# Anion Exchange Separation of Cobalt from Steel and other Ferrous Samples

ABDUL MAJEED, M.S.KHAN AND E.K.BALLANTYNE[**]
*Chemistry Department, Islamia University, Bahawalpur.*
*Pakistan*

**Summary:** A quick and accurate method for the determination of cobalt in iron and steel samples is reported. The separation of cobalt from iron and other elements present in iron and steel samples was affected on an anion exchange resin. It is based on selective adsorption of various ion chlorides present at different concentrations of hydrochloric acid. The amount of cobalt was determined photometerically by forming its nitroso-R-salt complex.

## Introduction

A comprehensive study of anion exchange behaviour of metal ions in chloride and flouride solutions has been reported in a series of papers [1-8]. It was observed that the adsorbability of these elements differed sufficiently as a function of hydrochloric acid concentration. The adsorption is due to the formation of negatively charged chloride complexes [9] such as $FeCl_4^-$ $CoCl_3^-$ and $NiCl_3^-$. Yashino and Kojima [10] and then Strelow [11] separated cadmium from zinc and other metal ions using hydrochloric acid as eluent. Similarly hydrochloric acid has been used for separation of $Fe^{+3}, Co^{+2}, Mo^{+6}, Al^{+3}$ and $Ni^{+2}$ on a cation exchange column [12], when both iron and cobalt were present in small amounts. This method was not successful when used to separate cobalt from steel samples due to the presence of iron in a large amount.

Estimation of $Co^{+2}$ from steel samples by British Standard Method [13] involves the separation of iron by precipitation and takes about 24 hours for complete determination. The present work was therefore taken in hand to develop a quick method for separation and then estimation of $Co^{+2}$ from steel samples in a shorter time by using an anion exchange column.

## Experimental

### Preparation of Reagents

All reagents used were of analytical grade (BDH) and distilled water was used whereever required. Solutions were freshly prepared and were filtered whenever necessary.

### Cobalt solution

Dissolved 0.1 g of high purity cobalt (BDH) by heating, in 10 ml of 9M HCl in a covered container. When cold, the solution was diluted to 100 ml with 9M HCl solution. 5 ml of this solution was further diluted to 200 ml with 9M hydrochloric acid.

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[**] British Steel Corporation, Clydebridge Works, Cambuslang, Glasgow, U.K.

## ii) Nitric acid (50%)

100 ml of conc. nitric acid was diluted to 200 ml with water.

## iii) Nitro-R-salt

Dissolved 0.3 g of sodium-1-nitroso-2-naphthol-3, 6-disulphonate (nitroso-R-salt) in 100 ml of water. Fresh solution was prepared for every determination.

## iv)Phosphoric-sulphuric acid solution (15:15) percent v/v

150 ml of phosphoric acid and 150 ml of sulphuric acid (sp.gr.1.84) were mixed with 600 ml of water. When cold, water was added to make a volume of 1000 ml.

## v)9M Hydrochloric acid solution

100 ml water mixed with 810 ml of conc. hydrochloric acid (sp.gr. 1.18).When cold, the solution was diluted to 1 litre with water.

## vi)4M Hydrochloric acid solution

To 500 ml of water, added 360 ml of hydrochloric acid (sp.gr.1.18) When the solution was cooled to room temperature, water was added to make a volume of 1000 ml.

## vii)Sodium acetate (50% w/v)

Dissolved 500 mg of sodium acetate ($CH_3$ $COON_a$:$3H_2O$) in water so as to make a total volume of one litre.

## Preparation of Column

30g of IRA 400 (Cl) analytical grade resin was mixed with 100 ml of water. The liquid was decanted as soon as the larger particles had settled. The resin was stirred with a fresh portion of water and separated by decantation of the liquid. The process was repeated until the supernatant slurry was clear. Transferred the slurry to a 35 cm long glass tube with a glass wool plug at the bottom, by constant tapping so as to prepare 22 cm.long, bubble free and well packed, resin column. Another glass wool plug was inserted on top of the column.

## Procedure

5g of the steel sample was dissolved in 25 ml of 9M HCl solution in a covered beaker by gentle heating. Oxidation of $Fe^{+2}$ to $Fe^{+3}$ was achieved by dropwise addition of conc. nitric acid (sp.gr. 1.42). The solution was evaporated to approximately 5 ml volume. Before transfering the sample to the column, 50 ml of 9M HCl was passed through the column which was drained almost to bed level. The sample was then transferred to the top of the resin column with a flow rate of 1 to 1.5 ml/minute. The beaker containing the sample was washed twice with measured amount (5-10 ml) of 9M HCl and the washings were transferred to the top of the column. A total of 50 ml (including washings of the beaker) of 9M HCl was passed through the column. The effluent, which contained $Ni^{+2}$, $Cr^{+3}$ and $Al^{+3}$ ions was collected in a beaker.

The column was then eluted with 50 ml of 4M HCl solution with a flow rate of 1 to 1.5 ml/minute and the eluate collected in a separate beaker (this contained $Co^{+2}$ and $Cu^{+2}$ ions). To this solution was then added 5 ml of phosphoric-sulphuric acid solution. The mixture was then evaporated by heating till it started fuming. When cooled to

room temperature, water was added to make a volume of 25 ml.

Two 10 ml portions of the aliquot were transferred into two separated 50 ml graduated flasks. To one of the flasks was added 10 ml of nitro-R-Salt solution and an equal amount of sodium acetate solution. The mixture was shaken and allowed to stand at room temperature for 5 minutes when 10 ml of 50% nitric acid solution was added and the volume made up with water.

To the other 10 ml portion of the aliquot were similarly added sodium acetate and 50% nitric acid solution in the same quantities as for the first flask. The absorption of the two solutions thus prepared was measured at 510 nm using 0.5 cm cell on SP 600 spectrophotometer. The blank was run concurrently with test determination and approximate corrections made [12].

After the elution of cobalt with 4M hydrochloric acid the column is regenrated by passing 200 ml of water through it, to remove iron and any other ion adsorbed on it. After this wash the column is ready for reuse.

### Calibrations

Nine standard solutions were prepared by dissolving 5g of high purity steel, (in this work B.C.S.149/S) as described above for sample preparation and then adding different amounts of standard cobalt solution (1 ml = 0.025 g of cobalt) and 9M hydrochloric acid solution as indicated below:

| No. | Cobalt Soln.(ml) | 9M HCl(ml) |
|-----|------|------|
| 1. | 0.0 | 25.0 |
| 2. | 2.5 | 22.5 |
| 3. | 5.0 | 20.0 |
| 4. | 7.5 | 17.5 |
| 5. | 10.0 | 15.0 |
| 6. | 12.5 | 12.5 |
| 7. | 15.0 | 10.0 |
| 8. | 17.5 | 7.5 |
| 9. | 22.5 | 2.5 |

The nine samples, thus prepared, were treated separately, and $Co^{+2}$ separated from them on ion exchange columns and the absorbance of 4M HCl solutions was recorded under similar conditions as for the sample above.

The absorbance for sample No.1 with added zero % cobalt was treated as a blank reading. Standard graph was prepared by plotting absorbance against concentration, using which the concentration of unknown sample found out.

As pure iron sample B.C.S. 149/3 contained 0.007% cobalt in it, this percentage of cobalt was taken into account while preparing the standard graph from the nine samples mentioned above.

The comparison of results for 3 standard samples of steel are reported in Table-1. Certified composition of three standard steel samples is given in Table-2.

Ten sample were processed for each standard.

Table-1

| B.C.S. No. | % of Co reported | % of Co found | Standard deviation |
|---|---|---|---|
| 326 | 0.0230 | 0.0238 | 0.0003 |
| 329 | 0.0700 | 0.0698 | 0.0005 |
| 330 | 0.0200 | 0.0205 | 0.0002 |

Standard deviation was calculated by the formula.

$$\delta = \sqrt{\frac{\varepsilon(\bar{X} - X_i)^2}{n-1}}$$

Where

$\delta$ = standard deviation
$\bar{X}$ = mean of 10 readings.
$X_i$ = individual reading
$n$ = number of samples

## Discussion

The standard method [13] available for estimation of cobalt in steel samples involves prior separation of iron by precipitation with α-nitroso-β-napthol. Complete separation takes from 20-22 hours. The cobalt from the remaining solution is then estimated photometrically by forming its nitroso-R-salt complex. The determi-
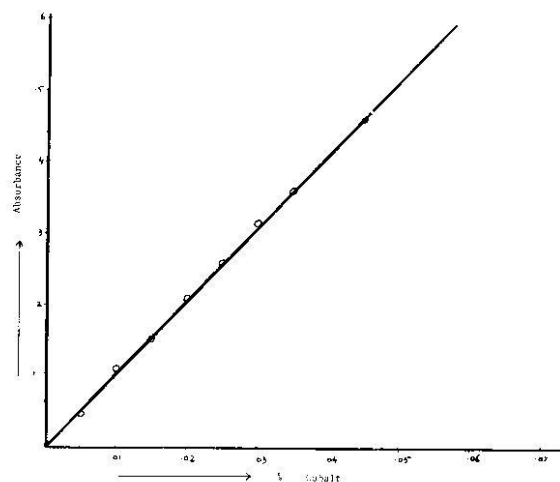


Fig.1: Standard graph for estimation of Cobalt

nation of cobalt thus takes about 24 hours. The present method is quick as separation of cobalt from steel samples and its determination takes only 3-4 hours. The accuracy of the method is also remarkable (Table-1).

The adsorption of various ions on an anion exchange column is due to the formation of negetively charged chloride complexes [9] such as $FeCl_4^-$, $CoCl_3^-$, and $NiCl_3^-$. Ion complexes of $Ni^{+2}$, $Al^{+3}$ and $Cr^{+3}$ are not stable at 9M HCl concentration and are not adsorbed on the column. However, $Co^{+2}$ and $Fe^{+3}$ chloride complexes being stable at this concentration are retained by the column. When the concentration of hydrochloric acid is changed to

Table-II: Percentage composition of mild steels B.C.S. 326,329 and 330

| No. | Co | Al | C | Si | S | P | Mn | V | Sb | Cu | Pb | B |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 326 | 0.023 | 0.005 | 0.23 | 0.36 | 0.009 | 0.019 | 0.32 | 0.057 | 0.005 | 0.260 | 0.014 | 0.001 |
| 329 | 0.70 | 0.058 | 0.16 | 0.15 | 0.020 | 0.029 | 0.12 | 0.083 | 0.018 | 0.072 | 0.050 | 0.008 |
| 330 | 020 | 0.019 | 0.20 | 0.46 | 0.031 | 0.029 | 0.45 | 0.027 | 0.018 | 0.047 | 0.003 | 0.007 |

4M, cobaltous chloride $(CoCl_3)^-$ being unstable at this concentration, is eluted from the column, which however retains $FeCl_4^-$ . Copper, if present in the sample, is also eluted along with cobalt.

Nitroso-R-salt is a very selective reagent and does not form complex with copper. Thus any amount of copper present, along with cobalt, would not interfere in spectrophotometric determination of the latter. Straub and Lewis[14], on the other hand, have used E.D.T.A. for complexing cobalt, which also forms a complex with copper. They therefore had to take extra caution in separating copper from cobalt prior to the latter's estimation. The method threfore becomes more laborious and any traces of $Cu^{+2}$ present would interfere in the determination of $Co^{+2}$. Moreover Straub and Lewis [14] faced difficulty in regenerating the column as tantalum, niobium or tungsten present in the samples were strongly adsorbed by the column and could not be removed and a fresh column was used for every determination. In the present case, however the column was easily regenerated by washing with water and can be used over and over again for a long time.

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