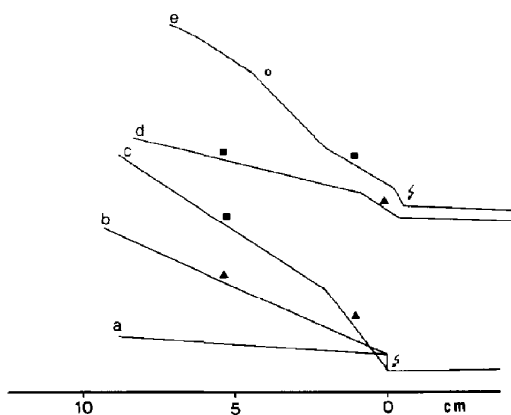


Fig. 1. Thermometric curves obtained by different Co(II) concentrations. (a) Catalytic reaction in absence of catalyst, ( $S = 50$  mV); (b) reaction catalyzed by 50 ppb of Co(II) ( $S = 50$  mV); (c) reaction catalyzed by 166 ppb of Co(II) ( $S = 50$  mV); (d) reaction catalyzed by 330 ppb of Co(II) ( $S = 200$  mV); (e) reaction catalyzed by 1000 ppb of Co(II) ( $S = 200$  mV).  $\blacktriangle$ , 1st zone;  $\blacksquare$ , 2nd zone;  $\circ$ , 3rd zone.

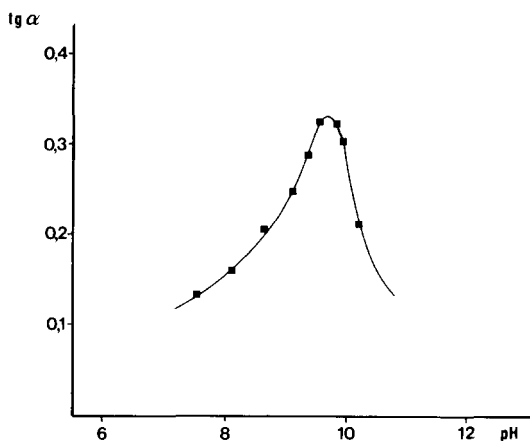


Fig. 2. The pH influence on  $tg \alpha$  values.

The thermometric curves obtained under either argon or oxygen atmospheres are compared with the standard thermometric titration in Fig. 3. The curves obtained under argon or standard conditions are similar, and both are different to that obtained under oxygen, which presents a less exothermic zone. Thus, the principal reaction catalyzed by the cobalt under argon or standard conditions is the same [1]. The first thermometric zone is similar in all cases, with the same  $tg \alpha$  values, and it may correspond to formation of a binuclear Co(II) complex, probably with hydrazine, hydroxo and/or peroxy ligands. This type of intermediate is known in Co(II) complex oxidation processes, as in the case of  $[(Co(NH_3)_6)^{2+}]$  [3,7-9]. The second part of the process may correspond to the oxidation of hydrazine and evolution of nitrogen with regeneration of initial Co(II) species, completing the catalytic reaction.

The less exothermic zone present in the thermometric curve obtained under oxygen, may be due to the simultaneous occurrence of reaction (2).

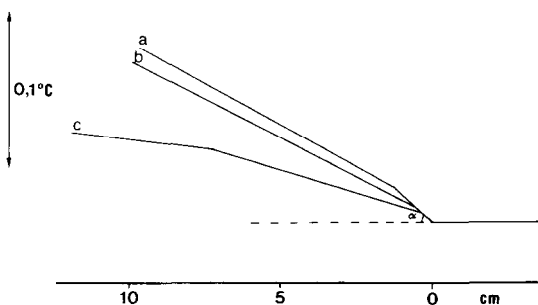


Fig. 3. Thermometric curves. Reaction catalyzed by 60 ppb of Co(II). (a) Standard conditions; (b) under argon atmosphere; (c) under oxygen atmosphere.

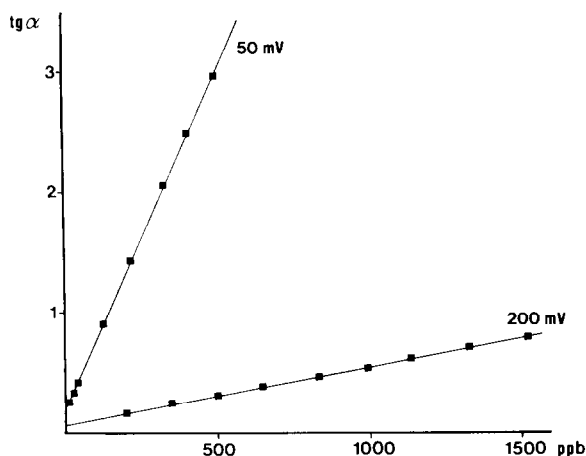


Fig. 4. Variation of response at different sensitivities as a function of Co(II) concentration.

In order to determine the application zone of the method, the variation of response as a function of Co(II) concentration was studied. The first and the second intervals of the thermometric curves were studied with 50 and 200 mV register sensitivity respectively. The results obtained are shown in Fig. 4 and Table 1. The method presents a good linearity between 5 and 1500 ppb of cobalt, taking account of the different register sensitivities listed. The relative standard deviation was 2.2% for a total of seven experiments carried out with 20 ppb of Co(II).

### Interfering cations

The effect of several potential interfering cations were studied as reported elsewhere [4]. The following cations, at final concentrations of 1000 ppm in solutions containing 20 ppb of Co(II), were studied: 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), Pb(II), Fe(II), Fe(III), Ti(IV), Mn(II) and Cu(II).

Only 20 ppm of Pb(II), 1 ppm of Mn(II) or Fe(III) and Cu(II) at a similar concentration to Co(II) interfere. The different thermometric curves ob-

TABLE 1

Variation of the response and application zone

S(mV)	Equation (ppb)	<i>r</i>	Application zone (ppb)
50	$tg \alpha = 0.1448 + 0.0057C$	0.9992	5-500
200	$tg \alpha = 0.0900 + 0.00045C$	0.9963	200-1500

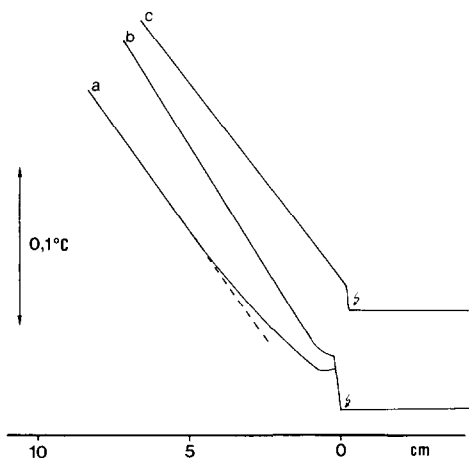


Fig. 5. Interference thermometric curves. (a) Reaction catalyzed by 24.4 ppm of Pb(II); (b) reaction catalyzed by 1.7 ppm of Mn(II); (c) reaction catalyzed by 29.6 ppm of Fe(III).

tained, and the cation responses as a function of its concentration are shown in Figs. 5 and 6.

Mn(II) and Fe(III) show a linear relation between  $\Delta T$  and time in thermometric curves. An induction time can be observed in the case of Pb(II), similar to that already reported in other catalytic thermometric studies [10]. The different types of thermometric curves obtained are due to the different catalytic species involved in the process.

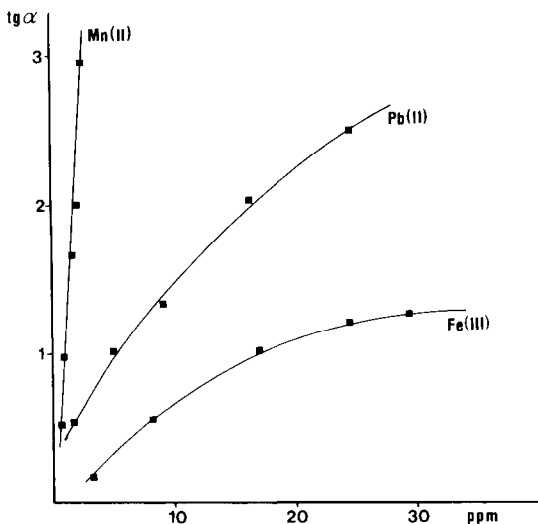


Fig. 6. Variation of response as a function of metallic concentration.

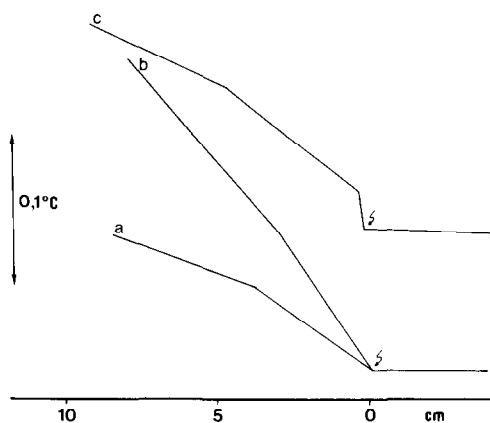


Fig. 7. Elimination of Fe(III) interference. (a) Reaction catalyzed by 82.6 ppb of Co(II); (b) reaction catalyzed by 82.6 ppb of Co(II), and 11.2 ppm of Fe(III); (c) reaction catalyzed by 82.6 ppb of Co(II) and 11.4 ppm of Fe(III) when 1 ppm of tartrate is present.

### *Elimination of interfering cations*

We have achieved elimination of Fe(III) interference by means of tartrate addition. The thermometric curves obtained are shown in Fig. 7.

### *Application*

The proposed method has been applied to Co(II) determination in a catalyst prepared by supporting  $\text{Co}_2(\text{CO})_8$  in an acid-modified  $\gamma$ -alumina [11]. Samples of size between 0.05 and 0.13 g were treated with nitric acid on a hot-plate. After mineralization they were diluted to 10 ml with water and analysed. Two samples containing about 1 and 0.2 ppm of Co(II) were analysed. The values obtained (mean of three determinations) were  $1.16 \pm 0.12$  and  $0.16 \pm 0.02$  ppm, close to the results obtained by atomic absorption spectroscopy ( $1.14 \pm 0.05$  and  $0.15 \pm 0.01$  ppm, respectively). Hence, for cobalt determination results obtained by the proposed thermometric method are comparable to those obtained by traditional methods [4,10,12,13].

### ACKNOWLEDGMENT

Financial support by EMP (Tarragona) is gratefully acknowledged.

### REFERENCES

- 1 H. Erlenmeyer, C. Flierl and H. Sigel, *Chimia (Aarau)*, 22 (1968) 433.
- 2 H. Erlenmeyer, C. Flierl and H. Sigel, *J. Am. Chem. Soc.*, 26 (1969) 1065.

- 3 F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th. Edn., Wiley-Interscience, London, 1985.
- 4 F. Borrull and V. Cerdà, *Thermochim. Acta*, 112 (1987) 335.
- 5 M. Calull, R.M. Marcé, P. Ramírez de la Piscina, N. Homs, J. Torres and F. Borrull, *Thermochim. Acta*, 125 (1988) 319.
- 6 R. Feys, J. Devynck, and B. Tremillon, *Talanta*, 22 (1975) 17.
- 7 A.G. Sykes and J.A. Weil, *Prog. Inorg. Chem.*, 13 (1970) 1.
- 8 V.M. Miskowski, J.L. Robbins, I.M. Treitel and H.B. Gray, *Inorg. Chem.*, 14 (1975) 2318.
- 9 N.N. Greenwood and A. Aernshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, 1985.
- 10 R.M. Marcé, M. Calull and F. Borrull, *Thermochim. Acta*, 117 (1987) 89.
- 11 N. Homs, P. Ramírez de la Piscina and J.E. Sueiras, *J. Catal.*, 89 (1984) 531.
- 12 F. Borrull and V. Cerdà, *Thermochim. Acta*, 113 (1987) 73.
- 13 F. Borrull, P. Ramírez de la Piscina, N. Homs, J. Torres and V. Cerdà, *Thermochim. Acta*, 127 (1988) 209.