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# The Extraction Spectrophotometric Determination of Cobalt(II) with 4-(2-Thiazolylazo)resorcinol and Zephiramin

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**Synopsis.** The cobalt(II)-4-(2-thiazolylazo)resorcinol chelate anion is quantitatively extracted into chloroform with a cation of zephiramin as an ion-pair complex. This process was applied to the spectrophotometric determination of cobalt. The effective separation and the sensitive determination for a trace amount of cobalt could be confirmed even in the presence of high concentrations of masking agents.

There are several ternary chelate extraction systems using *o*-hydroxyphenylazo dyes. Yotsuyanagi and Hoshino[1] systematically studied the 4-(2-pyridylazo)-resorcinol (PAR) chelates and found that the molar absorptivity of the ion-pair chelate increased when the non-coordinative *p*-hydroxyl group dissociated once. The homologous 4-(2-thiazolylazo)resorcinol (TAR) also has a noncoordinative *p*-hydroxyl group. The color reaction of TAR with cobalt[2] and its stability[3] in the aqueous phase have been investigated. The author[4] also studied the solvent extraction of 3d type transition metal–TAR chelate anions with the cation of zephiramin($Z^+Cl^-$) and recognized that TAR is superior as an ion-pair extraction reagent, especially for cobalt. In this research, the fundamental conditions for the spectrophotometric determination of cobalt were investigated. The interferences from the other transition metals could be effectively removed.

## Experimental

*Reagents.* TAR (Dojindo Co., Ltd.) was twice recrystallized from a 50 % ethanol-water mixture. $Z^+Cl^-$(Dojindo Co., Ltd.) was used as obtained. The standard cobalt(II) solution was prepared from cobalt sulfate and was standardized by EDTA titration.

*Apparatus.* A sample solution was prepared in a 50 ml graduated centrifuge tube with a glass-stopper; the solution was shaken in an Iwaki-KM type reciprocating shaker. A Kubota K-80 type centrifuge with 5000 r.p.m. was used for phase separation. A Hitachi-Horiba model M-5 pH meter equipped with a combined glass electrode was used for pH measurements. Absorption spectra and absorbance were measured with a Hitachi 124 recording spectrophotometer and a Hitachi Perkin Elmer 139 spectrophotometer using 10-mm quartz cells.

*Standard Procedure.* Transfer the sample solution containing up to 20 μg of cobalt in a centrifuge tube along with 1 ml of 0.05 % TAR, 2 ml of 0.1% $Z^+Cl^-$, and a suitable masking agent(*e.g.*, 5 ml of 10 % sodium salt of citrate, tartrate, or acetate). Adjust the pH of the solution to 8.0 with 2 ml of 0.05 M borax–phosphate buffer and dilute to 20 ml with redistilled water. Allow the solution to stand for 10 min, and shake it with 10 ml of chloroform for 10 min. After centrifugal separation, transfer the extract into an absorption cell, and measure the absorbance at 550 nm against the reagent blank.

## Results and Discussion

*Absorption Spectra.* The Co–TAR chelate anion and its ion-pair with $Z^+Cl^-$ in the aqueous phase have their absorption maxima at 540 nm; these shift to 550 nm in the chloroform extract.

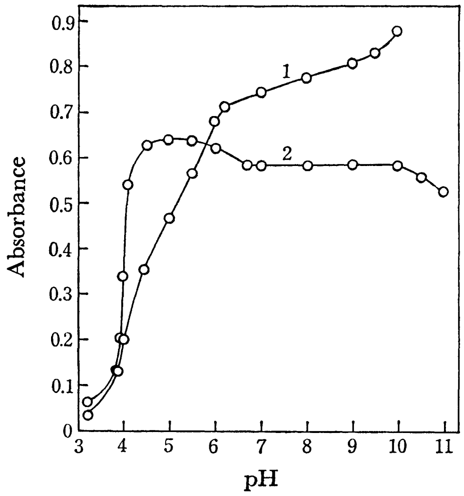

Fig. 1. Effect of pH on the extraction of Co–TAR–$Z^+Cl^-$ chelate.
1: Reagent blank (reference; chloroform), 2: Co; 10.1 μg (reference; reagent blank). 0.05% TAR: 1 ml, 0.1 % $Z^+Cl^-$: 2 ml. pH 3.5—6.0: 0.025 M succinic acid–borax, pH 6.0—9.2: 0.05 M borax–phosphate buffer.

*Effect of* pH. The effect of pH on the extraction of the ternary chelate was examined as shown in Fig. 1. The extract shows a constant absorbance at pH 6.7—10.0 with a broad peak at pH 5, where the absorbance of the reagent blank changes remarkably with an increase in pH. When hexamine–nitric acid buffer is used, the extract has a molar absorptivity of about $7\times10^4$ at 535 nm. An extractable higher order chelate, perhaps the quaternary chelate, may be formed. However, we could not obtain reproducible conditions because the complexation conditions were complicated.

*The Effect of TAR Concentration.* The effect of TAR concentration was examined and the constant absorbance was obtained by adding from 0.7 to 4 ml of 0.05% TAR solution for 10 μg of cobalt in 20 ml solution.

*The Effect of the $Z^+Cl^-$ Concentration.* The extract showed a constant absorbance with the addition of 0.1% $Z^+Cl^-$ over the ranges of 0.5—5 ml. The ternary chelate partially dissolved into aqueous phase upon the further addition of $Z^+Cl^-$.

*The Effect of Shaking Time, Color Stability, and the Aqueous Phase Volume.* The absorbance of the extract was constant for shaking times from 5 min to one hour. The extracted species was very stable and its absorbance was constant for at least 24 h at room temperature. A constant absorbance was also obtained up to 40 ml of the aqueous phase volume.

*Organic Solvents.* The chelate was effectively extracted into such polar solvents as chloroform, dichloromethane ($2.92\times10^4$, 552 nm), 1,2-dichloroethane ($2.80\times10^4$, 550 nm), and ethyl acetate ($3.27\times10^4$, 543 nm), but not into such nonpolar solvents as carbon tetrachloride, carbon disulfide, and hexane. The chelate was also extracted into such aromatic hydrocarbons as benzene, toluene, xylene, and chlorobenzene, where the extracts show a brilliant red color, but contain insoluble components. The other ketones and esters formed an emulsion or a third phase at the interface.

*Extractability and Molar Absorptivity.* The extractability of the ternary chelate was examined by the atomic absorption spectrometry; it was found that 99.6% of cobalt was extracted by a single extraction. The molar absorptivity of the ternary chelate is $3.42\times10^4$ $\text{l mol}^{-1}\text{ cm}^{-1}$, which is more sensitive than the ion-pair extraction methods, such as 1-(2-pyridylazo)-2-naphthol–Triton X-100 ($1.90\times10^4$),[5] but less sensitive than that of PAR–$Z^+Cl^-$ ($5.9\times10^4$)[6] methods.

*Calibration Curve.* A calibration curve for the determination of cobalt was made under the optimum conditions. The curve obeys Beer's law up to 20 μg of cobalt per 10 ml of chloroform, and Sandell's sensitivity for the absorbance of 0.001 is 0.0017 $\mu\text{g cm}^{-2}$. The variation coefficient of the absorbance is 0.92% for the 8 measurements.

*Effect of Masking Agents.* A constant absorbance is obtained in the presence of 5 ml each of 10% sodium salt of citrate, tartrate, acetate, oxalate, and thiourea. When the extract is washed with 5 ml of 0.05 M EDTA, the absorbance is constant because the chelate is rather stable once extracted. In the presence of sodium chloride, the extractions of ternary complexes of nickel, copper, and zinc were rapidly decreased as the number of the chloride ions increased, while the extraction of the cobalt complex was scarcely affected.[4] Thus, in the present method, the combined use of high concentrations of various masking agents is possible.

TABLE 1. EFFECT OF DIVERSE IONS

| Ions added | Tolerance limit, ppm |
|---|---|
| Mn(II), Zn(II),[a] Cd(II),[a] Al(III), Ti(IV),[b] Pb(II), Sb(V), Cr(VI), Mo(VI), W(VI), As(V), Se(IV), Rh(III), Ca(II), Mg(II), Sr(II), Ba(II) | 100 |
| Fe(II),[a] Fe(III),[a] Ni(II),[a] Cu(II),[c] Hg(II),[a] Cr(III), Sc(III),[d] In(III), Zr(IV), Hf(IV), Sn(IV), Th(IV) | 50 |
| Sn(II),[b] Ru(III), $CN^-$, $SCN^-$ | 20 |
| Be(II), Bi(III), Pt(IV) | 10 |

Cobalt taken: 1.01 ppm. a) Extracts were washed with 5 ml of 0.05 M EDTA solution. b), c), and d): Five ml each of 10% citric acid, thiourea, and tartaric acid solution were added, respectively.

*Effect of Diverse Ions.* The effect of diverse ions was investigated as shown in Table 1, where the tolerance limit was set to ±3% for cobalt recovery. Up to 10-fold amounts of nickel, and 20-fold of iron(II) and iron(III), were also tolerated by the addition of 5 ml each of 1% dimethylglyoxime and 5% sodium pyrophosphate, respectively. Five-fold amounts of nickel, and 2-fold of copper and zinc were left in the aqueous phase in the presence of 1 g of sodium chloride. Of the anions tested, chloride, sulfate, and nitrate did not interfere.

## References

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