

A Kinetic Method for the Spectrophotometric Determination of Cobalt using Flow Injection Analysis

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Summary: A flow injection manifold for the rapid and sensitive determination of cobalt(II) is described, based on its catalytic effect on the oxidation of Alizarin Red S (1,2-dihydroxy-anthraquinone-3-sulphonic acid) by hydrogen peroxide in alkaline media. The limit of detection is 10^{-7} M (6 pmol) at a sample throughput of 60 h^{-1} with a c.v. of 1.9% for 10^{-7} M cobalt and 0.3% for 10^{-5} M cobalt.

Introduction

Kinetic methods for analysis based on catalytic reactions have received considerable attention because of the sensitivity that can be achieved with inexpensive apparatus [1]. Many homogeneous redox reactions catalysed by cobalt have been used for the determination of cobalt in solution, the most common involving peroxide as the oxidant and aromatic oxy-compounds as the reductant [1-3]. Recently, such a method has been adapted for flow injection analysis [4].

Flow injection analysis (f.i.a), first developed by Ruzicka and Hansen [5-6], is a suitable technique for the kinetic measurement of metal ions because reaction conditions can be controlled by the optimisation of experimental parameters such as flow rate, coil length, diameter of tubing etc.

This paper describes a flow injection procedure for the determination of cobalt by its catalytic effect on the oxidation of Alizarin Red S (1,2-dihydroxy anthraquinone-3-sulphonic

acid) by alkaline hydrogen peroxide. The reaction was developed by Bognar [7] and has been used manually for the determination of cobalt in sea water [8].

Experimental

Reagents

All chemicals used were analytical grade and deionized water was used throughout. A stock cobalt solution (10^{-3} M) was prepared by dissolving 2.9103 g of cobalt nitrate (BDH) in deionized water [1]. Aqueous cobalt standards over the range 10^{-4} M 10^{-7} M were made by serial dilution of the stock.

Alizarin Red S (Sigma) was recrystallized from ethanol and an aqueous stock solution (1.5×10^{-3} M) was prepared. A stock solution of hydrogen peroxide (2 M) was prepared by diluting 112.5 ml of 27% (v/v) hydrogen peroxide (Fisons) to 500 ml. Disodium hydrogen phosphate (BDH) was used

as the buffer (0.2 M). The ion-exchange columns were filled with Dowex A-1 resin (100-200 mesh; BDH), to complex metal ions present in reagents.

Apparatus and procedures

The f.i.a. manifold is shown schematically in Fig.1. Carrier streams of Alizarin Red S (R1) and hydrogen peroxide (R2) were pumped at the same flow rate (1.2 ml min^{-1}) using a peristaltic pump (Ismatec Mini S-840). The catalyzed reaction was initiated by injecting cobalt standards ($60 \mu\text{l}$) into the stream containing Alizarin Red S (pH. 11.0) via a rotary injection valve (Rheodyne 5020). The sample (cobalt) and reagents were mixed in a 100 cm dispersion coil. As the dispersed sample zone reached the flow cell of the spectrophotometer (Pye Unicam SP-600), the decrease in absorbance (due to the oxidation of Alizarin Red S) was monitored at 510 nm. The manifold tubing was polyethylene (0.5 mm i.d.). The detector output was fed to a strip chart recorder and the peak height was related to cobalt concentration.

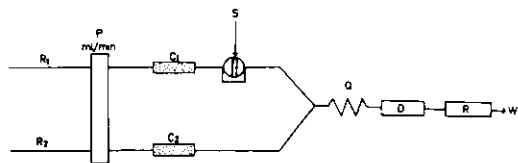


Fig.1: Manifold for the spectrophotometric determination of cobalt.

Results and Discussion

Optimization of Flow System

The sensitivity of the proposed method for cobalt is largely dependent upon parameters such as flow rate and

coil length. The effect of varying the flow rate was studied over the range 1.2 to 3.0 ml min^{-1} , while keeping all other variables constant. Decreasing the flow rate increased the detector response due to a longer sample residence time in the mixing coil and a reduced sample dispersion, as shown in Fig.2. However, a flow rate of 2.4 ml min^{-1} was used in order to achieve a reasonable sample throughput (60 h^{-1}). Increasing the coil length from 50-250 cm increased the detector response, again due to the longer residence time of the sample zone in the mixing coil, but peak broadening was observed at longer reaction coil lengths due to increased sample dispersion. The manifold shown in Fig. 1 was used to study the effect of pH on the rate of the catalysed reaction over the range pH 9.5-12.5. A fixed amount of cobalt (10^{-5} M) was

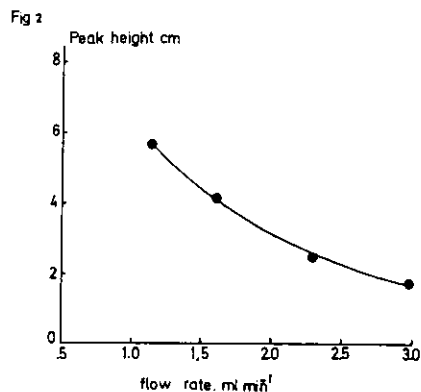


Fig.2: Effect of the flow rate on the peak height.

injected and the optimum pH obtained was pH 11.0.

The effect of hydrogen peroxide concentration on peak height is shown in Fig.3. The limiting value obtained

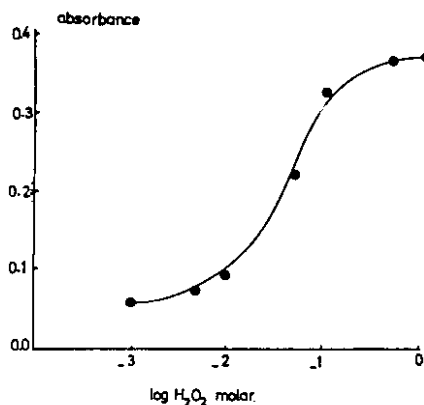


Fig. 3: Effect of hydrogen peroxide concentration on the absorbance.

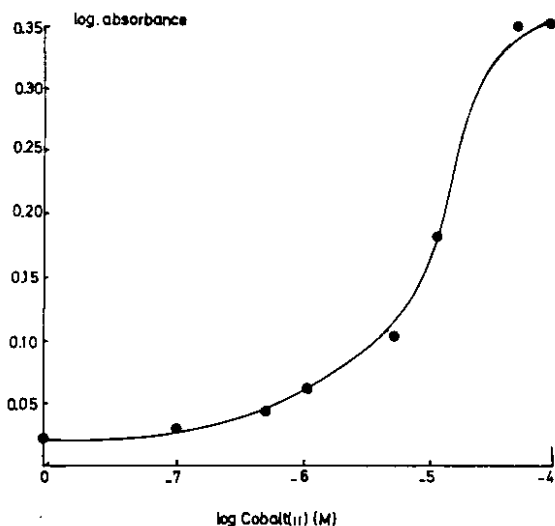


Fig. 4: A log-log calibration graph of cobalt (II) versus absorbance.

was 0.15 M, which represents an excess of hydrogen peroxide for the reaction conditions described above. The rate of oxidation of Alizarin Red S was measured for different substrate concentrations (1.5×10^{-3} - 7.5×10^{-3} M) with a fixed amount of cobalt (10^{-5} M). There was a linear relationship between the rate of oxidation and Alizarin Red S concentration, but higher concentrations gave a higher

background signal due to the increase in complex formation between Alizarin Red S and cobalt present as impurity in water and reagents [9]. Thus, 1.5×10^{-3} M Alizarin Red S was used for the analytical procedure.

Calibration for Cobalt (II)

Cobalt standards ($60 \mu\text{l}$) over the range 10^{-7} - 10^{-4} M were injected into a stream of Alizarin Red S. A plot of cobalt concentration versus change in absorbance is shown in Fig. 4. A background signal was observed when water was injected, due to dilution of the coloured reagent solution and contamination. The mean of triplicate injections (absorbance) and precision data for a series of cobalt standards is given in Table 1.

Table-1: Sensitivity and precision data for the determination of cobalt

Cobalt	absorbance mean of three (M)	c.v. injection%
0	0.02	2.4
1×10^{-7}	0.03	1.9
5×10^{-7}	0.04	4.4
1×10^{-6}	0.06	4.6
5×10^{-6}	0.11	0.6
1×10^{-5}	0.20	0.3
5×10^{-5}	0.35	0.2
1×10^{-4}	0.35	0.2

Interferences

One limitation of the above method is the lack of specificity of cobalt as a catalyst for the oxidation of Alizarin

Table-2: The catalytic effect of other cations on the oxidation of Alizarin Red S

Cation	conc. (M)	absorbance (ΔA)	cation	conc. (M)	absorbance (ΔA)
H ₂ O (blank)		0.02	NH ₄ ⁺	1.0 x 10 ⁻²	0.03
Co(II)	3.2 x 10 ⁻⁶	0.10	Mg(II)	1.0 x 10 ⁻⁴	0.03
Mn (II)	1.0 x 10 ⁻⁴	0.12	Cu(II)	1.0 x 10 ⁻⁴	0.02
Cr(III)	1.0 x 10 ⁻⁵	0.10	Cd(II)	1.0 x 10 ⁻²	0.02
Ni(II)	1.0 x 10 ⁻⁴	0.09	Pb(II)	1.0 x 10 ⁻⁴	0.02
Fe(II)	1.0 x 10 ⁻⁴	0.02	Zn(II)	1.0 x 10 ⁻²	0.02

Red S. Table 2 shows the absorbance change in the presence of a variety of cations relative to the absorbance change for the uncatalysed reaction (blank) and in the presence of 1.0 x 10⁻⁶ M cobalt. The only significant interferences are from manganese (II), chromium (III) and nickel(II). For real samples, manganese (II) and nickel(II) would have to be present in one hundred fold excess, and chromium (III) in ten fold excess, to cause any appreciable error. In cases where the level of interference was unacceptable, the interfering ions would have to be removed from the sample, by physical or chemical means, prior to analysis.

Conclusions

The results obtained above show that f.i.a. is a simple, sensitive and reproducible technique for the catalytic photometric determination of trace amounts of cobalt. Methods for eliminating interfering elements will allow a highly selective determination of cobalt in real samples.

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