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Flow Injection Analysis of Cobalt(II) by Catalytic Oxidations of Stilbazo and Pyrocatechol Violet

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Catalytic oxidations of ten organic dyes with an aromatic-hydroxyl or -amino functional group have been studied in the presence of metal ions such as cobalt(II), copper(II), and vanadium(V). Of these dyes, six were found to be effectively oxidized and decolorized specifically by one of these metals. 4,4′-Bis(3,4-dihydroxyphenylazo)stilbene-2,2′-disulfonic acid diammonium salt (Stilbazo) and 3,3′,4′-trihydroxyfuchsone-2″-sulfonic acid (Pyrocatechol Violet) were found to be promising for determining trace amounts of cobalt(II). The optimum analytical conditions have been studied for these two compounds with the aid of a flow injection analysis technique. The both reagents can be used to determine cobalt(II) down to 1 ppb.

It is well known that some metal ions, particularly transition metals with different oxidation states, catalyze the oxidation reactions of an arylamine, phenol, or some dyestuffs.[1] Indeed, a number of catalytic methods using a suitable oxidant such as H_2O_2 or BrO_3^- have been reported which permit trace analysis of some transition metal ions.[2-5] Concerning with the cobalt(II) determination, the following organic chromogenic substances have been so far used; Alizarin,[6] 3-(4-sulfophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid,[7] Gallocyanine,[8] chromotropic acid,[9] diphenylcarbazone,[10] Tiron,[11] gallic acid,[12] Luminol.[13] The last two have been used for the chemiluminescent reactions, and they are generally very sensitive. The other substances have been used for the photometric method. The organic chromogenic substances listed above are helpful to search for organic dyes with similar functional group(s) that might be expected to provide new catalytic systems.

Ten kinds of organic dyes were chosen, and the possibility of their metal-catalyzed oxidations have been investigated in view of trace analyses of cobalt(II), copper(II), and vanadium(V). 4,4′-Bis(3,4-dihydroxyphenylazo)stilben-2,2′-disulfonic acid diammonium salt (Stilbazo) and 3,3′,4′-trihydroxyfuchsone-2″-sulfonic acid (Pyrocatechol Violet) appeared promising for the determination of trace amounts of cobalt(II).

A flow injection analysis (FIA) technique was employed to find the optimum analytical conditions for these two organic dyes. The technique makes many different types of analysis be easily performed by controlling reaction conditions such as mixing of reactants at a fixed rate, reaction time, and temperature of reactant, and hence, particularly suitable for kinetic method of analysis which generally takes advantage of the difference between an indicator reaction (a reaction in the absence of the metal in question) and a catalytic reaction. By the use of FIA technique, an indicator reaction can be monitored continuously and the output signal is to be recorded as a baseline on a chart, and if a catalytic reaction does take place, it appears as a signal on the baseline.

Experimental

Reagents and Materials. Distilled and deionized water was used throughout. Commercially available 1000 ppm standard solutions of cobalt(II) and the other metal ions were diluted with water (a little acidic if necessary) to prepare the working solutions. Dotite 2,2′-dihydroxyazobenzene, Stilbazo, Pyrogallol Red, Pyrocatechol Violet, Beryllon II, and di-SNADNS-4 and Wako Pure Chemical's Evans Blue, Bismarck Brown, *m*-Cresol Purple, and Cresol Red were dissolved in water to give suitable concentrations. Potassium bromate and hydrogen peroxide (30%) were used as oxidants. Buffer solutions were prepared according to the literature;[14] CH_3COOH/CH_3COONa (pH 3—6), Na_2HPO_4/KH_2PO_4 (pH 6—8) and Na_2CO_3/$NaHCO_3$ or Na_2CO_3/NaOH (pH 9—12).

Apparatus. The FIA manifold employed in determining cobalt(II) with Stilbazo or Pyrocatechol Violet as a chromogenic substance is shown in Fig. 1. The system was

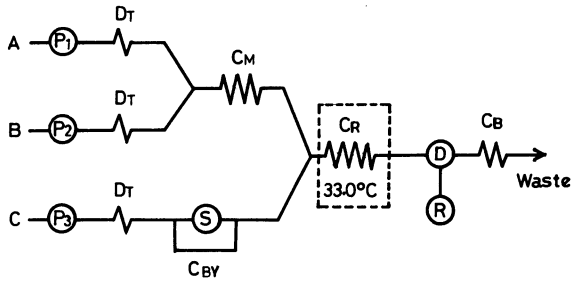


Fig. 1. Block diagram of FIA for determinations of cobalt(II) by catalytic oxidations of Stilbazo and Pyrocatechol Violet.
A: Stilbazo or Pyrocatechol Violet-hydrogen peroxide reagent solutions, B: buffer solution, C: distilled deionized water, P_1–P_3: pump, flow rates being fixed at 1 cm^3 min^{-1} (P_1), 1 cm^3 min^{-1} (P_2), and 2 cm^3 min^{-1} (P_3). D_T: damper tube(30 cm long, 2 mm i.d.), C_M: mixing coil (5 m long, 0.5 mm i.d.), C_{BY}: bypass coil (3 m long, 0.5 mm i.d.), C_R: reaction coil (4 m long, 0.5 mm i.d.), C_B: back-pressure coil(2 m long, 0.5 mm i.d.), S: sample injector(62 μl), D: detector, R: recorder.

built from Teflon tubing (i.d., 0.5 mm), Teflon connectors, two reciprocating pumps (Kyowa Seimitsu KHU-52, P_3, and KHU-W-52, double-plunger type, P_1, P_2), a spectrophotometer (Kyowa Seimitsu KLC-2290)(D), equipped with a flow-through cell (volume 8 μl, optical path-length 10 mm), a six-way loop valve injector (Seishin VHU-6)(S), and a recorder (Rikadenki R-22) (R). Elastic PVC tubes (Technicon 061 116-0536-15) of ca. 30 cm length, D_T, were placed immediately after each pump so that the pumping pulse was completely eliminated. A bypass coil, C_{BY}, which acts as a damper of sample injection shock, and a back-pressure coil, C_B, which serves to prevent the liberation of gas dissolved in reactant and carrier solutions upon heating, were incorporated into the system. The symbols, C_M and C_R, denote mixing and reaction coils, respectively.

Results and Discussion

Metal Ion-Catalized Oxidations of Organic Dyes. A suitable concentration of each chromogenic substance was prepared in pH 4 or pH 11 buffer solution in the presence of an oxidant (1.0×10^{-3} mol dm^{-3} $KBrO_3$ or 3.3% H_2O_2). To this solution a known volume of 1000 ppm metal standard solution was added with the aid of a micropipette so that the concentration of metal ion of interest became 1 ppm, and then the absorbance of the solution was followed as a function of standing time at room temperature or at an elevated temperature, if necessary. The results are summarized in Table 1. These substances listed in the Table were almost completely decolorized within 30 s in the presence of 1 ppm metal specified in the Table, while it took 30 min or more in the absence of the metal. A typical absorbance change with standing time is illustrated for Stilbazo-cobalt(II) system in Fig. 2, where the cobalt(II) concentration is lowered to 5 ppb for the sake of convenience of measuring the absorbance change with time.

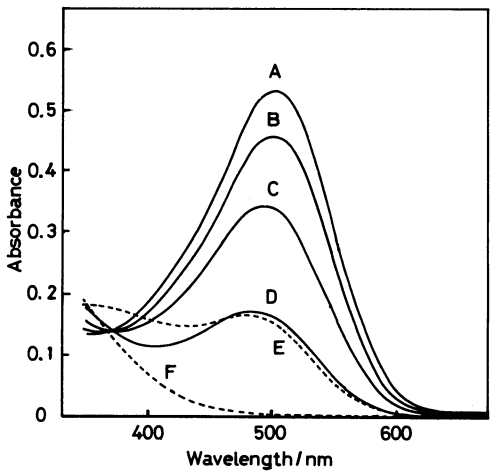


Fig. 2. Absorption spectra change with standing time. Solid line: reagent mixture of Stilbazo(1.0×10^{-5} mol dm^{-3}) and hydrogen peroxide(0.5%) at pH 11.7; A, 1.5 min; B, 15 min; C, 30 min; D, 40 min. Broken line: reagent mixture in the presence of 5 ppb cobalt at pH 11.7; E, 1.5 min; F, 15 min.

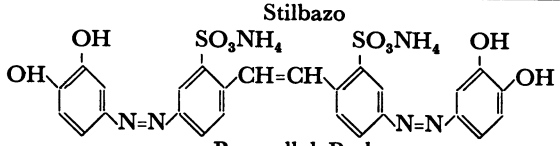
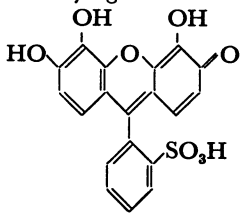
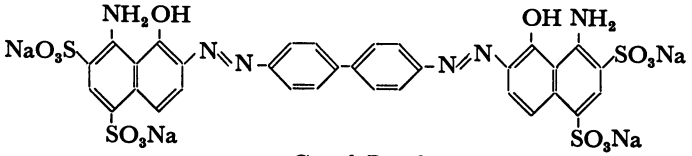
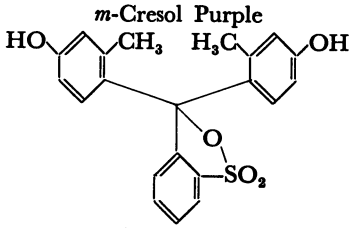
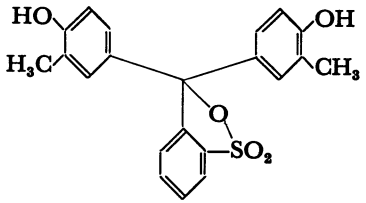
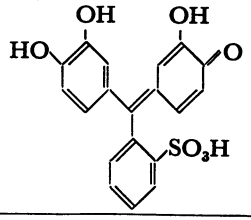
Concerning with cobalt(II) determination, Stilbazo, Pyrocatechol Violet, Pyrogallol Red, and Evans Blue are expected to be of potential utility. Among them, the first two seem better since Evans Blue is only effective at a fairly high temperature and Pyrogallol Red is of limited solubility in water.

The optimum conditions for determining trace amounts of cobalt(II) will be discussed in detail below. The experiments were carried out by using the FIA system shown in Fig. 1. The peak height recorded on a chart, which corresponds to a difference of absorbances between a metal blank and a metal-catalyzed reaction zone is a measure of analytical sensitivity.

Stilbazo Method—Effects of Operational Conditions—. The effects on the peak height were studied of such conditions as pH (9—12), concentrations of Stilbazo (4.8×10^{-5}—1.4×10^{-4} mol dm^{-3}) and hydrogen peroxide (0.05—0.6%), temperature (33, 43, 53, and 63 °C), and the FIA manifold including flow rate (P_1=P_2, 0.5—1.0 cm^3 min^{-1}; P_3, 1.0—2.0 cm^3 min^{-1}), tube length of the reaction coil (2—8 m), and sample volume (62, 91, and 110 μl). The peak height was found to (i) increase almost linearly with pH above 10, (ii) increase as the concentrations of Stilbazo and H_2O_2 increase (the peak hight become constant at Stilbazo concentrations greater than 9.6×10^{-5} mol dm^{-3} and at H_2O_2 concentrations greater than 0.15% at pH 11.9), (iii) increase by 1.4, 1.9, and 2.4 times as the temperature is raised from 33 °C to 43, 53, and 63 °C, respectively, (iv) increase with the tube length of the reaction coil to become constant at length greater than 6 m, but a longer coil tends to lead to broad peaks because of an increased axial dispersion of the sample zone, (v) increase as the flow rate decreases, but at the same time, there observed is the pronounced tailing of the peaks probably due to the adsorption of the reaction product onto the inside of the Teflon tube.

Stilbazo Method—Recommended Procedure for Cobalt(II) Determination—. Two solutions A and B are prepared; A: Stilbazo (9.6×10^{-5} mol dm^{-3})-H_2O_2 (0.15%), B: Na_2CO_3 (0.05 mol dm^{-3})-NaOH (0.006 mol dm^{-3}) mixed solution to give pH 11.9. Solutions A and B are both made to flow at the same flow rate of 1.0 cm^3 min^{-1}, while water at a flow rate of 2.0 cm^3 min^{-1}. A 62 μl portion of sample solutions which contain cobalt(II) higher than 1 ppb is injected via the loop valve injector into the carrier stream of water and mixed with the reagent stream before entering the reaction coil of 4 m which has been immersed in a thermostated bath (33 or 53 °C), and the absorbance is measured at 503 nm. A negative peak appears as a result of absorbance change due to the decolorization of Stilbazo.

Table 1. Metal Ion Catalysis in the Oxidative Decolorization of Organic Dyes

Compound examined	Oxidant	Catalyst	pH	Temperature	Color change of solution
Stilbazo 	H_2O_2	Co(II)	11	Room temp	Red ⟶ Colorless
Pyrogallol Red 	H_2O_2	Co(II)	11	Room temp	Purple ⟶ Colorless
	BrO_3^-	V(V)	4	Room temp	Orange ⟶ Colorless
Evans Blue 	H_2O_2	Co(II)	11	70 °C	Blue ⟶ Colorless
m-Cresol Purple 	H_2O_2	Cu(II)	11	70 °C	Red ⟶ Colorless
Cresol Red 	H_2O_2	Cu(II)	11	70 °C	Red ⟶ Colorless
Pyrocatechol Violet 	H_2O_2	Co(II)	11	Room temp	Violet ⟶ Colorless[a)]

a) This system was studied by a batchwise technique (Ref. 15).

Stilbazo Method—FIA Responses—. Figure 3 shows typical FIA responses obtained under the recommended procedure. It will be seen that cobalt(II) down to 1 ppb can be determined. A dip is observed in front of each peak, which is caused by an injection shock. The relative standard deviation observed for analysis of 60 ppb cobalt was 0.7% (n=13), and a sampling rate of 60 samples/h was achieved.

Stilbazo Method—Interferences—. Sample solutions containing 50 ppb cobalt(II) and various concentrations of foreign ions were injected according to the recommended procedure mentioned above (the temperature of bath was set at 33 °C). The results are shown in Table 2. Zinc(II) and cadmium(II) exhibited serious interferences when present above 500 ppb. The interferences, however, were completely eliminated up to 1 ppm concentration of these metals by making a 500 ppm sodium citrate solution flow instead of water. The serious interference by EDTA is due to its stable complex formation with cobalt(II). The other ions examined have no or only slight interference so far as their concentrations do not exceed 100 to 200 times the cobalt(II) concentration.

Pyrocatechol Violet Method—Effects of Operational Conditions—. The optimum conditions were

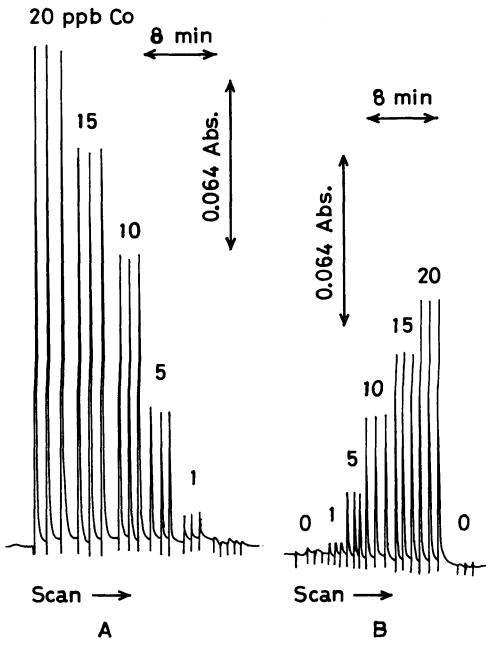


Fig. 3. Typical responses for cobalt(0–20 ppb) by FIA with Stilbazo (9.6×10^{-5} mol dm^{-3})–hydrogen peroxide(0.15%) system at 53 and 33 °C.
Experimental conditions: A, 53 °C; B, 33 °C; pH, 11.9. Other conditions and manifold as in Fig. 1.

Table 2. Effect of Diverse Ions on the Determination of 50 ppb Cobalt in the Catalytic Oxidation of Stilbazo at 33 °C

Foreign ion	Concentration/ppm	Relative error/%	Foreign ion	Concentration/ppm	Relative error/%
Al(III)	10	−4.8	Mg(II)	2	5.9
	5	0		1	3.0
Ag(I)	10	12	Ca(II)	5	11
	5	1.7		1	2.3
Cr(III)	5	−5.1	NH_4^+	50	1.8
	1	−2.6		10	1.9
Cr(VI)	10	0	F^-	50	0
Se(IV)	50	5.4	Cl^-	50	1.8
	10	0	Br^-	50	0
Fe(III)	1	−2.7	I^-	50	0
Ni(II)	5	−17	NO_3^-	50	0
	2	0	NO_2^-	50	−3.0
Mn(II)	0.5	−1.0	SO_4^{2-}	50	5.5
Cu(II)	1	0.9		10	0
Zn(II)	1	25	PO_4^{3-}	50	2.8
	0.5	14	Citrate	50	5.5
	1	0.8*		10	0
Cd(II)	1	17	Tartrate	50	0
	0.5	9.2	Oxalate	50	9.1
	1	0*		10	0
V(V)	10	2.9	Acetate	50	0
Pb(II)	10	0	EDTA	1	−100

* These values were obtained when pumping a 500 ppm of citrate aqueous solution through the pump(P_3). A negative relative error(%) means that the peak hights of 50 ppb cobalt in the presence of the diverse ions are lower than those for 50 ppb cobalt only.

studied by changing the concentration of Pyrocatechol Violet (4.0×10^{-5}—4.0×10^{-4} mol dm^{-3}) and that of H_2O_2 (0.075—0.55%) and pH (9—12). The peak height was found to (i) increase with the concentration of Pyrocatechol Violet up to 3.0×10^{-4} mol dm^{-3} and then decrease gradually beyond this concentration, (ii) increase with H_2O_2 concentration and become constant at 0.3% H_2O_2, (iii) increase with pH and remain constant above pH 11.8, and (iv) increase by 1.4 and 1.8 times as the temperature is raised from 33 °C to 42 and 51 °C, respectively.

Pyrocatechol Violet Method—Recommended Procedure for Cobalt(II) Determination—. Two solutions A and B are prepared; A: Pyrocatechol Violet (3.0×10^{-4} mol dm^{-3})-H_2O_2 (0.3%), B: the same solution as that used in the Stilbazo method (pH=11.8). Just in the same way and at the same flow rates as the Stilbazo method, solutions A and B and water are made to flow and a 62 μl portion of sample solutions is injected and the absorbance is measured at 585 nm.

Pyrocatechol Violet Method—FIA Responses—. Figure 4 shows typical responses obtained under the recommended procedure. The sensitivity of the cobalt(II) determination is approximately in the same order as that of the Stilbazo method. The relative standard deviation observed for analysis of 25 ppb cobalt was 0.5% (n=10), and a sampling rate of 60 samples/h was achieved.

Pyrocatechol Violet Method—Interferences—. Sample solutions containing 50 ppb cobalt(II) and various concentrations of foreign ions were injected (the temperature of bath was set at 33 °C). The results are shown in Table 3. In contrast to the Stilbazo method, zinc(II) and cadmium(II) do not interfere seriously, while iron(III) and manganese(II) exhibit serious interferences. The other ions examined show only slight interferences when present 100 to 200 times the cobalt(II) concentration.

The present paper is concerned with the cobalt(II) determinations based on the catalytic oxidations of Stilbazo and Pyrocatechol Violet. We had thought that these organic substances had not been used for the cobalt(II) analysis. On writing this paper,

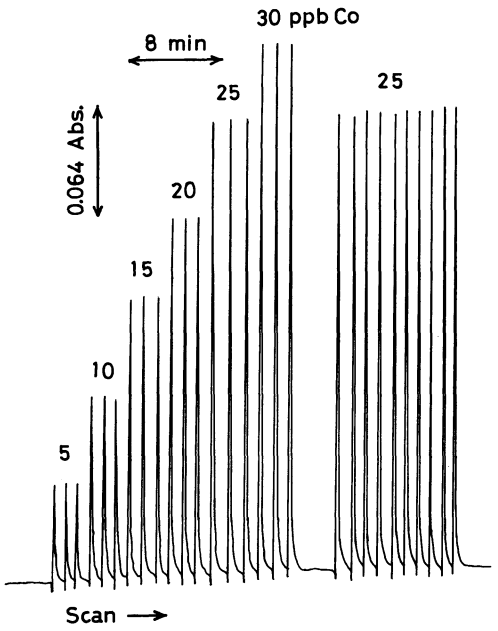


Fig. 4. Typical responses for cobalt(5—30 ppb) by FIA with Pyrocatechol Violet(3.0×10^{-4} mol dm^{-3})-hydrogen peroxide(0.3%) system at 33 °C.
Buffer solution: pH 11.8. Other conditions and manifold as in Fig. 1.

Table 3. Effect of Diverse Ions on the Determination of 50 ppb Cobalt in the Catalytic Oxidation of Pyrocatechol Violet at 33 °C

Foreign ion	Concentration/ppm	Relative error/%	Foreign ion	Concentration/ppm	Relative error/%
Al(III)	2	3.0	V(V)	50	−4.6
	5	6.0	Mg(II)	2	3.6
Cr(III)	5	0.6		5	18
Fe(III)	2	−25	Ca(II)	2	3.0
	5	−35		5	9.0
Ni(II)	5	−3.0	NH_4^+	50	2.4
	10	−15	F^-	50	2.9
Zn(II)	10	3.1	Cl^-	50	2.3
Cd(II)	2	−2.0	NO_2^-	50	3.0
	5	−6.9	NO_3^-	50	2.3
Cu(II)	2	−2.6	SO_4^{2-}	50	3.1
	5	−8.3	Citrate	50	1.7
Pb(II)	10	−4.0	Tartrate	50	2.9
Mn(II)	2	−14	Oxalate	50	0
	5	−25	Acetate	50	1.2

A negative relative error(%) means that the peak hights of 50 ppb cobalt in the presence of the diverse ions are lower than those for 50 ppb cobalt only.

however, we found the latter reagent used for the same purpose in a batchwise technique.[15] The analytical conditions such as H_2O_2 concentration and pH are almost the same between the present work and the literature, but the concentration of Pyrocatechol Violet employed by the literature[15] is lower by one order of magnitude than the present conditions. According to the literature,[15] cobalt(II) of 0.0065 ppb can be determined. The sensitivity is higher by two orders of magnitude than that attained in the present work using FIA technique and almost comparable to that obtained based on chemiluminescence methods.[12,13] The literature method, however, seems much laborious and time-consuming since it needs measurements of reaction rates and calculations of rate constants.

The sensitivity for the cobalt(II) analysis attained in the present work using Stilbazo and Pyrocatechol Violet appears to be comparable to that reported by investigators who used aromatic chromogenic substances with two 1,3-, or 1,4-dihydroxyl group.[8]

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