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Spectrophotometric Determination of Cobalt(II) with Eriochrome Black T after Extraction as Methyltrioctylammonium Tetrathiocyanatocobaltate(II)

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A sensitive extraction-spectrophotometric method for determination of cobalt(II) with Eriochrome Black T is described, which involves the preliminary separation of cobalt from aqueous solution by the benzene extraction of methyltrioctylammonium tetrathiocyanatocobaltate(II). The quantitative formation of ion pair between cobalt–Eriochrome Black T complex anion and the quaternary ammonium cation is attained by shaking the resulting extract with aqueous Eriochrome Black T solution of pH 5.5—8.2. Beer's law holds for 0.57—4.0 μg cobalt in 5 ml of the extract with the molar absorption coefficient of $\varepsilon_{587}=6.62\times10^4$ cm^{-1} mol^{-1} l (Sandell sensitivity 8.90×10^{-4} μg cm^{-2}). The composition of the extracted ion pair is estimated to be cobalt: Eriochrome Black T: methlytrioctylammonium ion=1:2:3.

The use of 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulfonic acid, sodium salt (Eriochrome Black T, abbreviated to EBT) for extraction-spectrophotometric determination of metal ions has been described by several authors.[1–5] Fukamachi *et al.*[3] and Pyatnitskii *et al.*[5] reported that the color intensity of magnesium(II) complex in the organic phase is higher than that in the aqueous solution.

In the present paper a sensitive method for extraction-spectrophotometric determination of cobalt(II) with EBT is described, in which cobalt(II) is first separated into benzene as the methyltrioctylammonium tetrathiocyanatocobaltate(II) and the resulting extract, without stripping, is subjected to the procedure for color development.

Experimental

Reagents. Commercial Eriochrome Black T(Dojindo Laboratories Ltd.) was used without further purification. The solution (0.1 mM nominal, 1 M=1 mol dm^{-3}) was daily prepared by dissolving the reagent in water and the concentration was corrected. The purity of EBT was evaluated as described in a previous paper[6] and found to be 52.6%.

A 5% benzene solution of methyltrioctylammonium chloride (Capriquat, Dojindo Laboratories Ltd., abbreviated as Q^+Cl^-) was converted into its thiocyanate form according to the method of Wilson and McFarland.[7] The stock solution was diluted with benzene as required.

A 0.01 M standard solution of cobalt(II) was prepared from its nitrate and standardized by means of the conventional chelatometric titration.

A mixture of 5 (v/v)% hydrogen peroxide and 10 μM manganese(II) buffered at pH 8.0 was freshly prepared before use by mixing the appropriate amounts of 30 (w/w)% hydrogen peroxide and 0.01 M manganese(II) chloride solutions and satd sodium tetraborate–0.1 M hydrochloric acid buffer solution.

Saturated sodium tetraborate–0.1 M hydrochloric acid or 0.1 M sodium hydroxide buffer and 0.2 M acetic acid–0.2 M sodium acetate buffer solutions were used. Deionized water was used. Other reagents used were all of analytical grade.

Apparatus. A Hitachi two-wavelength and double beam spectrophotometer 356 and a Shimadzu spectrophotometer, Model QV-50, 10-mm cells were used for absorptiometric measurements. A Yamato shaker, Model SA-31, was used for extraction. A Hitachi-Horiba glass electrode pH meter, Model F-5, was used for pH measurements.

Procedure. In a 100-ml separating funnel are taken 10 ml of the solution containing less than 4.0 μg of cobalt(II), 7 ml of a mixture of 1.5 M potassium thiocyanate, 1 M sodium citrate solutions and 0.15 M tris(hydroxymethyl)aminomethane–sulfuric acid buffer solution (pH 8.0). The mixture is shaken for 15 min with 5 ml of 0.5% benzene solution of methyltrioctylammonium thiocyanate(Q^+SCN^-). The organic phase is washed with 5 ml of a mixture of 0.5 M potassium thiocyanate, 0.7 M sodium citrate and 0.9 M sodium thiosulfate. After addition of 5 ml of 52.6 μM EBT solution and 10 ml of satd sodium tetraborate–0.1 M hydrochloric acid buffer solution (pH 7.5), the two phases are shaken for 5 min. The organic phase is washed twice with water and then shaken for 50 min with 15 ml of 5% hydrogen peroxide–10 μM manganese(II) solution of pH 8.0. The organic phase is transferred into a beaker containing anhydrous sodium sulfate and the absorbance of the extract is measured at 587 nm against a reagent blank.

Results and Discussion

Decomposition of the Excess EBT. The use of manganase(II)-catalyzed discoloration reaction for the decomposition of the excess *o,o'*-dihydroxy azo reagents was investigated in order to improve the sensitivity and selectivity of spectrophotometric determination of copper(II).[6,8,9] To apply this reaction to decompose the excess EBT in the benzene phase, effects of pH and shaking time were investigated. The decomposition of EBT proceeds efficiently (Fig. 1), when the extract is shaken for longer than 40 min with the aqueous solution of pH higher than 7.5 (5% in hydrogen peroxide and 10 μM in manganese(II)). Washing of the extract with water before this procedure is necessary for the complete decomposition of EBT.

Separation of Cobalt(II). A large number of metal ions such as copper(II), nickel(II), iron(III), and chromium(III) cause serious interference with the determination of cobalt(II) by forming colored, benzene-extractable complexes with EBT. In order to remove the interference a prior separation of cobalt(II) by means of the modified Vogel reaction was found to be useful. The procedure given here is based on the suggestion given by Wilson and McFarland,[7] except that the

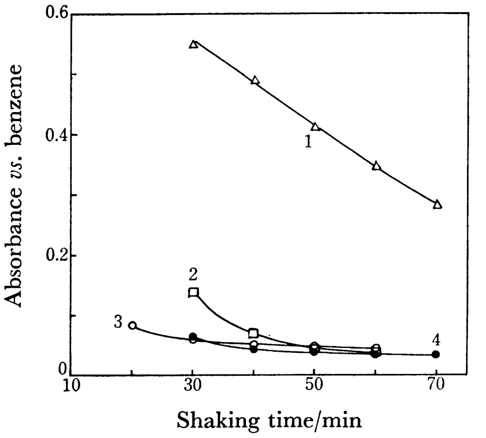

Fig. 1. Effects of pH and shaking time on the decomposition of 52.6 μM EBT in benzene with the aqueous solution of 5% hydrogen peroxide and 12 μM manganese(II).
$[QSCN]_0=0.01$ M, 587 nm, benzene as reference. pH (1): 7.0, (2): 7.5, (3): 8.0, (4): 9.0.

concentration of methyltrioctylammonium thiocyanate in benzene is lower than that recommended. The thiocyanate system is useful for the spectrophotometric determination of 1.2—59 μg of cobalt per milliliter. However, the extraction of smaller amounts of cobalt has not been reported. In order to determine the extractability of cobalt(II) at a few hundred ppb levels, the aqueous phase was repeatedly extracted with the benzene solution of methyltrioctylammonium thiocyanate and the extract was subjected to absorbance measurement. It was found that 2.3 μg of cobalt(II) is almost completely extracted by a single extraction with the 0.5% quaternary ammonium salt solution in benzene.

Absorption Spectra. Based on the observation that the methyltrioctylammonium cobaltothiocyanate in the benzene extract reacts with EBT forming an ion-pair of cobalt–EBT complex anion and the quaternary ammonium cation, the procedure for color development was determined as above. Absorption spectra of cobalt(II)–EBT complex in the aqueous solution and the ternary complex in the extract after the decomposition of excess EBT are shown in Fig. 2. A bathochromic shift of the absorption maxima, accompanied by the enhancement of the absorption intensity, is observed when the cobalt(II)–EBT complex anion is extracted as an ion-pair with the quaternary ammonium cation. The red-purple coloration of the ternary complex, the absorption maxima being 544 and 587 nm, is stable for at least 20 min.

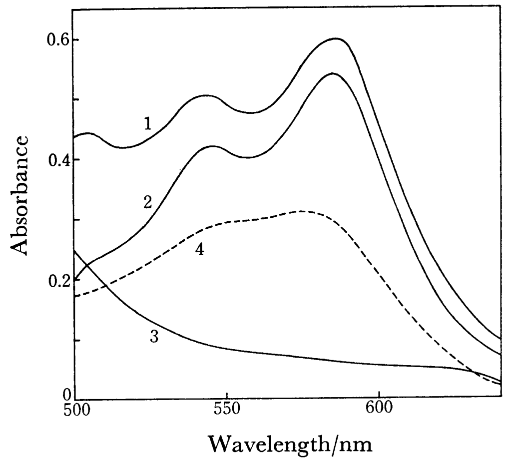

Fig. 2. Absorption spectra of cobalt–EBT complex in aqueous solution and the ternary complex in organic phase after decomposition of excess EBT.
1: Ternary complex *vs.* benzene; 2: ternary complex *vs.* reagent blank; 3: reagent blank *vs.* benzene; $[Co(II)]_0=7.79$ μM, $[EBT]_0=52.6$ μM, pH 8.0; 4: cobalt–EBT complex in aqueous solution *vs.* reagent blank; $[Co(II)]_w=7.79$ μM, $[EBT]_w=40$ μM, pH 10.5.

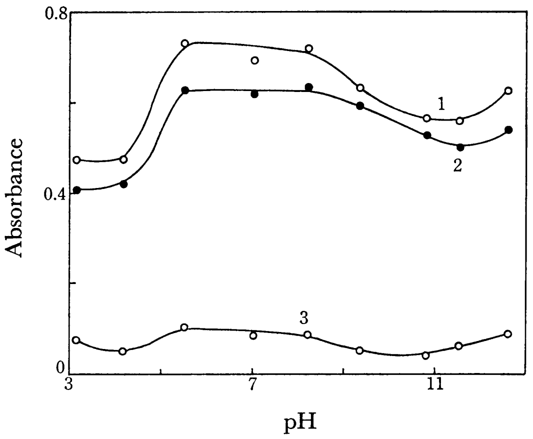

Fig. 3. Effect of pH on the absorbance of cobalt–EBT–Q ternary complex at 587 nm after decomposition of excess EBT. 1: Ternary complex *vs.* benzene; 2: ternary complex *vs.* reagent blank; 3: reagent blank *vs.* benzene; $[Co(II)]_0=9.73$ μM, $[EBT]_w=17.53$ μM, $[QSCN]_0=0.01$ M. Volume ratio of aqueous-to-organic phase is 3: 1.

Effects of pH *and EBT Concentration.* A constant and stable absorbance of cobalt–EBT–Capriquat ternary complex is obtained by shaking the extract with the EBT solution of pH 5.5—8.2 as shown in Fig. 3. For full development of color, addition of EBT in a small excess of the stoichiometrically necessary amount is sufficient.

Effect of Methyltrioctylammonium Thiocyanate Concentration. As described above, 0.5% methyltrioctylammonium thiocyanate in benzene is sufficient for the quantitative extraction of microgram amounts of cobalt(II) as the thiocyanate complex. It was found that the red-purple coloration of the ion-pair of cobalt–EBT complex anion and the quaternary ammonium cation is fully developed by shaking the extract for longer than 3 min with EBT solution. The ion-pair, once formed, is not stripped even by shaking with water and the mixture of hydrogen peroxide and manganese(II).

Calibration Curve and Sensitivity. The calibration curve conforms to Beer's law in the concentration range 0.57—4.0 μg cobalt in 5 ml of the extract, with the molar absorption coefficient of 6.62×10^4 cm^{-1} mol^{-1} l at 587 nm, which is higher than 4.04×10^4 cm^{-1} mol^{-1} l at 573 nm in the aqueous solution. The average of absorbance

Table 1. Effect of various ions

Ion added (X)	Amount µg	Cobalt(II) found µg	Error %
Al(III)	458	2.34	+2.2
Cd(II)	458	2.26	−1.3
Cr(III)	115	2.28	−0.4
Cu(II)	458	2.34	+2.2
Fe(III)	687	2.34	+2.2
Mn(II)	22.9	2.21	−3.5
Ni(II)	11.5	2.38	+3.9
Pb(II)	458	2.27	+0.9
Sn(II)	458	2.25	−1.7
Zn(II)	458	2.35	+2.6
MoO_4^{2-}	756	2.28	−0.4
VO_3^-	46	2.24	−2.2
WO_4^{2-}	618	2.21	−3.5
Cl^-	4580	2.26	−1.3
ClO_4^-	11450	2.28	−0.4
HPO_4^{2-}	2314	2.24	−2.2
SO_4^{2-}	6870	2.29	±0

Cobalt(II) taken: 2.29 µg.

obtained by three determinations was 0.386 and the range was 0.009 for 1.72 µg of cobalt(II) in the extract.

Effect of Foreign Ions. The results of tolerance test according to the above procedure are given in Table 1. The cations were added as nitrates, chlorides or sulfates and anions as sodium, potassium, or ammonium salts. Iron(III), copper(II), and nickel(II) form thiocyanate complexes which are extracted into benzene as the quaternary ammonium salts, interfering with the subsequent photometric analysis. The interference by these ions is removed by washing with the scrub solution mentioned above. Zinc(II) is extracted as the thiocyanate complex and reacts with EBT, forming a deep red complex. However, the complex is unstable and decomposed by shaking with the hydrogen peroxide–manganese(II) mixture.

Composition of the Extracted Species. Extraction of cobalt(II)–thiocyanate complex anion with amines and quaternary ammonium compounds has been investigated by many authors.[7,10–15] The blue color of the nonaqueous cobaltothiocyanate solution is attributable to $[Co(SCN)_4]^{2-}$ ion.[10,11,14,15] We might conclude that the faintly blue extract obtained with methyltrioctylammonium thiocyanate is due to the ion-pair of tetrathiocyanatocobaltate(II) anion with the methyltrioctylammonium cation. By using the familiar mole-ratio method, the molar ratio of EBT to cobalt(II) was found to be 2: 1 (Fig. 4). The molar ratio of methyltrioctylammonium cation to cobalt(II)–EBT chelate anion was determined by the method of equilibrium shift (Fig. 5). The distribution ratio *D* of cobalt(II) was evaluated from the molar absorption coefficient and the absorbance at 587 nm. The slope of the plot evaluated by the method of least squares is 2.87, indicating that the ternary complex has the composition of Co: EBT: Q=1: 2: 3. According to Kodama,[16] cobalt(II) ion forms a 1 to 1 complex with EBT in a weakly alkaline aqueous solution. If we assume that cobalt(II) ion forms the chelate anion with EBT which is extracted as the ion-pair with methyltrioctylammonium cation, the composition can be expressed by $[Co^{2+}(HEBT^{2-})(EBT^{3-})(Q^+)_3]_0$. The composition is comparable with $[Mg^{2+}(HEBT^{2-})(EBT^{3-})(Z^+)_3]_0$, that of magnesium complex reported by Pyatnitskii *et al.*,[5] where Z^+ indicates trioctylammonium ion. However, the possibility of +3 oxidation state of cobalt in the extract can not be excluded.

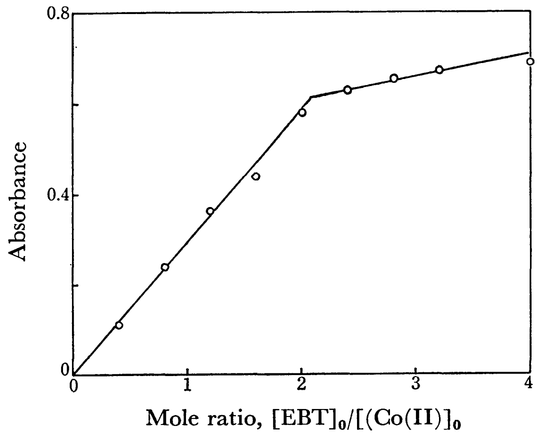

Fig. 4. Mole-ratio method applied to cobalt–EBT system in the extract. $[Co(II)]_w$=9.73 µM, $[KSCN]_w$=0.6 mM, $[QSCN]_0$=0.01 M, pH 8.9, 587 nm *vs.* benzene. The excess EBT was decomposed as above.

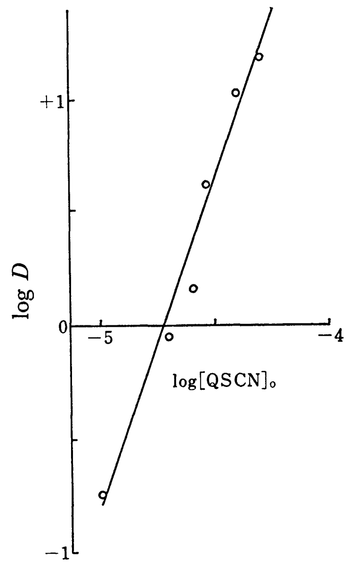

Fig. 5. The logarithm of distribution ratio *D* plotted *vs.* log $[QSCN]_0$ at pH 9.0 in the presence of 9.73 µM cobalt(II), 19.5 µM EBT and 0.5 mM KSCN.

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References

1) M. Nishimura and S. Nakaya, *Bunseki Kagaku*, **16**, 463 (1967).

2) C. Woodward and H. Freiser, *Talanta*, **15**, 321 (1968).

3) K. Fukamachi, H. Kohara, and N. Ishibashi, *Bunseki Kagaku*, **19**, 1529 (1970).

4) C. Woodward and H. Freiser, *Talanta*, **20**, 417 (1973).
5) I. V. Pyatnitskii, S. G. Pinaeva, and N. V. Pospelova, *Zh. Anal. Khim.*, **12**, 2316 (1975).
6) M. Sugawara, Y. Rokugawa, and T. Kambara, *Bull. Chem. Soc. Jpn.*, **50**, 3206 (1977).
7) A. M. Wilson and O. K. McFarland, *Anal. Chem.*, **35**, 302 (1963).
8) M. Sugawara, Y. Ozawa, and T. Kambara, *Bunseki Kagaku*, **23**, 1058 (1974).
9) M. Sugawara, Y. Sato, and T. Kambara, *Bunseki Kagaku*, **26**, 346 (1977).
10) A. R. Selmer-Olsen, *Anal. Chim. Acta*, **31**, 33 (1964).
11) H. Matsuo, S. Chaki, and S. Hara, *Bunseki Kagaku*, **14**, 935 (1965).
12) A. W. Ashbrook, *Analyst*, **84**, 177 (1959).
13) M. Fujimoto and Y. Nakatsukasa, *Anal. Chim. Acta*, **27**, 373 (1962).
14) H. Watanabe and K. Akatsuka, *Anal. Chim. Acta*, **38**, 547 (1967).
15) N. Gundersen and E. Jacobsen, *Anal. Chim. Acta*, **42**, 330 (1968).
16) M. Kodama, *Bull. Chem. Soc. Jpn.*, **40**, 2575 (1967).