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KINETIC THERMOMETRIC DETERMINATION OF Co(II) AND Cu(II) BASED ON THEIR CATALYTIC EFFECT ON PERMANGANATE DECOMPOSITION IN BASIC MEDIA

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ABSTRACT

The catalytic effect of several ions on permanganate decomposition is discussed. Based on their catalytic effect, a new thermometric method for Co(II) and Cu(II) determination is proposed. The linear response falls in the 2–8 ppm range with a relative standard deviation of 1.9% for Co(II) and in the 3–12 ppm range for Cu(II) with a relative standard deviation of 1.5%. Accuracy for different quantities of Co(II) and Cu(II) were also determined.

INTRODUCTION

There are a great number of reactions catalyzed by traces of metals. This catalytic effect has been studied by different researchers in order to determine very small quantities of these elements at ppm or ppb levels.

Spectrophotometry is the most widely used physical method for monitoring reaction rates, by measuring the absorbance either of a reacting or a resulting compound.

In this paper we propose a new method for Co(II) and Cu(II) determination based on the use of thermometric techniques. These are advantageous when colored samples or suspensions have to be analyzed.

The reaction selected was the catalytic permanganate decomposition in basic media, which has already been spectrophotometrically studied by various researchers. They have proved that permanganate transformation to manganate is catalyzed by traces of Ni(II), Co(II), Ag(I) and Cu(II) [1–3].

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EXPERIMENTAL

Apparatus

The thermometric system has been described elsewhere [4], and consists of an adiabatic cell, a stirrer, a 100 kΩ (at 25°C) thermistor and a Wheatstone bridge connected to a stabilized voltage source and to a recorder with high input impedance. A syringe was used to inject the sample.

Reagents

The reagents used were as follows: $KMnO_4$ (0.04 M standard solution), NaOH (1 M) with 0.5% of acetodiphosphonic acid [5], Co(II) stock solution (1000 ppm) (Titrisol Merck), Cu(II) stock solution (1000 ppm) (Titrisol Merck).

Procedure

Thirty milliliters of NaOH (1 M solution with acetodiphosphonic acid) and 30 ml of $KMnO_4$ solution were placed in the adiabatic cell. The Co(II) or Cu(II) samples were injected after thermal stabilization. The optimization of the procedure has been described in a previous paper [5].

RESULTS AND DISCUSSION

As already seen [6], when a metal is added to a permanganate solution in basic media, a precipitate appears which inhibits its catalytic effect. In order to prevent the precipitation of the catalyst it is recommended that a complexing agent is introduced to the reaction mixture. One of the best complexing agents found is acetodiphosphonic acid, which was added in a proportion of 5 ml per liter of NaOH.

The results observed when different quantities of Co(II) or Cu(II) were injected into the permanganate solution are shown in Figs. 1 and 2. The slope of the kinetic curve increases with an increase in the Co(II) or Cu(II) concentration.

We studied the effect of the $KMnO_4$ and NaOH concentrations on the reaction rate, in order to establish the best analytical conditions. The effect of the NaOH concentration was determined by adding different quantities of the base in 30 ml of $KMnO_4$ (0.04 M) and then diluting the mixture to a final volume of 60 ml. Results are shown in Fig. 3. Similar tests were performed by changing the $KMNO_4$ concentration; the results obtained are presented in Fig. 4.

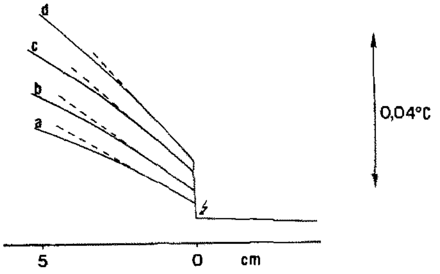

Fig. 1. Kinetic thermometric curves ([NaOH] = 1 M (0.5% acetodiphosphonic acid), [$KMnO_4$] = 0.04 M, [Co(II)] = 1000 ppm, V_0 = 60 ml, S = 20 mV (0.008° C min^{-1})): (a) 3.3 ppm; (b) 5.0 ppm; (c) 6.7 ppm; (d) 10.0 ppm.

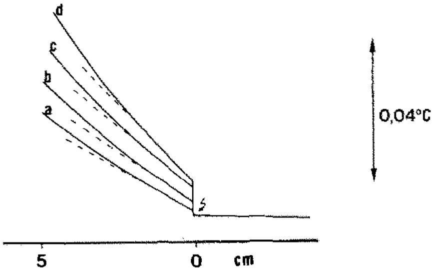

Fig. 2. Kinetic thermometric curves ([NaOH] = 1 M (0.5% acetodiphosphonic acid), [$KMnO_4$] = 0.04 M, [Cu(II)] = 1000 ppm, V_0 = 60 ml, S = 20 mV (0.008° C min^{-1})): (a) 3.3 ppm; (b) 5.0 ppm; (c) 6.7 ppm; (d) 10.0 ppm.

A linear relationship is observed between the NaOH concentration and the tg α values. The maximum quantity of NaOH was selected.

The linear response in front of each cation analite was studied by injecting different quantities of Co(II) and Cu(II) into the mixture of 30 ml

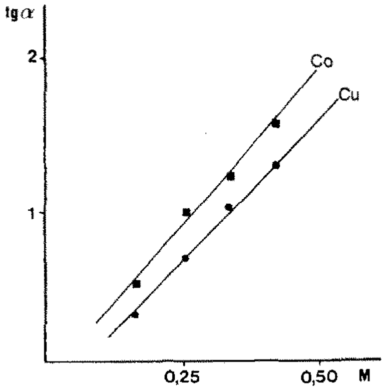

Fig. 3. Influence of the NaOH concentration.

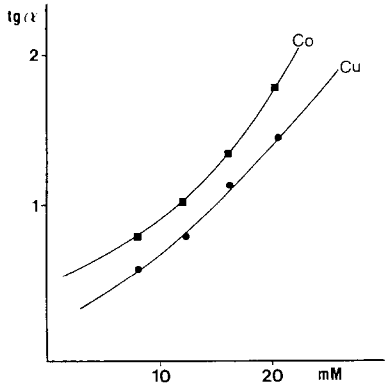

Fig. 4. Influence of the $KMnO_4$ concentration.

of $KMnO_4$ and 30 ml of NaOH with acetodiphosphonic acid. Good linearity between 2–8 ppm of Co(II) and between 3–12 ppm of Cu(II) was observed.

The accuracy of the method is summarized in Table 1. This was calculated for different quantities of Co(II) and Cu(II) using the proposed method. The relative standard deviations ($n = 7$) obtained for 5.8 ppm of Co(II) and 7.5 ppm of Cu(II) were 1.9% and 1.5%, respectively.

The study of interferences has been carried out in a previous paper using the spectrophotometric method [8]. The following metal ions were added (in 0.5 mg amounts) to the reaction solution in the presence of copper (5.8 ppm) or cobalt (7.5 ppm): Ag(I), Au(III), Bi(III), Cd(II), Cr(III), Fe(II), Fe(III), Ni(II), Mn(II), Mo(VI), Na(I), Os(VIII), Pb(II), Pd(II), Pt(IV), Sr(II), Ca(II) and Ba(II).

The only species that substantially catalyzed the reaction were as follows: Ni(II) at the 0.5 ppm level, Ag(I) at the 5 ppm level and Pb(II) and Fe(III) at the 10 ppm level. Fe(II) and Cr(III) did not catalyze the reaction, but were oxidized by the permanganate, and thus interfered when present in ppm concentrations.

TABLE 1

The analysis of unknown pure cobalt and copper solutions

Metal added (ppm)	Co(II)		Cu(II)	
	Found (ppm)	Diff. (%)	Found (ppm)	Diff. (%)
2.50	2.38	4.8	2.64	5.6
4.17	4.09	1.9	4.20	0.7
5.83	5.76	1.2	5.86	0.5
7.50	7.44	0.8	7.55	0.6
8.33	8.28	0.6	8.38	0.6
10.00	–	–	10.06	0.6

Several researchers have reported the catalytic activity of different ions in permanganate decomposition. The large differences observed using the spectrophotometric method induced us to study these catalytic activities using thermometric techniques.

Symons [8], proposed the following accepted mechanism for the permanganate decomposition

$$MnO_4^- + OH^- \overset{K_1}{\leftrightarrow} MnO_4^{2-} + {}^{\cdot}OH$$

$${}^{\cdot}OH + OH^- \xrightarrow{K_2} {}^{\cdot}O^-,\ {}^{\cdot}O_2H,\ {}^{\cdot}O_2H_2, \text{ etc.}$$

Later, Landsberg and Thiele [3] proved that traces of metals increase both K_1 and K_2 values, with the following order of activity: Cu(II) > Ag(I) > Pb(II) > Ni(II), Co(II) > Fe(III).

Using highly purified reagents, Veprek-Siska et al. [2] found the following order: Ni(II) > Co(III) > Fe(III), Ag(I), Cu(II), Pb(II).

In another study [7] with the introduction of acetodiphosphonic acid in the solution, the order of activity was found to be Ag(I) > Co(II), Ni(II) > Cu(II).

In this investigation we performed a similar study, by injecting different quantities of selected metals into a mixture of 30 ml of $KMnO_4$ (0.04 M) and 30 ml of NaOH (1 M with acetodiphosphonic acid). Results are shown in Fig. 5. Whereas Ni(II) acts as a catalyst at the 1 ppm level, Cu(II), Co(II) and Ag(I) are required in greater quantities.

The behavior of Ni and Co is quite different from that of Cu and Ag. The rate of reaction decreases in the usual way with time when Ni and Co are

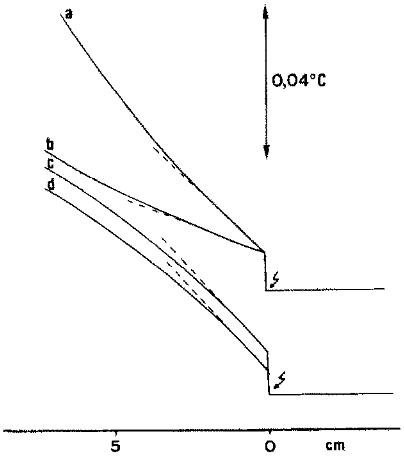

Fig. 5. Kinetic thermometric curves (30 ml of $KMnO_4$ (0.04 M), 30 ml of NaOH (1 M with acetodiphosphonic acid), $S = 20$ mV, $V_0 = 60$ ml): (a) 11.7 ppm of Cu(II); (b) 11.7 ppm of Ag(I); (c) 11.7 ppm of Co(II); (d) 1.2 ppm of Ni(II).

used as catalysts, whereas the reaction rate increases with time when Cu and Ag are used as catalysts. This might be due to the formation of an intermediate compound with higher catalytic activity.

The following order of activity was found in the presence of acetodiphosphonic acid: firstly, Ni(II), with a linear response between 0.5 and 1.2 ppm, then Co(II) and Cu(II) with a very similar response and, finally, greater quantities of Ag(I) were required to show catalytic activity; i.e. Ni(II) > Co(II) > Cu(II) > Ag(I).

This order of activity agrees with that proposed by Veprek-Sisca et al. [2]. However, if experiments had been performed using the fixed time method, this order of activity would have altered owing to the unusual behavior of Ag(I) and Cu(II), whose catalytic effect increases with time (quite the opposite to Ni(II) and Co(II)).

ACKNOWLEDGMENT

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