Extractive Spectrophotometric Determination of Cobalt with Thioglycolic Acid Anilide & Its Applications

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Cobalt in the concentration range 1 to 8 ppm is quantitatively extracted into chloroform as a 1:3 complex with thioglycolic acid anilide from solutions of pH 5.6-9.8 containing γ-picoline. The complex shows maximum absorption at 485 nm against solvent blank. The colour of the complex is stable upto 2 days and sufficient amounts of Zn^{2+}, Mn^{2+}, Ba^{2+}, Ca^{2+}, Sr^{2+}, V^{5+}, Ce^{3+}, Mo^{6+}, W^{6+}, Na^+, K^+, Cl^- and NO_3^- are tolerated. However, the separation from Be^{2+}, Cu^{2+}, Hg^{2+}, Cd^{2+}, Pb^{2+}, Sn^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Bi^{3+}, As^{3+}, Th^{4+} or U^{6+} has been effected using suitable masking agents. This method has been used to determine cobalt in ores, alloys and medicinal samples. The solid 1:3 complex of cobalt with thioglycolic acid anilide has been isolated. Its IR spectrum in KBr provides evidence for the coordination of metal through NH and SH groups of the ligand.

Thioglycolic acid does not appear to be an efficient reagent for the spectrophotometric determination of cobalt. However, some of its derivatives like the chloroanilide has been used for this purpose[1]. Thioglycolic acid anilide (mercaptoacetic acid anilide, $HSCH_2CONHC_6H_5$) has been recommended for the detection[2] of cobalt (gives brown precipitate), and it has also been used for the gravimetric determination of cobalt in the presence of nickel and zinc[3]. We have exploited this reagent for the extractive spectrophotometric determination of cobalt. The results of our studies are reported in this paper.

Materials and Methods

Thioglycolic acid anilide was prepared by refluxing a mixture of thioglycolic acid (AR, E Merck) and freshly distilled aniline in 1:1 proportion in an oil-bath (115-25°) for $3\frac{1}{2}$ hr under an air condenser. The solid mass obtained on cooling was recrystallised from aq. ethanol, yield 60% m.p. 110° (lit. m.p. 111°) (Found: C, 57.3; H, 5.48; N, 8.32; S, 19.25. Calc.: C, 57.46; H, 5.43; N, 8.38; S, 19.17%); IR(KBr): 3290 (νNH), 1640 (νC $=$O) (a weak band at 2560 cm^{-1} could be due to νSH, see ref. 10). A stock solution of the reagent (0.01 M) was prepared in 60% aq. ethanol whenever required.

Cobalt sulphate (AR, BDH) was dissolved in dil. sulphuric acid and the solution standardised gravimetrically with α-nitroso-β-naphthol[4]. Finally working solution ($9.7 \times 10^{-4} M$) was obtained by appropriate dilution of the stock solution.

Stock solutions of pure nitrates, chlorides and sulphates of various metal ions or other suitable salts were prepared to study the interference of the various diverse ions on the estimation of cobalt.

A stock solution (10%) of γ-picoline (AR, BDH) was prepared in aq. ethanol. Absorbance was recorded on a Beckman double beam (model 26) UV-visible spectrophotometer using a pair of matched 1 cm quartz cells. The pH values were measured with a Beckman 4500 digital pH meter. The IR spectrum was recorded on a Beckman Acculab 10 IR spectrophotometer.

Determination of cobalt

A known amount of a standard solution containing 11-90 μg of cobalt was taken and 5 ml of the reagent followed by 2 ml of 10% γ-picoline were added. The pH of the solution was adjusted to 6.2 by the addition of aq. ammonia. About 2 ml of 2% magnesium chloride solution were then added to facilitate the separation of the solvent layers. The cobalt complex was extracted with chloroform (2×5 ml), combined chloroform extract dried over anhydrous sodium sulphate and the absorbance of the red coloured chloroform extract measured at 485 nm against solvent blank.

Determination of cobalt in ore, alloy and vitamin samples

The ore (limonite) was decomposed following the standard method[5]. The ore (0.9-1.2 g) was dissolved by boiling with nitric acid (40 ml), cooled and potassium chlorate (8 g) added to it. The mixture was heated and evaporated to dryness. The residue was treated with hydrochloric acid (10 ml) and evaporated. This step was repeated twice and finally the residue was heated with dil. hydrochloric acid and filtered. The residue was fused with potassium hydrogen sulphate, extracted with hydrochloric acid, the two solutions were combined and the volume made upto 100 ml by adding dil. hydrochloric acid. An aliquot (5 ml) of this solution was used for the determination of cobalt. However, the pH was maintained at ~8 and

ammonium fluoride (0.2 g) was added as masking agent.

The alloy[5] (0.9-1.0 g) was boiled with a 1:3 mixture of nitric acid and hydrochloric acid for about 2 hr and then evaporated until crystals appeared. The mass was dissolved in water and ammonia was added carefully to almost neutralization. To this tartaric acid (0.15 g) was added and the volume made to 100 ml with dil. hydrochloric acid. An aliquot (10 ml) of this solution was further diluted to 100 ml in a similar fashion. A 1 ml portion of this final solution was used for the determination of cobalt.

Two ampoules (2 × 2 ml) of Macraberin Forte injection (Glaxo Lab., Bombay) were decomposed in a covered beaker with nitric acid, following a standard procedure for such samples[6], first at low temperature to avoid violent reaction. The mixture was cooled when reaction subsided and heated again with additional amount of nitric acid. The temperature was gradually raised and finally the residue was heated to about 400° on a hot plate. The ash was dissolved in dil. nitric acid (1:1) and evaporated slowly (1-2 hr) on a steam-bath. Finally, the residue was taken in water (25 ml) to which nitric acid was added in 0.25 ml portions until a clear solution was obtained on gentle heating. The cobalt content of this solution was determined by the procedure described above. The results of analysis are presented in Table 1.

Results and Discussion

Absorption spectra of cobalt-thioglycolic acid anilide complex

The absorption spectra of several extracts containing varying amounts of cobalt (1.1-7.9 μg/ml), recorded in the region 350-550 nm against the reagent blank, exhibited maximum absorption due to cobalt-thioglycolic acid anilide complex at 480-85 nm. The absorbance values increased below 420 nm, but no definite peak was noticed in the UV range. Therefore, all the measurements were carried out at 480-85 nm. The absorption spectrum of the reagent solution against solvent blank exhibited λ_{max} at 245 nm. The

reagent had no absorbance above 290 nm. Hence, solvent blank was recommended for the determination of cobalt.

Effect of γ-picoline and magnesium chloride

It was observed that complete extraction of cobalt was possible in the presence of γ-picoline otherwise only partial extraction[3] took place. Addition of 2 ml of 10% γ-picoline was sufficient. Studies on the extraction constant in the presence and absence of γ-picoline following the method due to Sekine and Ihara[7] failed to reveal adduct formation between cobalt-thioglycolic acid anilide complex and γ-picoline. It appeared that the raising of pH first with γ-picoline followed by ammonia prevented any localized hydrolysis and ensured complete extraction of cobalt. Such observations have been reported earlier[8]. Magnesium chloride helped in the separation of the two layers. The addition of aluminium chloride also served the same purpose.

Effect of pH

A set of cobalt(II) solutions was adjusted to different pH values with dil. ammonia or dil. hydrochloric acid, extracted with chloroform and the absorbance of the extract measured in each case. When the extraction was complete or almost complete, the aqueous layer after the extraction was evaporated, decomposed with nitric acid and tested both qualitatively and quantitatively with acetothioacetanilide[9]. The experimental results showed that the extraction was complete in the pH range of 5.6-9.8.

Effect of reagent concentration

Experiments under identical conditions but with varying amounts of the reagent showed that 4.5 mg reagent was sufficient for the quantitative extraction of cobalt in the range 5-9 μg/ml. It was also observed that a 10-fold excess of the reagent had no adverse effect.

Extracting solvent and stability of the complex

Of the various common organic solvents employed for the extraction of cobalt-thioglycolic acid anilide complex, chloroform was found to be the most suitable solvent. The complex was recovered to the extent of about 96% in the first step and the colour of the extract was stable upto 2 days.

Optimum concentration range and absorptivity

The plot of absorbance versus cobalt concentration was linear in the cobalt concentration range of 1.1 to 7.9 ppm in chloroform. The optimum concentration range for the determination was 1.1-6.5 ppm and the Sandell sensitivity was 5.2×10^{-3} μg/cm^2. The molar absorptivity was 1.128×10^4 litre mol^{-1} cm^{-1}.

Table 1—Determination of Cobalt in Ore, Alloy and Vitamin

Sample	Co		Relative error (%)
	Present	Found*	
Limonite (ore)	(a) 0.061%	0.062%	+1.6
	(b) 0.052%	0.051%	−2.0
Tata 66/4 (alloy)	5.30%	5.32%	+0.37
Macraberin Forte inj. (vitamin)	36.0 ppm	36.5 ppm	+1.39

*Mean of three determinations.

Effect of diverse ions

The tolerance limits of the various foreign ions in the determination of cobalt were as follows (values in parantheses refer to the amount of foreign ion in excess over that of cobalt taken): Na^+ (1000), K^+ (1000), Zn^{2+} (100), Mn^{2+} (100), Be^{2+} (100), Cu^{2+} (100), Ba^{2+} (100), Hg^{2+} (100), Cd^{2+} (100), Pb^{2+} (25), Ca^{2+} (100), Sr^{2+} (100), Sn^{2+} (50), Al^{3+} (100), Fe^{3+} (100), Cr^{3+} (100), Ce^{3+} (100), Bi^{3+} (100), As^{3+} (50), Th^{4+} (100), V^{5+} (100), Mo^{6+} (100), U^{6+} (100), W^{6+} (100), NO_3^- (1000) and Cl^- (1000). However, fluoride had to be used to mask Be^{2+}, Fe^{3+} and Al^{3+}. While Mg-EDTA masked As^{3+}, Bi^{3+}, Th^{4+}, Pb^{2+} and Cd^{2+} the interference due to Cr^{3+} was masked by Mg-EDTA in hot condition. The tolerance limit of Zn^{2+} was studied at higher pH within the limit in solutions buffered with ammonia-ammonium chloride. UO_2^{2+} and Cu^{2+} were masked by tartrate, but for Cu^{2+} warm (60-70°) condition was necessary. The tolerance limit of Sn^{2+} in the presence of sulphosalicylic acid and that of Hg^{2+} in the presence of potassium iodide were studied. In both the cases higher pH within the limit was necessary. The determination of cobalt was possible in the presence of nickel by proper adjustment of pH (6 to 8), and 15-fold excess of nickel did not interfere.

Effect of masking agents

The determination of cobalt was feasible in the presence of 200 mg of each of ammonium bifluoride, tartrate, acetate, citric acid, sulphosalicilic acid or iodide and 2 ml of 0.01 M Mg-EDTA. However, ascorbic acid, thioglycolic acid and EDTA were found to interfere.

Precision and accuracy

The relative standard deviation for 10 determinations of cobalt was $\pm 1.1\%$. The confidence range (95%) was calculated to be 5.67 ± 0.04 ppm.

Nature of complex

The composition of the complex in solution (50% ethanol) was verified by the conventional slope-ratio method and the cobalt:ligand ratio was found to be 1:3 indicating the presence of tripositive cobalt. This ready oxidation of cobalt(II) to cobalt(III) has also been reported for complexes with some soft bases[11,12] like nitrate, cyanide and monothio-β-diketones[13].

Thioglycolic acid anilide has coordination sites of an ambidentate ligand. So in order to determine the sites of coordination a small amount of the solid complex was isolated under the condition similar to that employed for extraction. But the mixture was allowed to stand for about 30 min, washed and the complex dried in a vacuum desiccator.

The infrared spectrum of the solid complex in KBr exhibited bands at 3280 (weak, vNH), 1650 cm^{-1} (vC = O). The weak ligand bands at 2560 cm^{-1} due to vSH disappeared. The shift of vNH to lower frequency region and the disappearance of vSH indicated coordination of metal through NH and SH groups of the ligand.

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