The Coagulated Ion-exchanger Colorimetry of Cobalt(II)-Thiocyanate Complex

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The coagulated ion-exchanger colorimetry was applied to the determination of a trace amount of cobalt(II). Cobalt(II)-thiocyanate complex was fixed by a batch method on the coagulated material composed of fine particles of anion and cation exchangers. The coagulated material was collected on a filter paper and a colored thin layer was prepared. The coloration of the compound was further intensified by dipping the thin layer in a concentrated thiocyanate solution, and the absorbance was determined by a densitometer. The calibration curve showed a good linearity in the range of 1—15 μg of cobalt(II). Iron(III) and copper(II) showed interfering coloration, but these ions were effectively masked by the addition of fluoride and egta, respectively. Zinc(II) gave seriously negative error.

The blue coloration of cobalt(II)–thiocyanate complex is specific for cobalt(II) and is applied to the spot test.[1] The coloration is intensified in the presence of organic solvents such as acetone and ethanol. The increase in the coloration is also observed when the complex is fixed on an anion exchange resin. Therefore, for cobalt(II), the spot test on the resin phase developed by Fujimoto[2] showed higher sensitivity than that for the ordinary solution method. The ion-exchanger colorimetry[3] was applied to the determination of cobalt(II) in which the thiocyanate complex fixed on the anion exchange resin was determined in a 1-mm cell. The combined use of finely divided anion and cation exchange resins was introduced to the colorimetric determinations of chromium(VI),[4] phosphate,[5,6] and hexacyanoferrate(III).[7] The mixed resins fixing the colored complex were collected on a filter paper as a thin layer and the coloration was determined by spectrophotometry[4,5,6] or densitometry.[7]

In the present study, cobalt(II)–thiocyanate complex is rapidly concentrated on the mixed resins and determined by densitometry. The sensitivity of the method and the effects of foreign ions are discussed.

Experimental

Reagents. All chemicals used were of analytical reagent grade.

Standard cobalt(II) solution, 1 mg Co dm^{-3}, was prepared by dissolving cobalt(II) chloride hexahydrate in 1 dm^3 of deionized water containing 10 ml (1 ml = 1 cm^3) of concentrated hydrochloric acid. More dilute standard solutions were prepared as required by diluting the stock solution.

The 0.5 M (1 M = 1 mol dm^{-3}) sodium fluoride and 8 M potassium thiocyanate solutions were prepared.

The dipping aqueous solution was composed of 80 w/v% potassium thiocyanate and 0.2% sodium fluoride.

Ion Exchange Resin Suspensions. The ion-exchangers used were macroreticular type Amberlyst 15 and A-27 (both Rohm and Haas Co.) in RSO_3H and $RN(CH_3)_3Cl$ forms, respectively. The anion exchange resin suspension (ARS) and the cation-exchange resin suspension (CRS) were prepared according to the reported method.[8] The stock suspensions were stored in 5-dm^3 polyethylene bottles, respectively, and were well shaken before being pipetted out. The exchange capacities, as determined by conductometric titration, were 4.40 μequiv. ml^{-1} for ARS and 8.02 μequiv. ml^{-1} for CRS. The resins in 4—6 ml of ARS were almost completely coagulated with those in 2 ml of CRS.[8] The combination of 4 ml of ARS and 2 ml of CRS was used throughout the following experiments.

Apparatus. A Shimadzu Chromatoscanner CS-920 was used for measurement of reflecting absorbance of colored complex in the thin layer of mixed resins. A Shimadzu UV-visible recording spectrophotometer, type UV-240, was used for measuring absorpion spectra. A Hitachi-Horiba pH meter, type F-7$_{LC}$, was employed. A Toyo KG-25 filter holder was served for the preparation of thin layer of the coagulated material by filtration with suction. Filter papers of No. 5B (Tokyo Roshi) were used. Micropipets were used for pipetting out the standard solution.

Procedure. An aliquot of sample solution containing more than 1 μg of cobalt(II) is placed in a 100-ml beaker. A 2-ml portion of 0.5 M of sodium fluoride is added for masking iron(III) ion in the sample. A 1 ml portion of 8 M of potassium thiocyanate is added. After the volume is adjusted to 40 ml with deionized water, 2 ml of CRS and 4 ml of ARS are added. The mixture is stirred by means of a magnetic stirrer for 10 min. The resulting coagulated material is collected on the filter paper, placed between cylindrical filter holder, by suction. A disk of thin layer of colored resin is formed, which is 17 mm in diameter and about 0.3 mm in thickness. It it then dipped into the dipping solution for 30 min, then the color becomes more intense. The wet filter paper holding the colored resin is placed on a white plastic plate fixed on a scanning board in the densitometer. A light beam (1.2 × 1.2 mm) scans the disk of thin layer in a range of 24 mm wide and 30 mm long and the integrated absorbance is printed out on the chart paper. The measurement is performed using linearizer in mode 1 at 625 nm against the filter paper substrate. All procedures were carried out at room temperature.

Results and Discussion

Absorption Spectra. Absorption spectra of cobalt(II)–thiocyanate complex in the resin phase are shown in Fig. 1. The spectrum against the blank thin layer was the same as that of the complex in acetone having an absorption maximum at 625 nm, which was prepared as described by Snell's.[9]

Effect of Dipping Solution. The coloration in the thin layer of mixed resins faded gradually during the strage in water. Therefore, for the stabilization of color, the resin phase was dipped in the thiocyanate solution together with filter paper before absorption

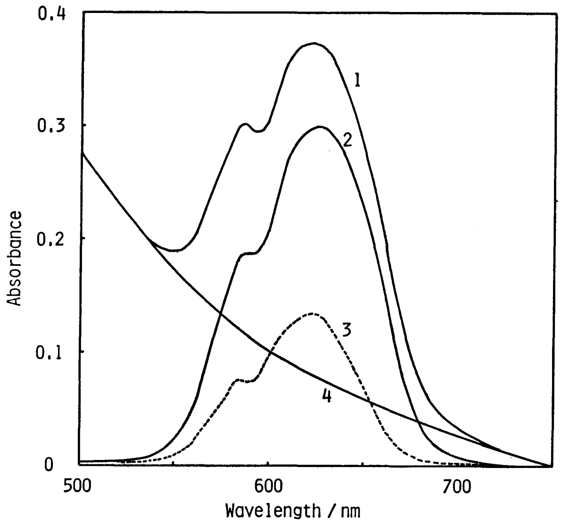

Fig. 1. Absorption spectra of cobalt(II)-thiocyanate complex.
——: Thin layer of mixed resin, ----: acetone solution; (1) and (2) 10 μg of cobalt(II), (3) 200 μg of cobalt(II), (4) blank; (1) and (4) *vs.* wet filter paper, (2) *vs.* blank thin layer, (3) *vs.* blank solution.

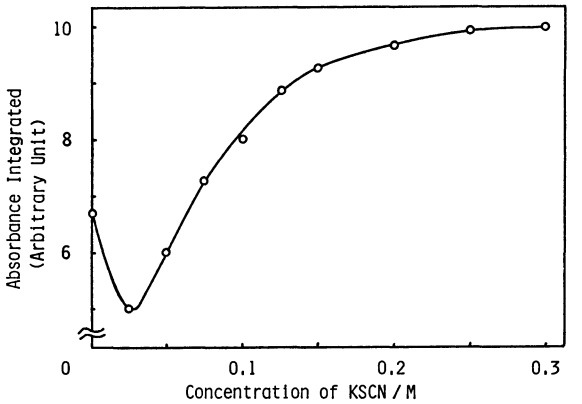

Fig. 2. Recovery of cobalt(II).
Cobalt(II) taken 10 μg; sodium fluoride 1 mmol; sample volume 40 ml; wavelength 625 nm.

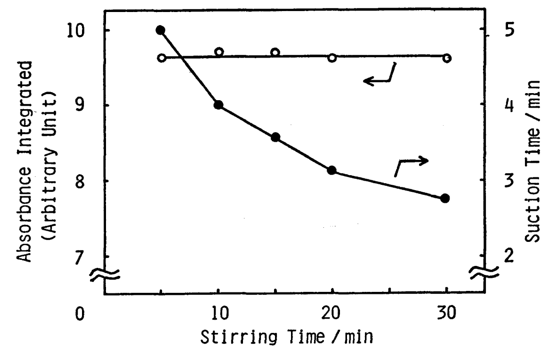

Fig. 3. Effect of stirring time.
Cobalt(II) taken 10 μg; sample volume 40 ml; wavelength 625 nm.

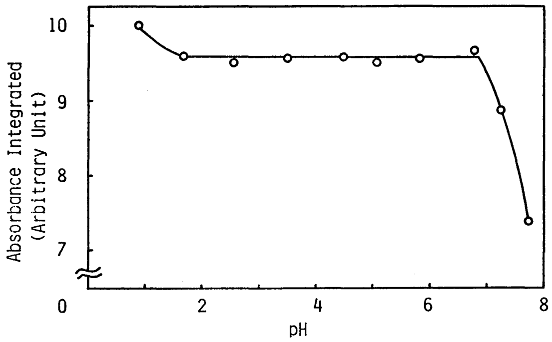

Fig. 4. Effect of pH of sample solution.
Cobalt(II) taken 10 μg; sample volume 40 ml; wavelength 625 nm.

measurement. The dipping solution containing 0.2% sodium fluoride was used for masking impurity iron(III). The coloration was intensified with increasing thiocyanate concentration. However, for the concentration over 85%, the solubility of sodium fluoride decreased. Consequently, 80% potassium thiocyanate solution was used throughout the experiments. About 15 min were necessary for obtaining a constant coloration, which was stable at least for 24 h.

Recovery of Cobalt(II). The effect of thiocyanate concentration on the recovery of cobalt(II) was investigated. The amount of cobalt(II) fixed on the mixed resin was first decreased with the addition of thiocyanate and then increased with increasing thiocyanate concentration (Fig. 2). The minimum recovery is probably due to the formation of neutral cobalt(II)–thiocyanate complex. The subsequent experiments were carried out in 0.2 M thiocyanate solution, since the longer filtration time was required with increasing thiocyanate concentration.

Effect of Stirring Time. During the course of stirring, cobalt(II)–thiocyanate complex is fixed on the anion exchanger in the coagulated mixed resins. The rate of adsorption is very fast and a constant coloration was obserbed in the range of 5 to 30 min studied. On the other hand, the suction time for collecting the mixed resins decreased with increasing stirring time (Fig. 3), since the mixed resins coagulated to form a bulky material during the longer stirring time.

Effect of pH. The effect of pH on the absorbance of complex at 625 nm is shown in Fig. 4. The pH was adjusted by the addition of hydrochloric acid or phosphate buffer solution. A constant absorbance was observed in the range of pH 1.7 to 6.7. The higher value was found at pH 0.9. This is due to the red coloration of iron(III)–thiocyanate complex, the masking of iron(III) by fluoride ion being impossible in this pH region. Above pH 7, cobalt hydroxide being formed, the absorbance decreased.

Calibration Curve. The calibration curve showed a good linearity in the range of 1—15 μg of cobalt(II). The relative standard deviation was 0.89% (n=6) for 10 μg of cobalt(II). The lowest determinable concentration was 25 μg dm^{-3} in 80 ml of sample volume.

Effect of Sample Volume. The effect of sample volume was studied, the thiocyanate concentration being kept to 0.2 M. A constant absorbance was obtained in the range of 30 to 80 ml. For the volume above 80 ml, the filtration time increased seriously. Moreover, the surface of the resulting thin layer did not become uniform and the absorbance decreased.

Effect of Foreign Ions. Most anions studied did

TABLE 1. EFFECT OF FOREIGN ANIONS ON THE DETERMINATION OF COBALT(II)$^{a)}$

Anion	Anion added(mg)	Cobalt(II) found(μg)	Error (%)
Chloride	350	10.17	+1.7
Fluoride	50	10.05	+0.5
Iodide	60	9.99	−0.1
Nitrate	10	9.91	−0.9
Sulfate	10	10.09	+0.9
Phosphate	10	10.06	+0.6
Pyrophosphate	10	9.80	−2.0
Thiosulfate	10	10.25	+2.5
Acetate	10	9.96	−0.4
Citrate	10	10.00	0
Tartrate	10	9.57	−4.3
Borate	10	10.44	+4.4
Oxalate	10	9.48	−5.2
Hexacyanoferrate(II)	1	5.05	−49.5
Hexacyanoferrate(II)	0.1	9.77	−2.3

a) Cobalt(II) taken: 10 μg.

TABLE 2. EFFECT OF FOREIGN CATIONS ON THE DETERMINATION OF COBALT(II)$^{a)}$

Cation$^{b)}$	Cobalt(II) found(μg)	Error (%)	Cation$^{b)}$	Cobalt(II) found(μg)	Error (%)
Mg	9.97	−0.3	$\mathrm{Cu^{II}}$	9.25	−7.5
Ca	9.84	−1.6	$\mathrm{Cu^{II}}$	10.35$^{c)}$	+3.5
Ba	10.22	+2.2	$\mathrm{Zn^{II}}$	4.13	−58.7
$\mathrm{Si^{IV}}$	10.18	+1.8	$\mathrm{Zn^{II}}$	10.08$^{d)}$	+0.8
$\mathrm{Al^{III}}$	10.16	+1.6	$\mathrm{Cd^{II}}$	9.88	−1.2
$\mathrm{Cr^{III}}$	10.64	+6.4	$\mathrm{Hg^{II}}$	9.32	−6.8
$\mathrm{Mn^{II}}$	10.32	+3.2	$\mathrm{Mo^{VI}}$	10.03	+0.3
$\mathrm{Fe^{II}}$	10.41	+4.1	$\mathrm{Pb^{II}}$	10.37	+3.7
$\mathrm{Fe^{III}}$	10.39	+3.9	$\mathrm{Ag^{I}}$	9.90	−1.0
$\mathrm{Ni^{II}}$	10.68	+6.8			

a) Cobalt(II) taken: 10 μg. b) Foreign cations added: 100 μg. c) The pH of sample solution was adjusted to 4 and 5 μmol of egta were added. d) The sample solution was passed through a column packed with anion exchange resin, Dowex 1-X8 (100—200 mesh, Cl-form). Eluting agent: 0.1 M HCl containing 5% NaCl.

TABLE 3. ANALYSIS OF COBALT(II) IN SYNTHETIC SAMPLE SOLUTION

Sample$^{a)}$ number	Concentration/μg ml^{-1}							Cobalt(II) found(μg)$^{b)}$	Error (%)
	$\mathrm{Co^{II}}$	Ca	Mg	$\mathrm{Zn^{II}}$	$\mathrm{Fe^{III}}$	$\mathrm{Cu^{II}}$	$\mathrm{Ni^{II}}$		
I	0.4	4.0	4.0	—	—	—	—	10.00	0
II	0.4	4.0	4.0	4.0	—	—	—	9.96	−0.4
III	0.4	4.0	4.0	4.0	4.0	—	—	10.18	+1.8
IV$^{c)}$	0.4	4.0	4.0	4.0	4.0	4.0	—	10.36	+3.6
V$^{c)}$	0.4	4.0	4.0	4.0	4.0	4.0	4.0	10.50	+5.0

a) All solutions contained HCl in 0.1 M and NaCl in 5%. b) Effluent taken: 25 ml, mean value of duplicate analyses. c) The pH of effluent was adjusted to 4 and 5 μmol of edta were added.

not interfere with the determination of 10 μg of cobalt(II) (Table 1). However, 100-fold hexacyanoferrate(II) gave negative error, since cobalt(II)–hexacyanoferrate(II) is more stable than the thiocyanato complex. The effect of divers cations was summarized in Table 2. Interference by iron(III) was eliminated with sodium fluoride, as stated before. Copper(II) salts, giving a red-brown coloration with thiocyanate, were masked by the addition of egta (3,6-dioxaoctane-1,8-diamine-*N*,*N*,*N*′-*N*′-tetraacetic acid). The 10-fold amount of chromium(III) and nickel(II) gave positive errors, while mercury(II) a negative one. Zinc(II) gave a serious negative error. No interference being found in the solution method, an additional reaction would occur between thiocyanate complexes of cobalt(II) and zinc(II) on the resin phase. Zinc(II) ions were easily removed from the sample solution as their chlorocomplex by use of an anion exchange resin of strong base type.[10)]

Analysis of Synthetic Sample Solution. The synthetic sample solutions containing 0.4 μg ml^{-1} of cobalt(II) and 4 μg ml^{-1} of various foreign ions were analyzed (Table 3). An anion exchange resin column was prepared to remove zinc(II). The column (25 cm × 1 cm i.d.) was packed with 1.5 g of Dowex 1-X8 (100—200 mesh) in the chloride form and washed with 50 ml of 2 M hydrochloric acid solution. The sample solution containing 0.1 M hydrochloric acid and 5% sodium chloride was passed through the column. The first 10 ml were discarded and the next 25 ml of effluent were taken and neutralized with sodium hydroxide. Then, the solution was submitted to the analysis according to the above method. The results obtained were satisfactory.

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