SENSITIVE REACTION-RATE DETERMINATION OF Co(II) BASED ON ITS CATALYTIC ACTION IN THE AERIAL OXIDATION OF SULPHITE BY USE OF A SIMPLE MONITORED THERMOMETRIC TECHNIQUE

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ABSTRACT

A very simple and sensitive kinetic ally-monitored thermometric technique is used for Co(II) determination in the range 5–30 p.p.b. The method is based on the catalytic effect of cobalt(II) on the autoxidation of the sulphite ion. The reaction is followed by measuring the rate of increase of temperature. The method suffers from very few interferences.

INTRODUCTION

In principle, 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 a catalyst. If the catalyst concentration is proportional to the heat produced in a fixed time or to the rate of heat production, catalyst determinations should have improved detection limits compared to stoichiometrically limited systems.

The measurement of a temperature (heat) change has several advantages over spectrophotometric or spectrofluorimetric assay procedures. The necessity 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.

The application of kinetic techniques is sometimes restricted by complex and expensive instrumentation. In the present paper a kinetic procedure for

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determination of Co(II) is described, by monitoring increase of temperature as a consequence of the development of a chemical reaction, by means of very simple instrumentation similar to that used in thermometric titrimetry. The method is based on the aerial oxidation of sulphite, this being catalyzed by the Co(II) cation. This reaction was applied to the determination of Co(II) in the concentration range 2×10^{-7}–2×10^{-5} M by monitoring the heat of reaction in a flow path with sensitive thermocouples. The rate of oxidation is linearly related to Co concentration in the above range with maximum errors of about 3% [1]. To date, very few examples of the use of calorimetry for direct measurement of heat changes during chemical reactions (reaction-rate methods) applied to the determination of inorganic species are found in the literature [2]; basically, this technique has been restricted to biochemical analysis [3,4].

EXPERIMENTAL

Reagents and solutions

Stock solutions included an aqueous solution of sulphite prepared from Na_2SO_3 (100 g l^{-1}), and a cobalt(II) nitrate solution containing 0.9870 g Co l^{-1} standardized compleximetrically. A buffer solution of pH 9 was prepared according to Clark and Lubs [5].

Calorimetric equipment

The temperature-monitoring system (Fig. 1) consisted of a thermistor (a miniature-type thermometer of rapid response), Wheatstone bridge and a recorder (Goerz, type Servogor RE 511). The circuit diagram of the thermistor and recorder coupling is also shown in Fig. 1. The thermistor was sealed in glass and had the following specifications: resistance, 100 kΩ at 25°C, power dissipation less than 0.134 mW, effective resistance 131 kΩ at 20°C. The e.m.f. for the Wheatstone bridge was supplied by 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. [6]. An adiabatic cell (Fig. 1) is also used. The dissolution in the cell was stirred with a magnetic stirrer.

Procedure for determination of cobalt (II)

10 ml of 0.8 M Na_2SO_3, 10 ml of pH 9 buffer and the volume of deionized water necessary for the final volume to be 25 ml were placed in the
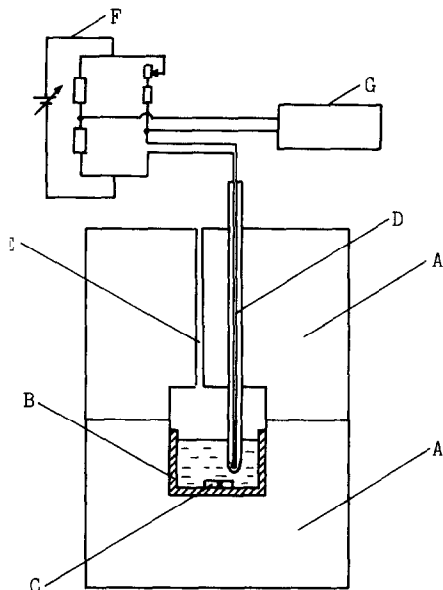
Fig. 1. Diagram of circuitry and apparatus used in reaction-rate thermometric analysis. A, polystyrene insulator; B, plastic beaker; C, magnetic stirrer; D, thermistor; E, pipette entrance; F, Wheatstone bridge; G, recorder.

cell compartment. 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 cobalt between 5 and 30 p.p.b. were added. From the curve obtained, the rate of reaction was calculated by the initial rate (tangent) method. All solutions were thermostatted previously at 20°C.

RESULTS AND DISCUSSION

Examples of the temperature–time curves, for determination of cobalt-II), are shown in Fig. 2. The slope of the curve should correspond to the temperature change due to catalytic reaction. To obtain rapidly stabilized measurements (horizontal temperature–time curves) before the addition of the cation, all solutions must be thermostatted at the same temperature and his must coincide with room temperature, therefore it is convenient that this is kept constant.

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

Kinetic studies

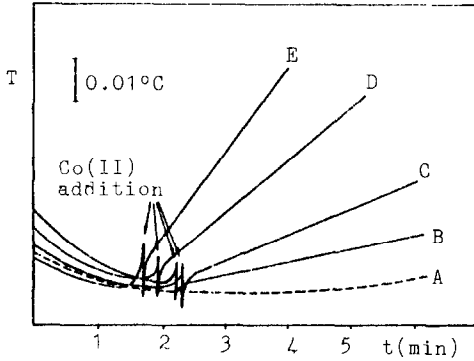For the purpose of finding the optimum conditions for the determination

Fig. 2. Temperature–time curves for various cobalt concentrations (p.p.b.): (A), reagent blank; (B), 5; (C), 10; (D), 20; (E), 30. The recommended procedure was used.

of Co(II), the influence of pH and concentration of sulphite on the reaction rate have been studied.

To optimize the concentration of each variable, its initial concentration was varied while the 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.

Figure 3 shows that the initial reaction rate is greatest at pH 9, and in a very small interval around this pH the order of reaction with respect to this pH is zero. For this reason a pH of 9 was chosen for the determination of cobalt.

The results shown in Fig. 4 correspond to the influence of the concentration of sulphite on the reaction rate. As can be seen, there is no region in
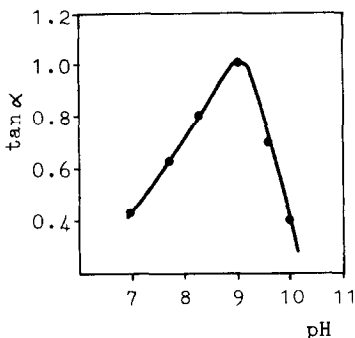

Fig. 3. Influence of pH on the initial rate: $[Na_2SO_3] = 5 \times 10^{-3}$ M, $[Co(II)] = 1$ p.p.m.
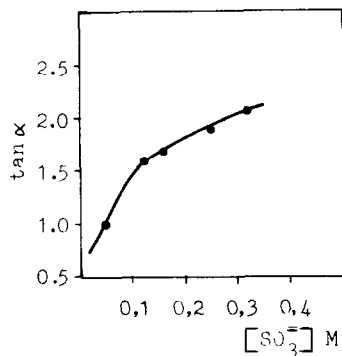
Fig. 4. Effect of concentration of reagent on the initial rate: $[Co(II)] = 0.05$ p.p.m., pH = 9.

which the order of reaction is zero and higher concentrations cannot be used because they would be too near to the solubility of the salt used. However, around a concentration of 0.32 M the reaction rate is maximum and the order of reaction is minimum, so this concentration was chosen for the determination.

Under these optimum conditions, there was a linear relationship between the initial reaction rate and the cobalt concentration in the range 5–30 p.p.b. in the final solution.

Characteristics of the analytical methods

The temperature–time curves were recorded for different amounts of cobalt(II) (Fig. 2), for the optimum pH values and concentration of sulphite. Owing to the shape of these curves, the tangent method was the only one applied for preparing the calibration graph and this was linear for 5–30 p.p.b. cobalt(II) and the relative standard deviation was 1.1% ($n = 11$, $\alpha = 0.05$).

The selectivity of the method has been assayed by studying the effects of

TABLE 1

Concentrations of foreign ions tolerated (error $\leqslant 1.1\%$) for 20 p.p.b. cobalt(II)

Ion added	Amount tolerated (p.p.b.)
Ca(II), Mg(II), Ba(II), Sr(II), Hg(II), Pb(II), Mn(II), Sn(II), Fe(III), Ni(II), Zn(II), Cd(II), Al(III), Bi(III), V(V), Mo(VI), NO_3^-, SO_4^{2-}, Cl^-	2000 [a]
Au(III)	1000
Cu(II), Pd(II), UO_2^{2+}	20

[a] Largest amount examined.

foreign ions on the reaction rate under the recommended conditions. The results are shown in Table 1. As can be seen, the method suffers from very few interferences.

CONCLUSION

The method proposed in this paper needs extremely simple instrumentation and for this reason it is inexpensive; the cost of the temperature-monitoring system (Wheatstone bridge and adiabatic cell) is not more than US$100. This instrumentation is also easily obtainable, therefore only requires a few electronic elements in common use. In spite of the simplicity of the instrumentation used, the method developed presents a great sensitivity (p.p.b. range) and an unusual selectivity. For this reason, practical interest in the development of such methods is understandable.

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