The Analytical Application of Sulfur Analogues of β-Diketones. I. The Extraction Spectrophotometric Determination of Cobalt(II) with 1,1,1-trifluoro-4-(2-thienyl)-4-mercaptobut-3-en-2-one (STTA)

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The solvent extraction of cobalt(II) with 1,1,1-trifluoro-4-(2-thienyl)-4-mercaptobut-3-en-2-one (abbreviated as STTA) in cyclohexane has been investigated, and a new spectrophotometric method for the determination of minute amounts of cobalt has been developed on the basis of the results obtained in the extraction study. When a sample solution the pH of which had been adjusted to 6.0—6.5 with hydrochloric acid or sodium hydroxide solution was shaken with a 10^{-3}M STTA organic solution, the extraction of cobalt(II) proceeded rapidly and quantitatively. The amount of cobalt up to 8 ppm in the final organic phase could be determined by measuring the absorbance at 480 or 490 nm against the reagent blank. All other interferring ions, such as Hg(II), Cu(II), Ni(II), Pb(II), Zn(II), and Fe(III), extractable together with cobalt(II) could be stripped out of the organic phase by shaking it with 1—12M hydrochloric acid, while cobalt remained in the organic phase as it was. After this treatment, the organic phase was shaken with an aqueous buffer solution of pH 9—11; thereby, the excess of the reagent was released to a great extent from the organic phase into the aqueous solution. The cobalt-STTA chelate was then the only one existing in the organic phase; therefore, the sensitivity and the selectivity of the method increased so much that a few ppb of cobalt(II) could be determined precisely by measuring the absorbance of the final organic phase at 360 nm against the reagent blank. In this work, the apparent mole ratio of STTA to cobalt in the complex formation was estimated to be 4: 1, and the molar absorption coefficients of the chelate in cyclohexane were found to be 4970000 (at 360 nm), 13200 (at 450 nm), 6500 (at 480 nm), and 5500 (at 490 nm) respectively. Anions, such as oxalate and citrate, as well as EDTA interfered with this extraction. By the recommended procedure, cobalt of a few ppb in an analytical-grade reagent of nickel nitrate hexahydrate could be determined.

Thenoyltrifluoroacetone (abbreviated as TTA) is a well-known chelating agent useful for the solvent extraction and for the colorimetric determination of various metal ions.[1] One of its substituents, monothiothenoyltrifluoroacetone (1,1,1-trifluoro-4-(2-thienyl)-4-mercaptobut-3-en-2-one, abbreviated as STTA), in which one oxygen atom of TTA is replaced with sulfur, has stimulated the interest of many investigators because of its chemical and physical behaviors. Because of the difficulty of its preparation, however, this attractive reagent has not been extensively investigated. However various monometric monothio-derivatives of β-diketones have appeared in the past seven years thanks to the efforts of Chaston *et al.*,[2,3] Uhlemann and Müller,[4] Berg and Reed,[5] and Yokoyama, *et al.*,[6] and many energetic investigations of the coordinative properties of the metal chelates are now under way. Among these reagents, STTA has been found to form its chelates with transition elements, each of them having a specific color and the attribute of being extracted with organic solvents.[5,7,8] Taking advantage of this behavior, the extraction spectrophotometric determination of copper,[9] palladium,[10] and mercury,[11,12] with STTA and the use of the isotope-dilution method for mercury[13] with monothio-dibenzoylmethane have been tried. Nevertheless, the chemical properties of monothio-derivatives of β-diketones and their metal chelates have not yet been reported in detail. The present authors aimed to investigate the extraction behavior of STTA chelates of various metals, and, as a first step, attempted to prepare the STTA reagent by their own method, based on the report by Berg and Reed.[5] After preliminary experiments, the STTA was found to react with the divalent cobalt ion to form a complex of extreme stability. The present paper will describe the extraction-spectrophotometric method for the determination of cobalt with STTA in cyclohexane. The method seems to be more sensitive and selective for cobalt than other methods consisting of synergistic solvent extraction and spectrophotometry, *i.e.*, with benzoyltrifluoroacetone in the presence of tri-*n*-octylphosphine oxide.[14]

Experimental

Apparatus. The visible and ultraviolet absorption spectra were obtained with a Hitachi EPU-2A type spectro-

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[1] J. Starly, "The Solvent Extraction of Metal Chelates," Pergamon, London, 1964, p. 70.

[2] S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles, and J. S. Shannon, *Aust. J. Chem.*, **18**, 673 (1965).

[3] S. H. H. Chaston and S. E. Livingstone, *Proc. Chem. Soc.* (London), **1964**, 111.

[4] E. Uhlemann and H. Müller, *Angew. Chem.*, **77**, 172 (1965).

[5] E. W. Berg and K. P. Reed, *Anal. Chim. Acta*, **36**, 372 (1966).

[6] A. Yokoyama, S. Kawanishi, M. Chikuma, and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **15**, 540 (1967).

[7] V. M. Shinde and S. M. Khopkar, *Chem. Ind.*, **1967**, 1785.

[8] E. Uhlemann and H. Müller, *Z. Chem.*, **8** (5), 185 (1968).

[9] V. M. Shinde and S. M. Khopkar, *Anal. Chem.*, **41**, 342 (1969).

[10] A. U. Rangneckar and S. M. Khopkar, *Chem. Ind.* (London), **10**, 293 (1969).

[11] H. Hashitani and K. Katsuyama, *Bunseki Kagaku*, **19**, 355 (1970).

[12] K. Itsuki and H. Komuro, *ibid.*, **19**, 1214 (1970).

[13] H. Tanaka, N. Nakanishi, Y. Sugiura, and A. Yokoyama, *ibid.*, **17**, 1428 (1968).

[14] T. Shigematsu and T. Honjyo, *ibid.*, **18**, 68 (1969).

photometer with 1-cm quartz cells. Radioactivity counting was done with a Kobe Kogyo NaI (Tl) well-type scintillation counter, Model PS-400, connected to a transistorized scaler, Model SA-250. A Hitachi-Horiba glass electrode pH meter, Model M-3, was employed for the pH measurement. A Iwaki shaking machine, type KM, was used for the agitation of the aqueous and organic phases in the solvent extraction. The melting point of the prepared STTA was measured with a Yanagimoto Micro Melting-point Apparatus, Model MP-J2. The infrared absorption spectra were obtained by the nujol method with a Japan Spectroscopic Infrared Spectrophotometer, Model DS 301.

Materials. A stock solution of cobalt(II) was prepared by dissolving a definite amount of cobalt(II) chloride hexahydrate of a guaranteed grade in distilled water, and it was standardized by EDTA titration, using MX as an indicator.[15] The concentration of the solution was estimated to be 0.97×10^{-3} M. The STTA was synthesized in the authors' laboratory by the following procedure, which was based on the method reported by Berg and Reed: the starting substance, TTA, was first stored in a desiccator containing silica gel in order to dry it satisfactorily. Anhydrous ethanol was prepared by adding 5 g of metallic sodium to 500 m*l* of commercial-reagent-grade ethanol (99.5%), by heating it under reflux for 5 to 8 hr, and by then distilling the alcohol. Hydrogen sulfide gas from a steel bomb (from Seitetsu Kagaku Co.) was introduced into a washing bottle containing distilled water dried through a glass tube containing anhydrous calcium chloride, and thereafter passed into the reaction vessel. Hydrogen chloride gas was generated by dropping concentrated sulfuric acid onto solid sodium chloride of a suitable amount in a distillation flask under occasional heating; the gas evolved was introduced from the outlet tube of the flask into a washing bottle containing concentrated hydrochloric acid, and then into another one containing concentrated sulfuric acid. After having been dried well, the hydrogen chloride gas was also passed into the reaction vessel. The dehydration of these three materials, ethanol, hydrogen sulfide, and hydrogen chloride, might lead a worker to a successful synthesis of STTA. This vital part of the process has, however, not been described, not even by Berg and Reed;[5] therefore, if one works according to their procedure, the result might fail. The synthesis in this work was done by a method modified by the present authors as follows. Into a 500-m*l* flask with four necks, 5 to 10 g of TTA and 150 to 200 m*l* of the dehydrated ethanol were put through the large central neck of the flask, and then the vessel was cooled to 0°C in an ice bath. The dried hydrogen chloride gas was introduced through the first slender neck into the vessel in order to saturate the gas in it. The dried hydrogen sulfide gas was then passed through the second slender neck into the reaction vessel for 3 to 4 hr under occasional shaking. Here the third slender neck was useful for letting the gases out under slow suction. The content of the vessel began to turn dark red even after the passing of hydrogen sulfide gas for only about thirty minutes, but the passing of the gas was continued for 3 to 4 more hr in order to complete the reaction. The dark red solution thus obtained was poured over ice in a beaker; the red precipitate of STTA began gradually to appear as the ice melted. The product was separated from the solution by filtration, washed with an appropriate amount of water and dried by sucking the air through the filter and finally on the silica gel in a desiccator. The dried substance was submitted to its recrystallization from the dehydrated ethanol and further purified by repeating the recrystallization twice or thrice. The purified STTA was sealed in a brown-colored bottle in a nitrogen atmosphere and stored in a refrigerator kept at 5°C. The reagent when stored in this manner was quite stable during the storage for as long a time as two years or more, but once it was placed in the air, it slowly turned dark by oxidation. The synthesis was repeated seven times; all were successful when the described procedure was followed exactly. The STTA purified by the recrystallization from dehydrated ethanol showed a melting point of 60—70°C, but the material insufficiently purified or incompletely dried showed a melting point lower than that. The STTA in cyclohexane showed its absorption maximum at 365 nm and a molar absorption coefficient of 1.90×10^4. The characteristic absorption frequencies and their assignments were as follows: 1623 (ref. 1612,[3] 1620[5]) ν (C=O); 1260 (ref. 1260,[3] 1258[5]) μ (C=S); 817 (ref. 817,[3] 819[5]) μ (C=S)+δ(C–H). The stock solution of STTA prepared by dissolving the reagent in cyclohexane so as to be 10^{-3}—10^{-2} M was stored in a brown-colored bottle placed in a refrigerator to avoid its decomposition before use. A dilute reagent solution has a yellow color, and the concentrated solution, a red color. The concentration of the reagent was checked from time to time by measuring the absorbance at 350—450 nm. The cyclohexane was purified by distillation, and the chloroform, by washing it successively with a dilute sodium hydroxide solution, water, dilute hydrochloric acid, and three portions of water, and by finally distilling it. Thenoyltrifluoroacetone of a guaranteed reagent grade was purchased from the Dojindo Research Laboratory Co., Ltd., and was used as a starting substance for the synthesis of STTA after drying the commercial reagent in a desiccator containing silica gel. All the other reagents were of a reagent grade and were employed without further purification.

Procedure. An aqueous solution containing cobalt(II) ions was made to have 0.1 M acetic acid (in the acidic region) or 0.1 M boric acid (in the basic region), and its pH was adjusted to a desired value. Ten milliliters of this solution and 10 m*l* of 10^{-3} M STTA in cyclohexane were put together in a 30-m*l* glass-stoppered centrifuge tube and agitated by means of a mechanical shaker for 15—30 min at room temperature (25—29°C). After the separation of the two phases by centrifugation, the amount of cobalt(II) in the cyclohexane was determined by measuring the absorbance at 480 or 490 nm. The extractability of cobalt(II) was also determined by using a ^{60}Co tracer and by counting the radioactivity in both phases with a NaI (Tl) scintillation counter. The pH of the aqueous phase was checked again after each extraction.

Results and Discussion

Absorption Spectra. The absorption spectra of STTA in cyclohexane and those of the extracted cobalt(II)-STTA chelate are shown in Fig. 1. The absorption curve of the chelate has its maximum at 450 nm, but the absorbance of the reagent blank is remarkably large around this wavelength. The measurement of the absorbance of the chelate was, therefore, performed at 480 or 490 nm.

Effect of pH. The effect of the pH on the extractability of cobalt(II) of 10^{-4}M with 10^{-3} M STTA in cyclohexane was examined; the results are shown in Fig. 2 in terms of the absorbance of the chelate. A complete and quantitative extraction is found to be accomplished in the pH region between 5.5 and 7.5. The decrease in the distribution in the basic region may be due to

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[15] K. Ueno, "Chelatometric Titration" (in Japanese), Nankodo, Tokyo, 1967, p. 243.

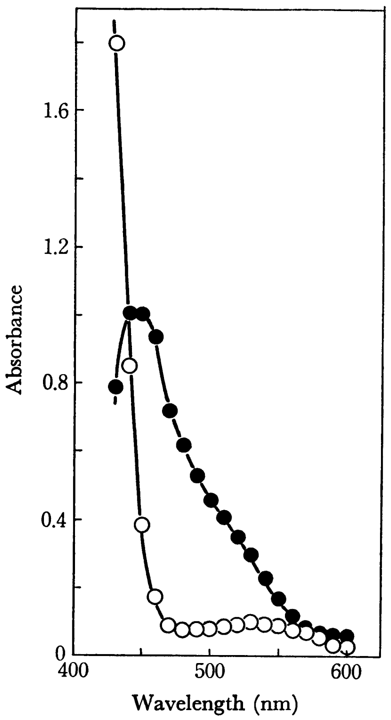

Fig. 1. Absorption spectra of STTA and cobalt-STTA in cyclohexane.
Aqueous phase: 10 m*l* of 0.97×10^{-4}M Co(II) solution of pH 6.0.
Organic phase: 10 m*l* of 10^{-3}M STTA-cyclohexane.
Shaking time: 30 min.

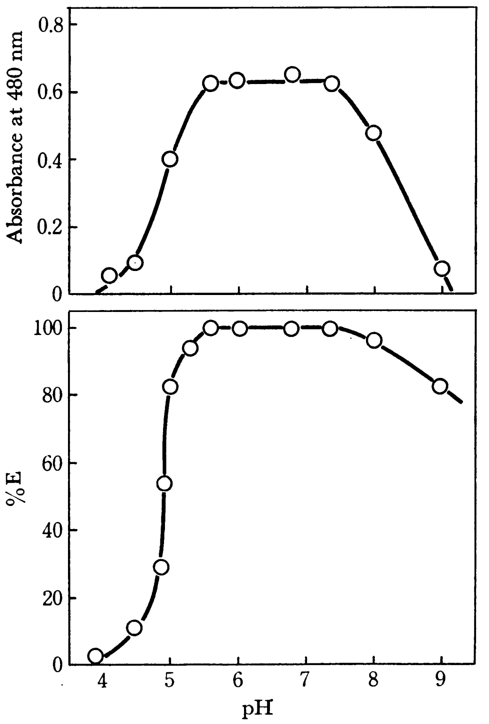

Fig. 2. Dependence of pH on the extraction of Co-STTA in cyclohexane.
Aqueous phase: 10 m*l* of 0.97×10^{-4}M Co(II) solution.
Organic phase: 10 m*l* of 10^{-3}M STTA-cyclohexane.
Shaking time: 30 min.

the increasing solubility of STTA into the aqueous phase, since a yellow color appears in the aqueous beyond pH 6.0. This gradually turns yellowish red with an increase in the pH, while the original color of the reagent in the organic phase fades little by little. Some yellow deposit of an unknown composition is observed in the aqueous phase at pH 9.0.

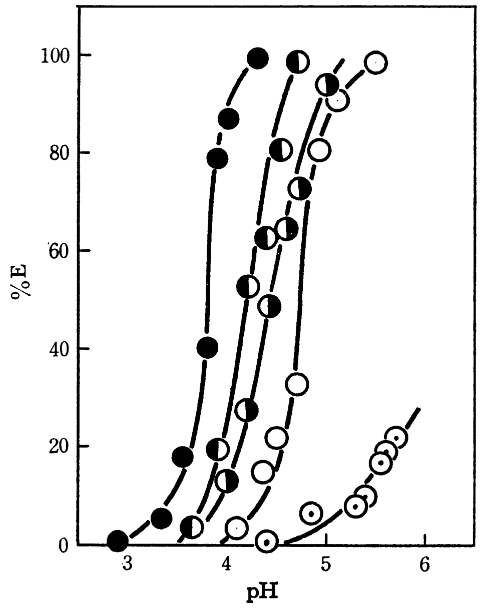

Fig. 3. Extraction of cobalt(II) with STTA in various solvents.
Aqueous phase: 10 m*l* of solution containing only radioactive tracer.
Organic phase: 10 m*l* of 10^{-3}M STTA-solvent.
Shaking time: 10 min.
—●— cyclohexane, —◐— carbon tetrachloride,
—◑— methyl isobutyl ketone, —○— benzene,
—⊙— chloroform.

Effect of Organic Solvents. STTA was dissolved in various organic solvents to make various 10^{-3}M STTA solutions, and the extraction of ^{60}Co in concetrations lower than 10^{-10}M was performed with these organic solutions. Among cyclohexane, benzene, carbon tetrachloride, chloroform, and methyl isobutyl ketone, cyclohexane was found to be the most excellent solvent to extract cobalt in the lower pH region, as can be seen in Fig. 3. In the lower pH region, hydroxo-complexes of many metals are not formed; therefore, serious interference can be avoided spontaneously. This is the reason for our preferring cyclohexane as a solvent in this study. The distribution of cobalt from a 10^{-4}M solution was found to be somewhat lower than that of radioactive cobalt in a trace amount. This might be attributed to the decrease in the effective concentration of STTA in the organic phase caused by the consumption of the reagent during the chelate formation and also to the time-lag needed to reach the extraction equilibrium.

Effect of the Reagent Concentration. The extraction of cobalt from a 10^{-4}M aqueous solution with cyclohexane containing STTA of varying concentrations was done; the absorbance of the organic phase is given in Fig. 4 in terms of the initial concentration of STTA in cyclohexane. The results show that it is enough to keep the

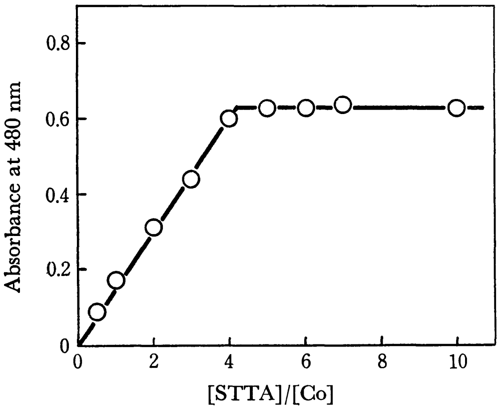

Fig. 4. Effect of the concentration of STTA in cyclohexane.
Aueous phase: 10 m*l* of 0.97×10^{-4}M Co(II) solution of pH 6.5.
Organic phase: 10 m*l* of cyclohexane containing various amounts of STTA.
Shaking time: 30 min.

concentration of STTA four times that of cobalt in order to achieve the quantitative extraction of the metal.

Effect of Shaking Time. The extractability of 10^{-4}M cobalt with 10^{-3}M STTA in cyclohexane at pH 6.0 is given in Fig. 5 as a function of the shaking time. The quantitative result is attained in about ten minutes of shaking.

Effect of the Volume of the Aqueous Solution. When the volume of the organic phase of 10^{-3}M STTA in cyclohexane was kept at 10 m*l*, when that of the aqueous phase was varied from 10 m*l* to 100 m*l*, and when the absorbance of the organic phase was measured at 480 nm after every extraction, almost the same absorbance was obtained in each case, as is shown in Fig. 6. Therefore, the volume of the initial aqueous solution seems to have no effect on the extraction recovery of cobalt, even at a ten-fold volume of the organic phase.

Stability of the Extracted Chelate. By measuring the absorbance of the cobalt-STTA chelate in cyclohexane at 480 nm at long intervals, the brown color of the chelate was found to be quite stable; it showed no change in the absorbance for several weeks. The extraction was carried out in natural daylight and also in the dark, but no differences in the distribution as in the absorbance could be found between the two cases.

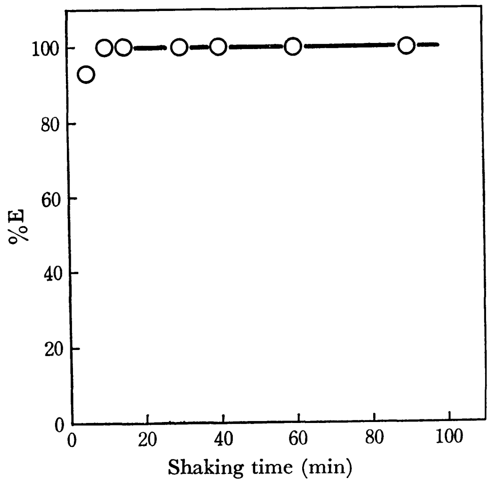

Fig. 5. Effect of shaking time.
Aqueous phase: 10 m*l* of 0.97×10^{-4}M Co(II) solution of pH 5.9.
Organic phase: 10 m*l* of 10^{-3}M STTA-cyclohexane.

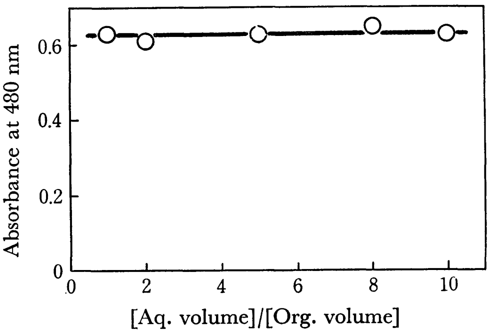

Fig. 6. Effect of the volume of the aqueous phase.
Aqueous phase: varying volume containing 0.97×10^{-3}m mol Co(II) of pH 6.0.
Organic phase: 10 m*l* of 10^{-3}M STTA-cyclohexane.
Shaking time: 30 min.

Back-extraction of the Chelate from the Organic Phase. The back-extraction of the extracted chelate was attempted by shaking the organic phase with hydrochloric acid of from 1 to 12M for thirty minutes. It was found that the back-extraction of cobalt did not occur at all. On the other hand, when the organic phase was shaken with an aqueous buffer solution of pH 9.0—11.0, the excess of the STTA reagent was almost entirely transferred into the aqueous solution, leaving only the cobalt-STTA in the organic phase. Thus, by the above two treatments, other interferring ions could be stripped out and the excess of the STTA be back-washed from the organic phase; therefore, the spectrophotometric determination of cobalt might be more sensitive and selective. This can be readily seen in Fig. 7, in which the absorbance of the organic phase after shaking with aqueous solutions of varying pH values, one at 480 nm when cobalt-STTA is present and another at 440 nm when only STTA is present, are shown together for the sake of comparison. The

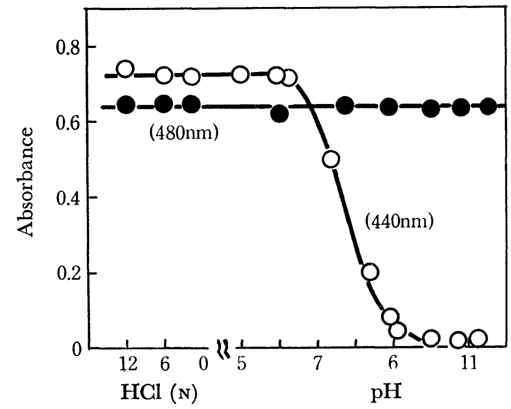

Fig. 7. Back-washing of STTA and Co-STTA with an aqueous solution of different pH/acidity.
Aqueous phase: 10 m*l*. Organic phase: 10 m*l* containing 10^{-2}m mol STTA and 0.97×10^{-3}m mol Co(II).
Shaking time: 30 min.

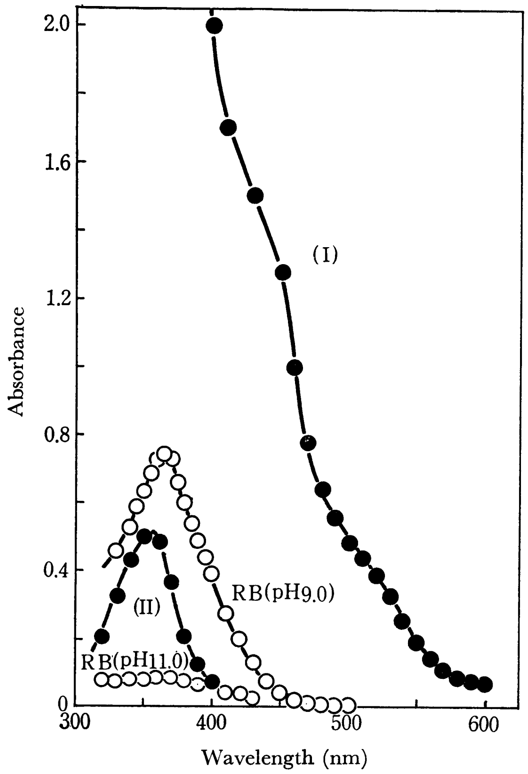

Fig. 8. Absorption spectra of STTA and Co-STTA in cyclohexane after back-washing of the organic phase prepared as in Fig. 1, (I) with a solution of pH 9.0 and (II) with that of pH 11.0. Organic phase: 10 m*l* of (I) 0.97×10^{-4}M Co-STTA and of (II) 0.97×10^{-7}M Co-STTA, both containing the excess of the STTA;
Aqueous phase 10 m*l*. Shaking time: 30 min.
—●— Co-STTA, —○— reagent blank.

STTA in the organic phase is found to begin to transfer itself into the aqueous phase at pH 6.0; it completely dissolves into the aqueous solution of pH above 9.5. On the other hand, the cobalt-STTA remains in the organic phase, as before. The absorbance of this cobalt-STTA could keep its value constant for at least several hours. The absorption spectra of the cobalt-STTA chelate remaining in the organic phase after back-washing with an aqueous solution of pH 9 and pH 11 are shown in Fig. 8, in which the reagent blank is found to have remarkably decreased, particularly at pH 11, without any effect on the STTA chelate. Thus, when the uncombined STTA was removed from the organic phase, the quantitative determination of cobalt could be extended to the order of ppb in the final organic phase.

Recommended Procedure and Working Curve. From the experimental results described above, a useful procedure for cobalt could be developed as follows. From 10 to 100 m*l* of an aqueous sample solution, the pH of which had been adjusted at 6.0—6.5 with 0.1M acetic acid and 0.1M sodium hydroxide, was put in a 30—300 m*l* glass-stoppered centrifuge tube or separating funnel, and 10 m*l* of 10^{-3}M STTA cyclohexane solution was then added into the vessel. The content was agitated by a mechanical shaker for 15 to 30 min at room temperature (25—29°C). After the lower aqueous phase had been separated off, the remaining organic phase was shaken again with 1M hydrochloric acid and then with a buffer solution of pH 9.0—11.0. After centrifugation, the organic phase was taken out to determine its absorbance at 450, 480, or 490 nm arbitrarily against the reagent blank. The analytical working curves prepared at each wavelength are shown in Fig. 9, in which it is found that Beer's law is obeyed up to 8 ppm of cobalt in the final organic solution and in which the molar absorption coefficients are found to be 13200 (at 450 nm), 6500 (at 480 nm), and 5500 (at 490 nm).

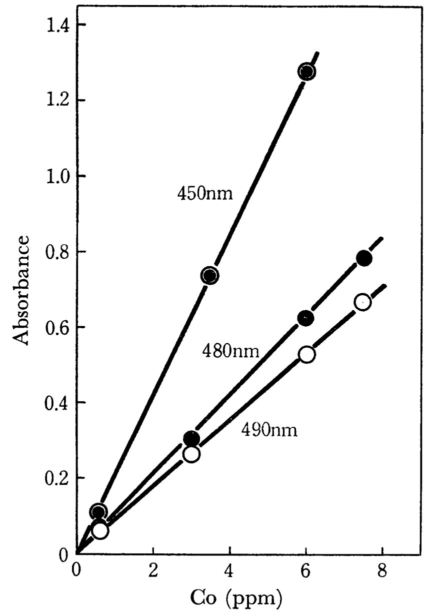

Fig. 9. Working curves for cobalt(II) at different wavelength.
Aqueous phase: 10 m*l* of pH 6.0.
Organic phase: 10 m*l* of 10^{-3}M STTA-cyclohexane.
Shaking time: 15—30 min.

Effect of Diverse Ions. The effect of foreign ions on the determination of cobalt according to the above procedure is noted in individual cases in Table 1. Mercury(II), Pb(II), Cu(II), Ni(II), Zn(II), and Fe(III) could form their extractable, colored complexes with STTA and, therefore, interfered with the spectrophotometric detemination of cobalt(II) if they could not be removed from the organic phase. However, when the organic phase containing the chelates of these metals was shaken with hydrochloric acid of 1.0—12M for thirty minutes, all these ions other than cobalt could be readily back-extracted into the acid. This fact was examined by the tracer method and by the colorimetric method to make sure that the separation was complete. On the other hand, these metal ions existing in the original sample solution consume the STTA reagent, being competitive with the formation of cobalt-STTA, and therefore hinder the extraction of the latter. When a large amount of these other ions are present a larger amount of the reagent should be employed to permit the complete extraction of all the metal ions. The back-extraction with hydrochloric acid could remove all the metal ions other than cobalt from the organic phase; this process seemed indispensable for the purpose. Strange to say, the cobalt-

Table 1. Effect of foreign ions on the absorbance of Co–STTA in cyclohexane

Ion coexisting in aq. phase	Taken µg/10m*l*	Absorbance of org. phase		Absorbance after back-washing with 1.0M HCl		Remark
		480 nm	490 nm	480 nm	490 nm	
none	—	0.620	0.535			
Ag(I)	6000	0.605	0.515			oxide ppt.
Pb(II)	6000	0.705	0.585	0.625	0.528	
	600	0.670	0.568			
	60	0.630	0.540			
Hg(II)	6000	0.642	0.548	0.635	0.545	
	600	0.635	0.545			
	60	0.632	0.535			
Cu(II)	6000	1.40	1.08	0.215	0.170	
	600	0.970	0.818	0.350	0.330	
	60	0.665	0.570			
Ni(II)	6000	2.02	1.75	0.362	0.315	
	600	1.22	0.975	0.340	0.322	
	60	0.690	0.590			
Mn(II)	6000	0.625	0.540			
Sr(II)	6000	0.628	0.535			
Zn(II)	6000	0.655	0.555	0.595	0.510	
	600	0.648	0.555	0.350	0.330	
Cd(II)	600	0.632	0.545			
	60	0.623	0.538			
Mg(II)	6000	0.630	0.540			
Fe(III)	6000	1.32	1.19	0.620	0.532	
	600	0.980	0.880			
	60	0.640	0.555			
Cr(III)	6000	0.615	0.520			
Bi(III)	6000	0.860	0.665			hydroxide ppt.
Al(III)	6000	0.565	0.478			hydroxide ppt.
Cl^-	60000	0.620	0.532			
CH_3COO^-	60000	0.630	0.540			
SO_4^{2-}	60000	0.618	0.530			
$C_2O_4^{2-}$	60000	0.410	0.350			
PO_4^{3-}	60000	0.620	0.530			
BO_3^{3-}	60000	0.638	0.555			
Cit^{3-}	60000	0.522	0.445			
$EDTA^{4-}$	60000	0.040	0.050			
NO_3^-	60000	0.622	0.538			

In each case 57.2 µg of cobalt(II) was taken in 10 m*l* of the aqueous solution of pH 6.0—6.5 and extracted with 10 m*l* of 10^{-3} M STTA-cyclohexane.

STTA chelate was scarcely back-extracted from cyclohexane, even with 1—12M hydrochloric acid, 70% perchloric acid, and 18M sulfuric acid as well as an aqueous buffer solution of pH 9—13, each after one hour's shaking. The chelate could, however, be back-extracted to the extent about 15% with 1.0M sodium hydroxide after thirty minutes' shaking and to the extent about 10% and 90% under shaking with concentrated nitric acid for thirty and sixty minutes respectively. With concentrated sulfuric acid, all the cobalt was transferred immediately from the organic phase into the acid accompanying the decomposition of the organic matter.

Some Aspects of the Nature of Co-STTA. As has been described above, the cobalt-STTA once formed in the extraction system is remarkably stable. At pH 6.5, all of the cobalt in the aqueous solution was extracted into the organic phase (as is shown in Fig. 2), while a small amount of the STTA reagent was back-extracted into the aqueous phase under the same contitions (as is shown in Fig. 7). The absorbance of the extracted cobalt-STTA was examined in terms of the mole ratio of STTA to cobalt; the absorbance was found to become constant in the region above the 4:1 ratio, as is shown in Fig. 4. This confirms that the apparent mole ratio of STTA to cobalt in the complex formation was 4:1. Similar investigations have been done for Co(II)-1-nitroso-2-naphthol,[16,17] Co(II)-dithizone,[18,19] and Co(II)-monothio-dibenzoylmethane.[6,20]

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[16] R. Paulais, *Bull. Soc. Chim. Fr.*, **1951**, 206.

[17] N. Suzuki and H. Yoshida, *Nippon Kagaku Zasshi*, **80**, 1008 (1959).

[18] J. F. Duncan and F. G. Thomas, *J. Inorg. Nucl. Chem.*, **4**, 376 (1957).

[19] J. F. Duncan and F. G. Thomas, *J. Chem. Soc.*, **1960**, 2814.

[20] E. Uhlemann and H. Müller, *Anal. Chim. Acta*, **41**, 311 (1968).

In all cases involving the present study, it may be assumed that the original cobalt could no longer be present as divalent, but must be trivalent or something else after its chelate formation. A detailed report concerning the composition of this stable cobalt-STTA will be presented in the near future.

TABLE 2. RECOVERY OF COBALT(II) IN THE PRESENCE OF NICKEL

Co(II), taken in 10 m*l* mmol	Ni(II), taken in 10 m*l* mmol	Recovery of Co(II) %
1.94×10^{-3}	1.0×10^{-3}	98.0
0.97×10^{-3}	1.0×10^{-3}	98.4
0.97×10^{-4}	1.0×10^{-3}	97.8
trace ($<10^{-9}$)	1.0×10^{-3}	97.4

TABLE 3. DETERMINATION OF COBALT IN NICKEL NITRATE REAGENT

$Ni(NO_3)_2$ solution prepared M	Taken m*l*	Absorbance of Co–STTA at 360 nm	Recovery by ^{60}Co tracer %	Cobalt, found	
				M $\times10^{-7}$	%
1.0×10^{-4}	10.00	0.412	96.9	0.855	0.088
1.0×10^{-4}	10.00	0.375	97.6	0.778	0.080
1.0×10^{-4}	10.00	0.420	98.0	0.871	0.088

Application of the Recommended Method. The extraction spectrophotometric procedure for cobalt recommended by the present authours will find extensive application for various purposes. First of all, the method has been applied to the determination of a minute amount of cobalt in a nickel nitrate reagent of the guaranteed analytical grade. The recovery of cobalt was ascertained at the same time by employing a radioactive tracer, $^{60}Co(<10^{-10}M)$; it was found to be 97.4—98.4% from an aqueous solution of 10^{-4}M nickel(II). The results obtained are shown in Table 2, while the practical analysis of a trace amount of cobalt in nickel nitrate of an analytical grade gives the data shown in Table 3. In the latter case, the recovery of cobalt was checked by using ^{60}Co in order to confirm the spectrophotometric data. In this case, when a minute amount of cobalt is to be determined, the absorbance of cobalt-STTA at 360 nm is preferred. As is shown in Fig. 8, when the organic phase was back-washed with a solution of pH 11.0, the proper absorption spectra of cobalt-STTA appeared distinctly since the reagent blank was reduced to an almost indetectable value. Therefore, as little as 5.89 ppb of cobalt(II) in a sample aqueous solution could be determined by using a 10 m*l* of the initial solution and by measuring the absorbance of the final organic phase as being 0.482, corresponding to 0.97×10^{-7}M Co-STTA. The molar absorption coefficient of Co-STTA was found to be 4970000 at 360 nm. In the determination of a trace amount of cobalt in the nickel nitrate reagent, a working curve was prepared at 360 nm for cobalt of 0.6 to 60 ppb in the final organic phase; each measured absorbance was adopted to this working curve, and the amount of cobalt was evaluated. The results after three experiments are shown in Table 3; the standard deviation is also estimated to be 0.004%.

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