Original Contribution

CATALYTIC SPECTROPHOTOMETRIC DETERMINATION OF COBALT(II) BY SULFANILIC ACID - HYDROGEN PEROXIDE SYSTEM

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ABSTRACT

A kinetic spectrophotometric method for the determination of trace Co(II) is developed. It is based on the catalytic effect of Co(II) on the oxidation of SA by hydrogen peroxide in alkaline media. The reaction was monitored spectrophotometrically by measuring the increase in absorbance of the reaction product at 370 nm. A fixed-time method of 15 min from the initiation of the reaction was used. The parameters affecting the sensitivity were optimized. The proposed catalytic method permits determination of Co(II) over the range $6 - 60$ ng mL^{-1} with detection limit of 1.77 ng mL^{-1}. The relative standard deviations (n=10) are 2.8 % and 4.2 % for 6 and 60 ng mL^{-1} Co(II), respectively. The method was applied successfully to the determination of cobalt in synthetic samples.

Key words: cobalt determination, sulfanilic acid, kinetic methods.

INTRODUCTION

Cobalt is very important mineral element for environmental chemistry, and human biochemical metabolism (1-3) Low concentrations of cobalt in living organisms and in the environment make it very difficult for analytical determination and therefore often preconcentration steps are necessary (4-7). Various methods for cobalt determination have been reported including spectrophotometry (5, 8, 9), AAS (10-13), ICP-AES (6), ICP-MS (14), stripping voltametry (7), FIA (15) *etc.*

Catalytic methods with spectrophotometric monitoring for Co(II) determination are reported (15-22). Catalytic kinetic methods have the advantages of low cost apparatus, rapid analysis and extremely low detection limits comparable with those of the instrumental methods (11, 21, 23). Most of these methods are based on the catalytic action of cobalt on the oxidation of various organic compounds. Sulfanilic acid (SA) is involved as a substrate in catalymetry by Bontchev and coworkers for catalytic determination of silver (24). The choice of SA

was based on the theoretical considerations on its structure and properties. As an aromatic amine it forms intensive colored reaction products, which contributes to improving sensitivity and detection limits of the reactions with spectrophotometric monitoring. On the other hand, due to the high standard redox potential (E^o=1.808 V) of the couple Co^{3+}/Co^{2+}, strong oxidants are necessary for the determination of cobalt. Their interaction with readily oxidizing substrates, possessing relatively low redox potentials – from -0.20 to 0.30 V (25), would lead to the lower selectivity, high and unstable background of the reactions. Unlike them, SA has relatively high redox potential E^o=0.58 V. The presence of the electron-accepting sulfonic group in the aromatic ring significantly raises the redox potential of the substrate, thus leading to the low background and good selectivity. The advantages of sulfanilic acid made it a convenient and to a some extend a universal substrate for catalytic determinations. Combining it with appropriate oxidizers and activators several redox reactions with spectrophotometric and thermometric monitoring for silver, cysteine, copper, manganese and iron were developed (26-32). Most of them have already found analytical application.

In this work a kinetic method for the determination of cobalt in solutions of its salts is proposed based on the catalytic effect of

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Co(II) on the reaction between sulfanilic acid and hydrogen peroxide.

EXPERIMENTAL

Reagents

All solutions were prepared from analytical reagent grade substances and doubly distilled water. Laboratory glassware was immersed for 12 h in aqua regia, washed ten times with distilled water and five times with doubly distilled water and dried at 140 ^{o}C. The glassware was kept in hermetically closed vessels before and after taking the samples.

A 0.01 mol L^{-1} stock solution of Co(II) was prepared by dissolving 0.2379 g of CoCl$_2$.6H$_2$O (Fluka) in 100 ml of 0.01 mol L^{-1} HCl (Merck). Its exact concentration was controlled complexometrically. Working solutions (1×10^{-4}-1×10^{-5} mol L^{-1}) were prepared by suitably diluting the stock cobalt solution with water. The initial 2.2 mol L^{-1} solution of hydrogen peroxide was prepared from 30 % H$_2$O$_2$ (Merck) and its exact concentration was standardized permanganometrically. Because of their limited stability, working solutions of 1.1 mol L^{-1} H$_2$O$_2$ and 1×10^{-4} - 1×10^{-5} mol L^{-1} Co(II) were prepared just before use. A 3.8×10^{-2} mol L^{-1} solution of the substrate SA (Fluka) was prepared by dissolving 0.6581 g of SA in water and by diluting to 100 mL in a standard flask. These solutions were stabile for at least one week, when kept in dark glass vessels at 5 – 10°C.

The medium pH in the range 5.02-11.98 was maintained with universal buffer solution prepared by 0.04 mol L^{-1} acetic acid, boric acid and orthophosphoric acid (solution A) and brought to the required pH by using appropriate volumes of 0.2 mol L^{-1} sodium hydroxide (solution B) (33). Buffer solution of pH 9.15 was prepared by mixing 70.0 mL of solution B and 100.0 mL of solution A.

The initial concentrations of the reagents in the reaction mixture and the experimental conditions are described in the text where necessary.

Apparatus

Absorbance measurements were made on a Specol 11 spectrophotometer (Germany) fitted with 5-cm cells. The spectrophotometer cell compartments were thermostatted by means of circulating water. A NBE thermostat (Germany) was used to control the temperature. The absorption spectra were taken on a Specord UV-Vis recording spectrophotometer (Germany). The pH-values of solutions were determined by a PHM 64 research pH meter.

Initial rate method

The indicator reaction was monitored spectrometrically and initial-rate method was used for processing the kinetic data. In a three-compartment reaction vessel were placed: 2.00 mL of SA (3.8×10^{-2} mol L^{-1}) in the first compartment, 2.00 mL of H$_2$O$_2$ solution (1.1 mol L^{-1}) in the second compartment and 0.00 - 0.80 mL of cobalt standard solution (to give a final concentration between 0 and 10×10^{-7} mol L^{-1}) in the third compartment. Then 6.0-5.2 mL of buffer solution (pH 9.15) were added to each compartment in approximately equal portions, so that the total volume of the reaction mixture was the same in each experiment (10.00 ml). After the components had been brought to the reaction temperature (40°C) and mixed by vigorous shaking, the reaction mixture was transferred into a 5-cm temperature-controlled cell in the spectrophotometer. The change in the absorbance (*A*) at 370 nm as a function of time (*t*) was measured. The initial rate of the indicator reaction, as tg α=d*A*/d*t*, was calculated from the slope of the absorbance-time kinetic curves. Using the initial rate method, the dependencies of the reaction rate on the temperature, acidity and reagent concentrations were studied.

Fixed-time method

For the determination of Co(II) in the concentration interval studied, the fixed-time method was chosen. This method is simple and suitable for laboratory work and automation. When using this approach there is no need for the entire kinetic curve and a simpler test-tube can be used instead of the three-compartment reaction vessel. The effect of the reaction time was studied in the range 10-20 min. The most acceptable values of the intercept, slope and detection limit were obtained at a fixed time of 15 min. Therefore, the fixed time of 15 min was selected.

The experimental conditions, i.e. temperature, pH, concentrations of the oxidant, substrate and catalyst, volumes of the reagents, total volume of the reaction mixture and wavelength for absorption measurement, were the same as for the initial rate method. Into a test tube, to a Co(II) solution, buffer and H$_2$O$_2$ solutions were successively added,

the mixture was kept at 40^0 C for 15 min, then the substrate solution was added and the start of reaction was registered. After 15 min from the start of the reaction, the reaction mixture was placed back in the thermostat and the absorption was measured. A calibration graph of absorbance (A) vs. Co(II) concentration was constructed.

Catalytic method for the determination of cobalt in synthetic samples

For the determination of cobalt in synthetic samples, to 0.6 mL Co(II) solution (1×10^{-5} mol L^{-1}), known amounts of different ions were added instead of the corresponding volume of buffer solution and the above described fixed time procedure was applied.

RESULTS AND DISCUSSION

Optimum reaction conditions

During the oxidation of SA by hydrogen peroxide in the presence of Co(II) as a catalyst, a yellow colored reaction product was yielded, which exhibits an absorption maxima (λ_{max}) at 360 – 380 nm (**Figure 1**). Figure 1 indicates that the oxidation of SA by hydrogen peroxide is catalysed by the presence of small amounts of Co(II) in the system. The greatest difference between the absorbances of the catalysed and uncatalysed reaction occurred at 370 nm. This wavelength was selected for further studies.
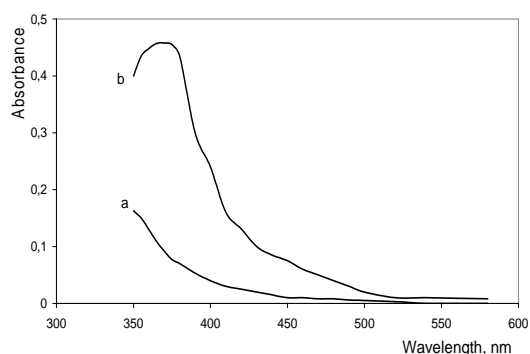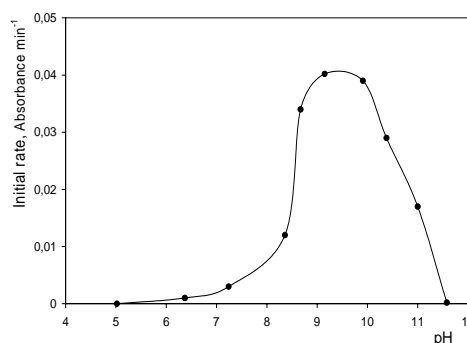

***Figure 1**. Absorption spectra of the reaction product (a) in the absence of the catalyst; (b) in the presence of 1×10^{-6} mol L^{-1} Co(II). Conditions: 7.6×10^{-3} mol L^{-1} SA; 0.22 mol L^{-1} H$_2$O$_2$; pH 9.15; time 15 min, and temperature 40 ^{o}C.*

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The influence of the reaction variables (reagent concentrations, temperature, acidity) on the reaction rate was studied to establish the optimum reaction conditions. The system was optimised by altering each variable in

turn, while the others were kept constant.

The effect of the acidity on the rates of the catalysed and uncatalysed reactions is presented in **Figure 2**. The preliminary studies showed that for buffering of the reaction mixture, the universal buffer was the most appropriate, because it had no side-effects. The rate of the catalysed reaction increased quickly with pH up to 9.15, at which maximal reaction rate was observed. Moreover, at this pH the difference between the reaction rates of the catalysed and uncatalysed reactions was maximal. That is why a pH of 9.15 was selected as the optimum acidity for the remainder of the studies.
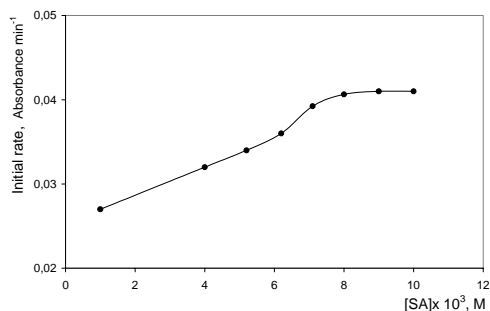

***Figure 2.** Influence of pH on the initial reaction rate in the presence of 1×10^{-6} mol L^{-1} Co(II). Conditions: 7.6×10^{-3} mol L^{-1} SA; 0.22 mol L^{-1} H$_2$O$_2$; λ 370 nm, and temperature 40 ^{o}C.*

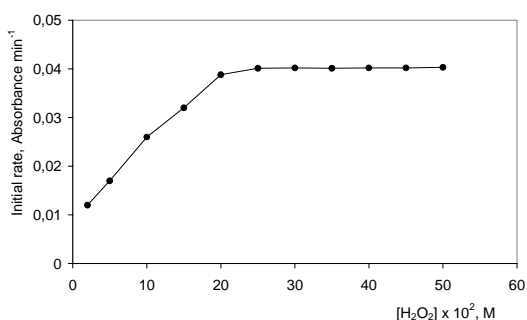*M.G. Angelova, A.M. Stoyanova, A.A. Alexiev*

In the dependences of the reaction rate on the concentrations of SA and hydrogen peroxide (**Figs. 3, 4**) in the presence of the catalyst Co(II), initially, sharp increase was observed, followed by saturation at concentrations above 6.5×10^{-3} mol L^{-1} and 0.20 mol L^{-1}, respectively. On the other hand, under the studied conditions, the change in the concentrations of the reagents had no effect on the initial rate of the uncatalysed reaction, thus the greatest difference between the rates of the catalysed and uncatalysed reactions was achieved. Therefore, concentrations of $7.6.10^{-3}$ M SA and 0.22 mol L^{-1} H$_2$O$_2$ were chosen as the optimal.

The influence of temperature on the reaction rate is shown in **Figure 5**. The rates of both - catalysed and uncatalysed reactions increased with increase of the temperature and the difference in the reaction rates became larger, furthermore up to 40°C the uncatalysed reaction practically did not proceed. For practical purposes, such as no reaction background, high slope of the calibration graph and good reproducibility, a temperature of 40^{0}C was selected.
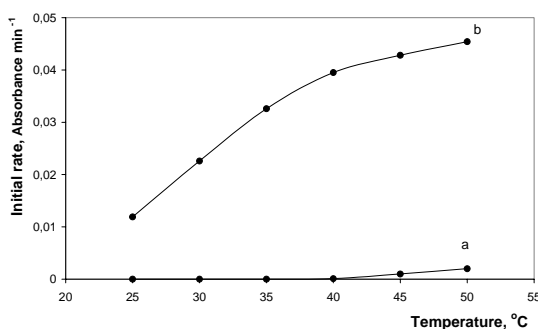
Figure 3. Influence of SA concentration on the initial reaction rate in the presence of 1×10^{-6} mol L^{-1} Co(II). Conditions: 0.22 mol L^{-1} H_2O_2; pH 9.15; λ 370 nm, and temperature 40 ^{o}C.

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Figure 4. Influence of H_2O_2 concentration on the initial reaction rate in the presence of 1×10^{-6} mol L^{-1} Co(II). Conditions: 7.6×10^{-3} mol L^{-1} SA; pH 9.15; λ 370 nm, and temperature 40 ^{o}C.

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Figure 5. Influence of temperature on the initial reaction rate (a) in the absence of the catalyst; (b) in the presence of 1×10^{-6} mol L^{-1} Co(II). Conditions: 7.6×10^{-3} mol L^{-1} SA; 0.22 mol L^{-1} H_2O_2; pH 9.15 and λ 370 nm.

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Under the optimal reaction conditions (λ=370 nm; pH=9.15; 40 ^{o}C; 7.6×10^{-3} mol L^{-1} SA; 0.22 mol L^{-1} H_2O_2), the dependence of the reaction rate was linear in the range 6 – 60 ng mL^{-1} of the concentration of Co(II).

After characterization of the influence of each variable on the reaction rate, the corresponding kinetic equation can be formulated in a general form:

$$rate = dP/dt = k \; C(SA) \; C(H_2O_2)$$

$$C(Co(II)) + k_o \, C(SA) \, C(H_2O_2)$$

where P is the concentration of the reaction product, k and k_o are denoting the rate constants of the catalysed and uncatalysed reactions.

Under optimum conditions, the background reaction was nearly zero, and at the concentrations of SA above 6.5×10^{-3} mol L^{-1} and of hydrogen peroxide above 0.2 mol L^{-1}, the reaction rate was independent on the concentrations of the substrate and the oxidant. Therefore, the kinetic equation can be written as follows:

$$dP/dt = k' \, C(Co(II))$$

where k' is a constant proportional to the rate constant of the catalysed reaction. This equation shows a linear dependence of the reaction rate on the concentration of the catalyst.

Calibration graph, detection limit and precision

Under optimum experimental conditions, a linear calibration graph was obtained by the fixed-time method of 15 min from the initiation of the reaction. For the range of 6 – 60 ng mL^{-1} Co(II), the regression equation of the calibration graph was $A = 0.0917 + 0.006$ C, with a regression coefficient of 0.9906, where A is the absorbance and C is concentration of Co(II) expressed in ng mL^{-1}. The relative standard deviation for 5 replicate analyses of 6 ng mL^{-1} and 60 ng mL^{-1} of Co(II) was equal to 2.8 % and 4.2 %, respectively. The detection limit was 1.77 ng mL^{-1}, calculated as three times the standard deviation of the blank divided by the slope of the calibration graph.

Interference Studies

The possibility of analytical application of the proposed method was assessed by examining the effect of various ions which potentially interfere with the determination of cobalt. Solutions containing 6×10^{-7} mol L^{-1} Co(II) and excess amount of foreign ions were investigated. The tolerable concentration of each foreign ion was taken as the highest concentration causing an error of less than ± 5 %. Most ions did not interfere with cobalt determination. Mg(II), CH_3COO^-, Cl^-, PO_4^{3-} did not interfere even at 10000-fold excess; Ca(II), SO_4^{2-}, $C_2O_4^{2-}$ did not interfere up to 5000-fold excess; Cu(II), Mo(VI), Fe(II), $Cr_2O_7^{2-}$, Cd(II), Zn(II), Pb(II), Ag(I) up to 100-fold excess and Ni(II), Mn(II), Fe(III) did not interfere up to 5, 10 and 50 fold excess over Co(II), respectively. Hence, it can be

concluded that the selectivity of the method is good.

Determination of cobalt(II) in synthetic mixtures

In order to check the accuracy and reproducibility of the proposed method, it was applied to the analysis of synthetic samples, containing Co(II) and various amounts of common cations. The analytical results for cobalt determination in model samples are shown in **Table 1**. All data are an average of three replicate determinations. The results obtained showed good reproducibility and accuracy of the method.

Table 1. *Catalytic determination of Co(II) in synthetic samples*

Synthetic sample composition, ng mL^{-1}	Found, ng mL^{-1}	Recovery, %
35.4 Co(II), 670 Fe(III)	35.87	101.33
35.4 Co(II), 650 Ag(I), 760 Cu(II)	34.92	98.67
35.4 Co(II), 780 Zn(II), 670 Pb(II), 150 Mg(II)	34.04	96.17
35.4 Co(II), 650 Ag(I), 780 Zn(II), 670 Pb(II), 240 Ca(II)	36.40	102.83

CONCLUSION

The catalytic effect of Co(II) on the oxidation of SA with H_2O_2 was investigated. A kinetic spectrophotometric method for the determination of trace Co(II) was developed. It can be used for the determination of Co(II) in the range 6 – 60 ng mL^{-1} by the fixed-time method. The method proposed is highly sensitive and simple, and the precision is very acceptable for the determination of low ranges of Co(II). With its detection limit of 1.77 ng mL^{-1}, this method is comparable to analytical techniques with detection limits in the ng mL^{-1} range, such as AAS, ICP-AES, ICP-MS. The method was applied successfully to the determination of cobalt in synthetic samples.

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