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Determination of Iron and Chromium by Precipitation from Homogeneous Solution Methods

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Iron and chromium are precipitated quantitatively as their hydroxides by urea hydrolysis method from homogeneous solution. The pH for complete prcipitation for iron is 7.4 and for chromium is 7.2. The method has the advantage that the precipitates can be weighed as hydroxides after drying at 110°C. These methods are advantageous over earlier methods since the precipitate need not to be ignited. Thermogravimetric and X-ray diffraction studies were made on the precipitates. These methods can be applied in the preparation of shift catalysts.

INTRODUCTION

Willard and Tang[1] utilised the technique for the precipitation of basic aluminium sulphate by the controlled hydrolysis of urea to yield ammonia and called it a Precipitation From Homogeneous Solution (PFHS) which is the basis for development. Since then a large number of methods were developed and they were reviewed[2–5]. Iron can be precipitated as hydroxide by conventional methods[6] and by PFHS method[7] but iron can be weighed as Fe_2O_3 after ignition. Chromium was determined mostly as chromate. Chromium can also be precipitated conventionaly as hydroxide[6] but can be weighed as Cr_2O_3.

Present work deals with the development of quantitative method for the determination of iron and chromium by precipitating them as hydroxide from homogeneous solution by urea hydrolysis method.

EXPERIMENTAL

Ferric ammonium sulphate $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 12H_2O$, chromium sulphate $Cr_2(SO_4)_3 \cdot 6H_2O$, urea NH_2CONH_2 (all from Loba Chemicals), nitric acid and sulphuric acid were all of analytical reagent grade.

A stock solution of iron was prepared by dissolving about 48.28 g of ferric ammonium sulphate (0.1 M) in concentrated sulphuric acid and diluting to 1 L with double distilled water.

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A stock solution of chromium was prepared by dissolving about 49.5 g of chromium sulphate in double distilled water and diluted to 1 L.

Natzsch thermobalance mode STA 409 (BARC, Bombay) was used for taking thermograms. X-ray diffractograms were recorded on a Phillips PW1051 diffractometer. Systronics UV-Visible Spectrophotometer was used for colorimetric measurements and Elico pH meter was used for pH measurements.

Procedure

(A) Precipitation of ferric hydroxide

0.5 mL of concentrated nitric acid and 5 g of urea were added to 10 mL of the stock solution containing about 56 g of iron in a 250 mL conical flask and the volume was adjusted to approximately 100 mL. The initial pH of the solution was found to be 1.8. The conical flask was fitted with a rubber cork and was heated on a steam bath for about 4 h maintaining the volume by occasional addition of distilled water. The final pH of the supernatant liquid after complete precipitation was found to be 7.4. The precipitate was filtered in a G_4 sintered glass crucible and washed with small amount of distilled water. It was dried at 110°C for about 1 h and weighed as $Fe(OH)_3$. The conversion factor $Fe/Fe(OH)_3$ is 0.5234.

(B) Precipitation of chromium hydroxide

5 g of urea was added to 10 mL of the stock solution containing 104 g of chromium in a 250 mL conical flask and the volume was adjusted to 100 mL. The initial pH of the solution was found to be 3.3. The conical flask was fitted with rubber cork and heated on a steam bath for about 2 h maintaining the volume by addition of distilled water. The final pH of the supernatant liquid after complete precipitation was found to be 7.2. The precipitate was filtered in a G_4 sintered glass crucible and washed with small amount of distilled water. It was dried at 110°C for about 1 h and weighed as $Cr(OH)_3$. The conversion factor $Cr/Cr(OH)_3 = 0.5048$.

RESULTS AND DISCUSSION

The results of precipitation and determination of iron as iron hydroxide using the recommended PFHS method are reported in Table-1. The results indicate that 50 to 300 mg of iron can be determined accurately. The precipitate obtained is pure amorphous and it does not adhere to the walls of the beaker. No suitable anion is necessary in this method. The precipitate can be weighed as iron hydroxide after heating to 110°C. Thermogram of the precipitate was shown in Fig. 1. From the figure it is clear that the precipitate has constant weight at 470°C. From 470° to 850°C there is no weight loss. Conversion of $Fe(OH)_3$ to Fe_2O_3 is completed at 470°C. DTA curve indicates the endothermic nature of the precipitate. X-ray diffractograms were taken for the ferric hydroxide samples dried at 110°C for 1 h and ignited at 400°C and were shown in Fig. 2. The precipitate dried at 110°C is amorphous while that of ignited precipitate is crystalline. It is clear from the figure that crystalline ferric oxide contains two phases and is a mixture of α-Fe_2O_3 and γ-Fe_2O_3. The iron content in $Fe(OH)_3$ was determined colorimetrically[6] and was found to be 52.34%.

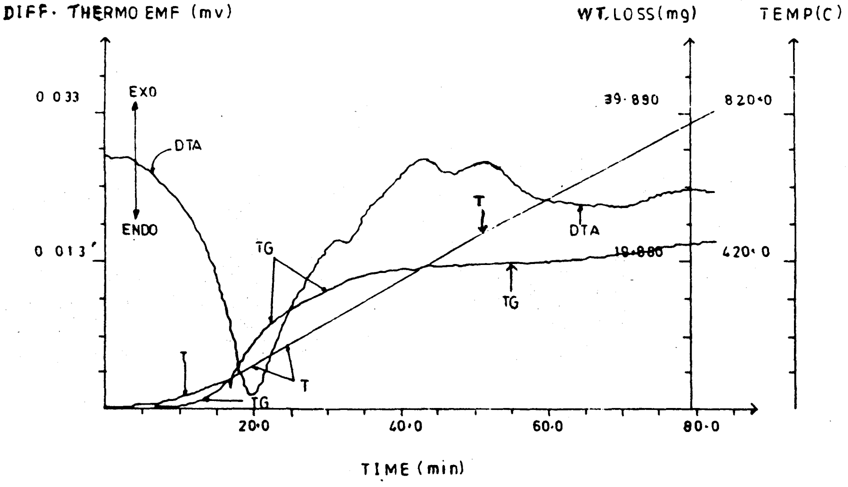

Fig. 1. Thermogram of iron hydroxide.

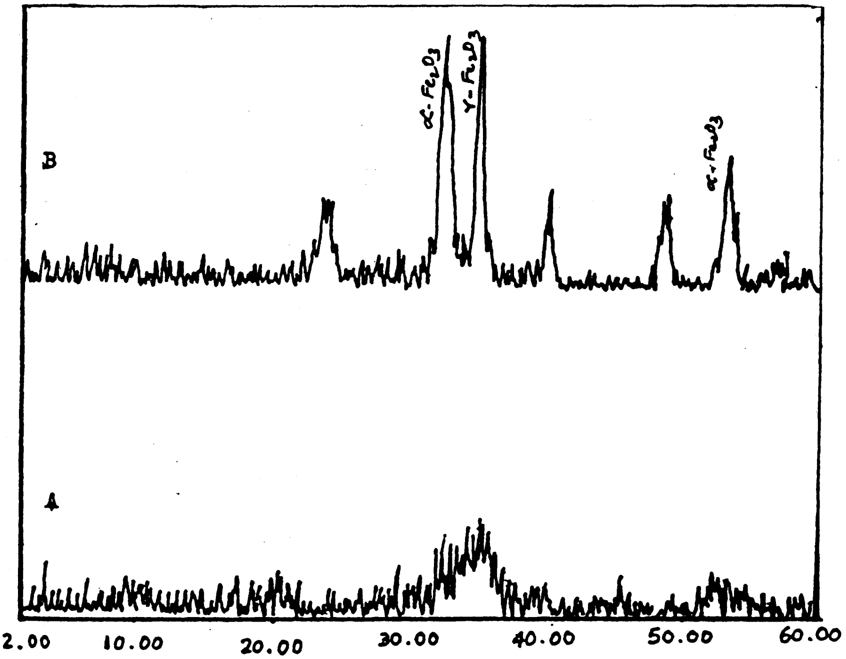

Fig. 2. X-ray diffractogram of iron hydroxide dried at (110°C (A) and 400°C (B).

TABLE-1
PRECIPITATION OF VARYING AMOUNTS OF IRON

Wt. of iron taken (mg)	Wt. of iron found (mg)	Per cent recovery
56	53	94.64
56	55	98.21
56	54	96.43
112	110	98.21
112	113	100.89
112	111	99.11
168	166	98.81
168	167	99.40
168	168	100.00
280	279	99.64
280	280	100.00
280	281	100.36

The results of determination of chromium as chromium hydroxide using the proposed method are tabulated in Table-2. From the results it is clear that 100–500 mg of chromium can be determined accurately. Experiment was repeated in presence of ammonium chloride and ammonium nitrate. Presence of ammonium salts effects the precipitation since the optimum pH is not attained. Thermogram of the chromium hydroxide precipitate was shown in Fig. 3. The curve rose up due to weight loss continuously and attain horizontal stretch at 640°C. The formula of the compound at this temperature was found to be CrO_2. X-ray

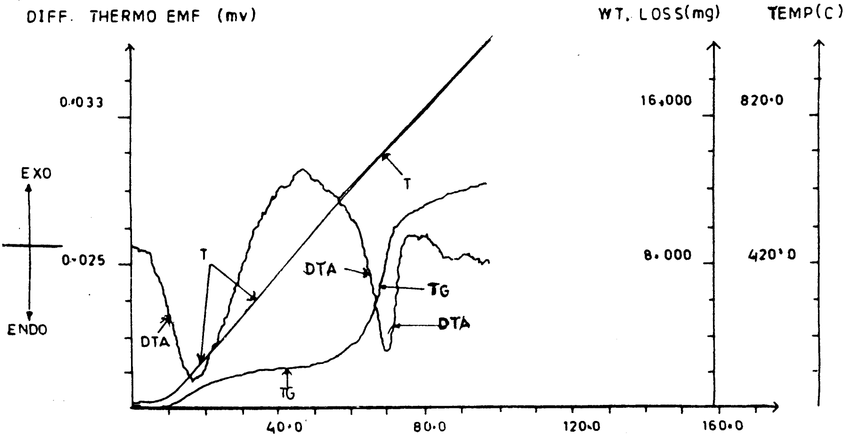

Fig. 3. Thermogram of chromium hydroxide.

diffractograms for the samples of the chromium hydroxide precipitate (A) heated at 110°C and (B) ignited at 400°C were shown in Fig. 4. Curve-A shows the amorphous nature. It is clear from the curve-B that precipitate becomes crystalline on ignition to 400°C and forming hxagonal Cr_2O_3. To know the purity of the precipitate, the chromium content was determined by spectrophotometric method[6]. The percentage of chromium was found to be 50.48.

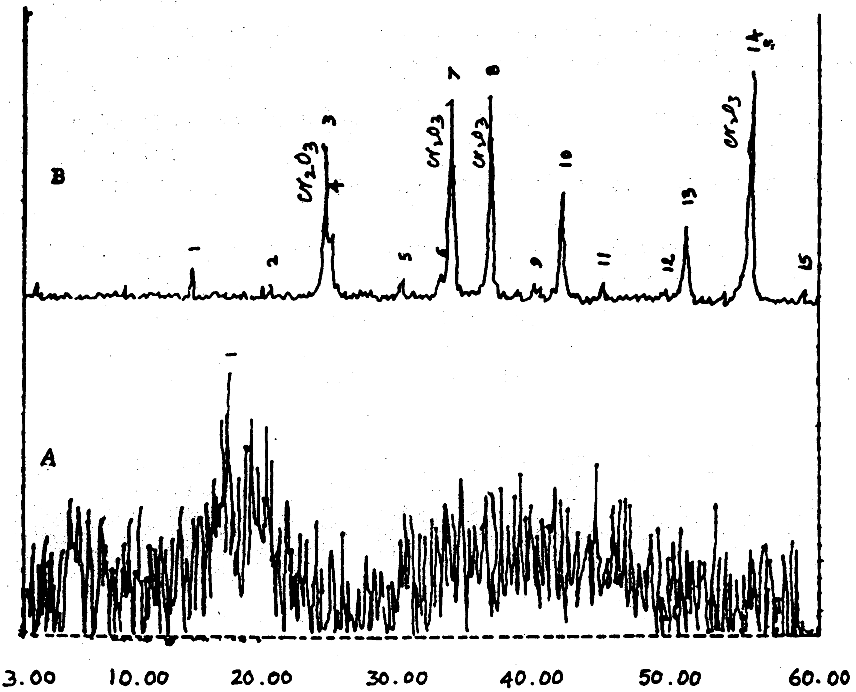

Fig. 4. X-ray diffractogram of chromium hydroxide dried at (110°C (A) and 400°C (B).

Conclusion

The recommended method for the precipitation of $Fe(OH)_3$ can be used for quantitative determination and also in the preparation of shift catalyst. The determination of iron is advantageous since it can be weighed as $Fe(OH)_3$ by drying at 110°C. In other earlier methods it has to be ignited to Fe_2O_3 at higher temperature of about 850°C weighed as Fe_2O_3. In this method, in the absence of suitable anion, the precipitate is obtained in a pure form and does not adhere to the walls of beaker as in the earlier PFHS method. The recommended procedure for the precipitation of $Cr(OH)_3$ can be used for quantitative determination. Usually chromium can be dtermined after converting chromium to chromate but in the recommended method it can be directly determined by precipitating chromium hydroxide which is an advantage. The method was applied elsewhere[8] for preparation of Fe_2O_3-Cr_2O_3 shift catalyst.

TABLE-2
PRECIPITATION OF VARYING AMOUNTS OF CHROMIUM

Wt. of chromium taken (mg)	Wt. of chromium found (mg)	Per cent recovery
104	103	99.04
104	104	100.00
104	105	100.96
208	206	99.04
208	205	98.56
208	208	100.00
312	310	99.36
312	311	99.68
312	313	100.32
520	518	99.62
520	520	100.00
520	522	100.38

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