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Spectrophotometric Determination of Cobalt(II) with Thiocyanate. A Modification for Increasing Sensitivity and Selectivity

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Synopsis. The ion association complex formed between $[Co(SCN)_4]^{2-}$ and 3,3′-(1,1′-biphenyl-4,4′-diyl)bis[2,5-diphenyl-2*H*-tetrazolium] dichloride, commercially known as neotetrazolium chloride, has been extracted into isobutyl methyl ketone and used for the photometric determination of 2.5—9.8 μg cm^{-3} cobalt at pH 3.5—5.0 (acetate buffer). Sandell's sensitivity of the method (0.02 μg cm^{-2}) is better than most of the other thiocyanate methods known so far. Interference of diverse ions has been studied. Using the higher tolerances of anions, many cations interfering in the other thiocyanate methods have been masked, thus making the present procedure more selective. The method has been applied to wire alloys.

Thiocyanate is among the most commonly used spectrophotometric reagents[1] of cobalt. The tetrathiocyanatocobaltate(II) as well as its ion associates with a variety of counter ions have been employed for the determination of the metal,[2,3] but the sensitivity exceeding 0.04 μg cm^{-2} (for 0.001 absorbance) has been rarely reported. In the course of studies on tetrazolium salts it has been observed that the ion pair formed between neotetrazolium chloride (NTC) and $[Co(SCN)_4]^{2-}$ is highly absorbing in isobutyl methyl ketone (MIBK) medium in comparision to other ion pairs of the anions investigated so far (Sandell's sensitivity 0.02 μg cm^{-2}). The detailed results of these investigations are reported in the present note.

The aqueous solution of $[Co(SCN)_4]^{2-}$ on mixing with NTC solution forms a greenish blue precipitate which is extractable into organic solvents. However the absorbance of this ion pair has been found maximum in MIBK. The tolerance of anions is more in this system than other Co–SCN systems and therefore can be utilized to create a more selective method for the determination of cobalt(II) with thiocyanate.

Experimental

Apparatus. Unicam SP 500 and 700 spectrophotometers were used for absorbance measurements and a Elico LI-10 pH meter for measuring pH.

Reagents. A stock solution 0.01 M (1 M = 1 mol dm^{-3}) of cobalt(II) was prepared by dissolving $CoSO_4 \cdot 7H_2O$ (BDH, A. R.) in doubly distilled water. It was standardized by titration with ethylenediaminetetraacetic acid (EDTA) before use. The solution of NTC, procured from Aldrich (U. S. A.), was prepared in 50% ethanol. Thiocyanate solution(10%) was prepared by dissolving the requisite amount in doubly distilled water. All other solutions of cations and anions were prepared by dissolving analytical grade chemicals in doubly distilled water.

Recommended Procedure. To a suitable aliquot containing 20 to 70 μg of cobalt add acetate buffer of pH 4.5, 10% ammonium thiocyanate and 0.4% NTC solution(4.0 cm^3 each). To this mixture add 2 cm^3 of water and 5 cm^3 (*N,N*-dimethylformamide) (DMF) to dissolve the precipitate. Extract the complex with 7 cm^3 MIBK and measure the absorbance of organic layer after centrifugation, at 620 nm against water blank. Deduce the metal content from calibration curve.

Results and Discussion

Spectral Behavior of the Complex and Effect of pH. The ion associate absorbs maximum at 620 nm. Absorbance remains maximum in the pH range 2.5 to 5.0. The variation in pH does not affect the absorbing characteristics of the complex. Reagent blank does not absorb at 620 nm. Acetate buffer is most suitable for pH adjustment .

Effect of Thiocyanate and NTC Concentration. For 1 cm^3 of 1 mM cobalt solution the maximum absorbance is attained in the presence of 3.7 cm^3 NTC solution (0.04 %). At least 3 cm^3 of 10 % thiocyanate solution should be added for full color development. The excess of either reagent does not affect the absorbance.

Effect of DMF and Stability of the Complex. At least 4.5 cm^3 of DMF should be added in the estimation of 1 cm^3 cobalt(II) to dissolve the precipitate. Excess up to 8 cm^3 does not have any effect but beyond this the extraction becomes erratic due to very slow irreproducible separation of the immiscible layers. The color does not fade even on keeping the solution for 12 h.

Characteristics of the Complex. Beer's law is obeyed up to 13 μg cm^{-3} at pH 4.5. The optimum concentration, evaluated by Ringbom method, is 2.5 to 9.8 μg cm^{-3}. The Sandell's sensitivity is 0.02 μg of cobalt cm^{-2}. The molar absorptivity is 3.0×10^3 l mol^{-1} cm^{-1}. The metal: NTC ratio, as found by Job's method of continuous variation, is 1 : 1. The species $(NTC)^{2+} \cdot [Co(SCN)_4]^{2-}$ are most probably responsible for the absorption. The standard deviation for the mean absorbance 0.345 has been found to be 0.003.

Effect of Diverse Ions. Synthetic solutions containing known amounts of diverse ions and cobalt(II) were prepared and the recommended procedure was followed for determination of the metal. An error of 2 % in the absorbance measurement was considered tolerable. In the determination of 8.4 μg cm^{-3} cobalt the anions tolerated (in μg cm^{-3} given in parentheses) are as follows: fluoride, chloride, iodide, nitrate(1000 each); phosphate (1250); oxalate(1280); nitrite (1200); bromide(625); thiosulfate (600); citrate, tartrate (480), and thiourea (150). The metal ions tolerated are: Ca(II), Sr(II), Ba(II), Ni(II), Cd(II), Mn(II), Al (III), Ti(IV) (250 μg cm^{-3} each); Zn(II) or Fe(II) (50 μg cm^{-3}); and Cu(II) (10). EDTA interferes seriously. All other metal ions which form colored complex with thiocyanate also interfere in this system. However, 100 μg cm^{-3} of iron can be masked with

Table 1. Determination of cobalt in alloys

Alloy	Cobalt/%		No. of detn.	Relative standard deviation
	Reported	Found		%
"K" Monel wire	0.51	0.50	6	3.8
Nilo "K" wire	17.4	17.6	6	2.0

fluoride. Tolerance of copper can be improved up to 60 μg cm^{-3} by using thiourea as masking agent. Similarly mixture of citrate and tartrate improves the tolerance of nickel up to 1000 μg cm^{-3}.

Determination of Cobalt in Alloys. To exhibit the advantages of higher sensitivity and selectivity of this method, the contents of cobalt in some wire alloys have been estimated using SCN and NTC as chromogenic reagent. The detailed procedure is given below.

Weighed samples of "K" Monel wire and Nilo "K" wire were dissolved in concentrated nitric acid. Excess acid was evaporated off and the residue was dissolved in doubly distilled water. By applying the recommended procedure the cobalt contents of the samples were determined. To mask copper, nickel, and iron present in these alloys requisite amounts of thiourea, citrate, tartrate, and fluoride were added. The results are reported in Table 1.

Comparision with Other Methods Based on Thiocyanate. The present method is better in sensitivity than most of the other methods based on thiocyanate. Sensitivities are compared in Table 2. The high molecular weight and conjugation of NTC^{2+} ion is responsible.

Table 2. Sensitivities of thiocyanate methods for the photometric determination of cobalt(II)

Method	Sensitivity (μg Co cm^{-2})	Reference
Thiocyanate (isopentyl alcohol)	0.055 (620 nm)	1, 4
Thiocyanate + tetraphenylarsonium ion (chloroform)	0.034 (620 nm)	1, 4
Thiocyanate + 1,1-diantipyrinylethane	0.075 (625 nm)	4
Thiocyanate + tributylammonium salt	0.045 (615 nm)	4
Thiocyanate + 2,3,5-triphenyltetrazolium salt	0.055 (625 nm)	1, 5
Thiocyanate + Neotetrazolium chloride	0.020 (620 nm)	Present method

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