Separation of nickel from cobalt as its chlorosulphate on silica gel layer with solvents containing formic acid

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Three-component solvent systems, viz formic acid-propanol-2-acetone, formic acid-butanol-1-ethyl methyl ketone, formic acid-dimethyl sulfoxide-ethyl methyl ketone and formic acid-propanol-2-1,4-dioxane have been used to separate nickel from cobalt as its chlorosulphate on silica gel layer. The mobility of nickel chlorosulphate is found to be greater in solvent systems with higher formic acid concentration and it increases with the increase in formic acid concentration in the mobile phase. The mobility of cobalt chlorosulphate also changes slightly with the change in concentration of formic acid in the mobile phases. Both the chlorosulphates are strongly adsorbed on silica gel layers in absence of formic acid.

Mutual separation of nickel from cobalt is of great analytical importance because of their potential application in the analysis of various ores and alloys. Nickel is slightly poorer reductant than cobalt, however, forms several complexes like cobalt. Amongst the analytical methods, thin layer chromatography, gas chlorination voltammetry and hydrometallurgical techniques have been used to lesser extent for the separation of nickel from cobalt, copper and iron. Because of several favourable features, formic acid has found interesting applications in inorganic TLC for achieving analytically important separations. The investigations indicate that it produces better separations when used in combination with oxo-solvents (alcohols, ketones) or nitrogen containing organics.

The present work is an attempt to develop a rapid and reliable thin layer chromatographic method for the separation of nickel from cobalt as its chlorosulphate using acidic mixed organic solvent systems containing formic acid. It is probably the first report on the separation of nickel from cobalt as its chlorosulphate.

Experimental procedure—Silica gel, formic acid (FA), ethyl methyl ketone (EMK) acetone and 1,4-dioxane from E Merck; chlorosulphuric acid, thionyl chloride, butanol-1, propanol-1, and propanol-2 from S D Fine Chem; dimethyl sulphoxide (DMSO) and dimethylglyoxime (DMG) from Qualigen; acetic anhydride from Sarabhai Chemicals; and cobalt and nickel acetates from CDH were used. All other chemicals used were also of AR grade. The commercially obtained metal acetates were dehydrated with acetic anhydride for about 2 h. DMF and thionyl chloride were distilled before use.

Anhydrous metal acetate (5 g) was taken in a reaction vessel and an excess of chlorosulphuric acid was slowly added to it. When the reaction subsided, the contents were magnetically stirred for about 12 h. The precipitated compound was vacuum filtered, washed several times with neat chlorosulphuric acid and finally dried in vacuum to a constant weight. The solid, thus, isolated was hygroscopic in nature and kept under unhygroscopic conditions. Chlorosulphates were prepared by using trifluoroacetate, benzoate or chloride of respective metals. Chlorosulphuric acid was handled in a manner described previously. Chlorosulphates of nickel and cobalt were taken as 5 or 10% solutions in dimethylformamide for spotting on the chromatoplates.

The following solvent mixtures were used as mobile phase:

(A) Formic acid-propanol-2-acetone

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(B) Formic acid-propanol-2-1,4-dioxane

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(C) Formic acid-dimethyl sulphoxide-ethylmethyl ketone

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(D) Formic acid-butanol-1-ethyl methyl ketone

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Preparation of plates—A slurry of silica gel G was prepared by mixing 20 g silica gel with 60 mL of demineralized water and shaking the contents mechanically for 5 min. The slurry was spread over fine even-glass plates (20 x 3 cm) with the help of a TLC applicator (Toshniwal, India), to give a 0.25 mm layer. The plates were air dried at room temperature followed by activation at 120°C for 2 h. The plates were cooled to room temperature and kept in a closed chamber until used.

The silica coated plates were spotted with 20 μL aliquots of 5 or 10% solution of nickel or cobalt chlorosulphate in DMF with the help of a micropipette. The spots were completely dried and the plates were developed in glass jars (24 x 6 cm) with desired solvent system by ascending technique. The solvent ascent was fixed to 10 cm in all cases. After the development is over, the plates were withdrawn from the glass jars, dried and sprayed with 1% alcoholic solution of dimethylglyoxime to locate the positions of the spots.

To study the effect of anions on the separation of nickel from cobalt, synthetic mixture (0.1 mL of nickel and cobalt chlorosulphates (3.2%) was spotted on the chromatoplates followed by spotting of different volumes (0.01-0.05 mL) of anion solution (1%). After drying the spot completely, plates were developed with S₁ and the R_f values for nickel and cobalt chlorosulphates were determined. The R_f values for anions were also determined using another set of experiment under identical condition. The R_f values obtained for anions are given in parenthesis as: IO_4^-, BeO_3^-, MnO_4^-, I^-, S_2O_3^2-, Fe(CN)_6^3-, or S^2- (00); SCN^-, (0.95); NO_3^- or NO_2^- (0.1); Fe(CN)_6^3-, CrO_4^2- or Cr_2O_7^2- (0.5, tailed spot) and IO_4^-, MoO_4^2- or MoO_2^4- (00 and 0.95).

The limit of detection of nickel and cobalt chlorosulphates were determined by spotting different amounts of chlorosulphate solutions on the chromatoplates. The plates were developed and detected. The method was repeated with successive lowering of the amount of analyte until no detection of the spot was achieved. The minimum amount of analyte just detectable was taken as the limit of detection.

Results and discussion—It is evident from Fig. 1 that good separation of nickel from cobalt as its chlorosulphate can be successfully accomplished on silica gel layer using any solvent of choice (S₁-S₁₀). The mobility of nickel chlorosulphate increases with the increase in formic acid concentration in mobile phase (S₁₀-S₁₆). The R_f value reaches to 0.70 in S₁₆ through gradual increase from 0.38 in S₁₀. Cobalt chlorosulphate also shows a slight increase in its R_f value with the increase in formic acid concentration. An additional spot with R_f value around 0.20 is appeared for cobalt chlorosulphate along with original spot at R_f 0.85 when the chromatogram is developed with S₁₃-S₁₆ solvent systems.

Experimentally, well resolved mutual separation of nickel and cobalt chlorosulphates at microgram level from their mixture has been achieved on silica gel layer using any solvent of choice (S₁-S₁₀). Therefore, for a better separation, the loading rate the maximum possible amount of nickel from cobalt at microgram levels is always possible. However, sometimes the larger amounts of an analyte are required to be separated from complex mixture. Therefore, an attempt to separate the maximum possible amount of nickel chlorosulphate from a fixed amount of cobalt chlorosulphate at milligram levels was made. It was always possible to separate cobalt chlorosulphate (4.0 μg-5 mg, maximum R_f value = 0.88) from 5 μg-200 mg of nickel chlorosulphate (R_f = 0.28). It has been experimentally noticed that higher loading of cobalt chlorosulphate (>10 mg) halted its separation from nickel chlorosulphate because of the formation of tailed spot of cobalt.

Therefore, for a better separation, the loading
amount of cobalt chlorosulphate should not exceed 5 mg per spot.

The presence of inorganic anionic impurities (NO$_3^-$, SCN$^-$, PO$_4^{3-}$, IO$_3^-$, Fe(CN)$_6^{3-}$, Fe(CN)$_6^{4-}$, I$^-$, Br$^-$, F$^-$, CrO$_4^{2-}$, Cr$_2$O$_7^{2-}$, MoO$_4^{2-}$ and Mo$_7$O$_{24}^{6-}$) exceeding to 1 µg in the mixture of cobalt and nickel chlorosulphates hurts the separation. Anions such as NO$_3^-$, IO$_4^-$, BrO$_3^-$, MnO$_4^-$, Cl$^-$, SO$_4^{2-}$ and S$_2$O$_3^{2-}$ interfere at all concentration levels in the separation of nickel from cobalt.

The magnetic moment for fairly regular tetrahedral complexes of nickel falls in the range 3.5-4 BM whereas for octahedral cobalt complexes it lies in the range 4.7-5.2 BM. The reported values of magnetic moments for nickel and cobalt chlorosulphates are 3.6 and 5.11 BM, respectively. It is, therefore, concluded that tetrahedral complex of nickel has strong binding interactions with silica gel compared to octahedral cobalt complex.

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References
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