CCLV.—*The Estimation of Ferro- and Ferri-cyanides.*

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BY making use of the fact that solutions of ferrocyanides precipitate, from a solution of benzidine dihydrochloride, a sparingly soluble white salt, $3C_{12}H_{12}N_2,H_4Fe(CN)_6,H_2O$, Cumming (J., 1924, **125**, 240) estimated gravimetrically and volumetrically the ferrocyanides of sodium, potassium, and calcium. Satisfactory results were obtained, but the use of hypobromite as an external indicator in the volumetric process required some practice. By altering the method of estimation, however, it is possible to replace it by phenolphthalein. Mr. R. Fleming, of The Cairo School of Medicine, has kindly informed us that benzidine gives a blue coloration with a mixture of copper sulphate and ammonium thiocyanate solutions. The coloration, however, is produced only under certain conditions of concentration.

The gravimetric method outlined in the previous paper has now been extended to other soluble and also to insoluble ferrocyanides,

and the volumetric method has been improved so as to render the end-point easy of detection. Both methods have also been applied to soluble ferricyanides, which give with benzidine dihydrochloride (Cumming, J., 1924, **125**, 1107) a sparingly soluble, bluish-violet precipitate, $3C_{12}H_{12}N_2,H_3Fe(CN)_6,3H_2O$ (Found : Fe, 6·8. Theory requires Fe, 6·8%).

*Estimation of Ferrocyanides.*—For soluble ferrocyanides, the gravimetric method (*G.M.*) is that already described, 0·2 g. of the salt being used. An insoluble ferrocyanide (0·5 g.) is dissolved in sodium hydroxide or decomposed by carbonate solution, and the metal removed by suitable means (see later). The filtrate is exactly neutralised with dilute hydrochloric acid, methyl-orange being used as indicator, and an excess of a saturated solution of benzidine dihydrochloride is added. The precipitate is filtered off, washed, dried, and ignited as before. By multiplying the weight of ferric oxide obtained by the factor given, the weight of anhydrous ferrocyanide is obtained.

The principle of the new volumetric method (*V.M.*) consists in adding to a neutral solution of the ferrocyanide a measured quantity (excess) of a standard solution of benzidine dihydrochloride. The precipitated benzidine hydroferrocyanide is filtered off, and the hydrochloric acid in the filtrate estimated with standard alkali and phenolphthalein. In the case of the insoluble ferrocyanides, the heavy metal is removed as in the gravimetric method, and the measured excess of the benzidine then added to the carefully neutralised filtrate.

The volumetric method depends on the reaction $3[B,2HCl] + M_4Fe(CN)_6 = 3B,H_4Fe(CN)_6 + 4MCl + 2HCl$. The hydrochloric acid produced is equivalent to one-third of that present in the benzidine dihydrochloride used in the reaction. Hence, if 1 c.c. of alkali solution is equivalent to $b$ c.c. of benzidine dihydrochloride solution and $n$ and $x$ are the number of c.c. of benzidine dihydrochloride solution added, and used in the reaction, respectively, then the total alkali (c.c.) required after the reaction, $a = (n - x)/b + x/3b$, whence $x = 1·5(n - ab)$. Hence, since the concentration of benzidine dihydrochloride is known, the amount of the original ferrocyanide can be calculated; or $x/3b$ represents the volume of standard alkali equivalent to the free hydrochloric acid produced, and this is proportional to the amount of ferrocyanide originally present.

*Estimation of Ferricyanides.*—The gravimetric method is similar to that used in the case of the ferrocyanides, but a large excess of benzidine dihydrochloride (250 c.c. of the saturated solution for 0·2 g. of ferricyanide) is required to complete the precipitation

of the benzidine hydroferricyanide. A test should be made, however, to ascertain if precipitation is complete.

The volumetric method is the same as for ferrocyanides, but again a large measured excess of benzidine dihydrochloride is required. The reaction is represented by $3[B,2HCl] + M_3Fe(CN)_6 = 3B,H_3Fe(CN)_6 + 3MCl + 3HCl$. The hydrochloric acid produced is equivalent to one-half of the quantity present in the benzidine dihydrochloride used in the reaction. In the same notation as before, $x = 2(n - ab)$. The quantity of ferricyanide can therefore be calculated; or, as before, the amount of ferricyanide $\propto$ HCl produced $\propto x/2b$ (c.c. of standard alkali).

Both the gravimetric and the volumetric method give accurate results, and are very easily carried out. Both methods may be applied to the same sample of the salt; the former estimation is obtained from the precipitate of the organic salt, the latter from the filtrate after removal of the organic salt.

## EXPERIMENTAL.

Standard benzidine dihydrochloride solution is prepared by dissolving, with the aid of slight heat, about 3·5 g. of pure benzidine in a litre of water containing the calculated quantity of chlorine-free hydrochloric acid, or by dissolving about 4 g. of pure benzidine dihydrochloride in a litre of water. In the former case, if the benzidine is not quite pure, the solution should be standardised, gravimetrically, against a pure ferrocyanide. In the latter case, if the salt contains some monohydrochloride, as it often does when recrystallised from water (see Cumming, *J. Soc. Chem. Ind.*, 1923, **42**, 168), the solution should be titrated with standard sodium hydroxide and the quantity of hydrochloric acid adjusted to that required to form the dihydrochloride (compare equations of the reactions).

*Estimation of Ferrocyanides.*—*Potassium ferrocyanide* (standardisation). Found (by *V.M.*): $K_4Fe(CN)_6,3H_2O = 99·9, 99·8$ %.

*Ammonium ferrocyanide* was prepared by adding a large excess of alcohol to a solution of the crude salt in the minimum quantity of cold water; after prolonged and vigorous shaking, the salt was thrown out as lustrous, light green, stable plates. It was filtered off, washed with a little alcohol and finally with ether, and dried in the air at the ordinary temperature. *G.M.* Factor = 3·556. Found : $(NH_4)_4Fe(CN)_6 = 81·9, 82·0$%. *V.M.* The salt was estimated by titrating the filtrate with alkali and methyl-red, or by boiling the alkaline solution of the salt until all the ammonia was expelled. After dilution and neutralisation, excess of standard benzidine dihydrochloride solution was added, the precipitate filtered off, and

the filtrate titrated with standard alkali and methyl-orange [Found : $(NH_4)_4Fe(CN)_6 = 81.9$, 82.1 %. This result was confirmed from a second preparation of the salt. $(NH_4)_4Fe(CN)_6,3\frac{1}{2}H_2O$ requires $(NH_4)_4Fe(CN)_6$, 81.85%]. Williams ("Cyanogen Compounds," Churchill, 1915) assigns $4H_2O$, and Etard and Bémont (*Compt. rend.*, 1885, **100**, 108) $3H_2O$ to the salt precipitated from alcohol.

*Magnesium ferrocyanide* was purified in the same way as the ammonium salt. There is, however, no difficulty in mixing the aqueous solution with alcohol. *G.M.* Factor $= 3.263$. Found : $Mg_2Fe(CN)_6 = 54.5$, 54.3%. *V.M.* Found : $Mg_2Fe(CN)_6 = 54.3$, 54.2%. [$Mg_2Fe(CN)_6,12H_2O$ requires $Mg_2Fe(CN)_6$, 54.7%]. The salt, when recrystallised from alcohol, had the same composition [Found : $Mg_2Fe(CN)_6 = 54.7\%$].

*Barium ferrocyanide* was boiled with a little concentrated potassium carbonate solution until decomposition was complete. The liquid was cooled, diluted to complete the precipitation of the barium carbonate, filtered, and the ferrocyanide in the filtrate estimated as before. *G.M.* Factor $= 6.094$. Found : $Ba_2Fe(CN)_6 = 82.1$, 81.7%. *V.M.* Found : $Ba_2Fe(CN)_6 = 81.6$, 81.7% [$Ba_2Fe(CN)_6,6H_2O$ requires $Ba_2Fe(CN)_6$, 81.8%]. This salt was also estimated as a soluble ferrocyanide, but bulky solutions were involved [Found : $Ba_2Fe(CN)_6$, 81.8%].

*Lead ferrocyanide* was prepared by adding cold dilute potassium ferrocyanide in excess to a dilute solution of lead acetate, washing the salt with warm water until free from soluble ferrocyanide, and drying it in the air. In the estimation, the lead was removed with potassium carbonate as in the case of barium, or by saturating a warm solution of the ferrocyanide in a little concentrated sodium hydroxide solution with carbon dioxide and diluting and filtering it. *G.M.* Factor $= 7.844$. Found : $Pb_2Fe(CN)_6 = 86.3$, 86.3%. *V.M.* Found : $Pb_2Fe(CN)_6 = 85.8$, 86.3%. The salt appears to contain $5\frac{1}{2}$ molecules of water [theory requires $Pb_2Fe(CN)_6$, 86.3%]. The degree of hydration is given as 3, 4, 5, and $6H_2O$ by different investigators.

*Zinc ferrocyanide* was prepared from zinc sulphate as in the case of the lead salt. Sodium and potassium carbonates convert zinc ferrocyanide partly into a basic salt, so the following method of estimation was adopted. The salt was dissolved in a small excess of sodium hydroxide solution, and yellow ammonium sulphide solution added drop by drop until precipitation was complete. The precipitated zinc sulphide was filtered off and washed with hot water, and the filtrate boiled to expel ammonia. The filtrate and washings were carefully neutralised and cooled. (In most cases a

slight separation of sulphur takes place, but it is unnecessary to remove this. It is also unnecessary to remove any hydrogen sulphide formed. Hydrogen sulphide may be used to precipitate the zinc, but the solution should not be saturated.) After neutralisation the ferrocyanide in the filtrate was estimated as before. *G.M.* Factor = 4·292. Found: $Zn_2Fe(CN)_6 = 79·4$, 79·9%. *V.M.* Found: $Zn_2Fe(CN)_6 = 79·2\%$. [$Zn_2Fe(CN)_6,5H_2O$ requires $Zn_2Fe(CN)_6$, 79·2%]. A specimen of zinc ferrocyanide obtained from the British Drug Houses was found to have the same composition. Friend ("Text-Book of Inorganic Chemistry," IX, p. 2220) gives 3 or 4 $H_2O$.

*Estimation of Ferricyanides.*—Sodium ferricyanide was purified from a well-agitated, aqueous solution of alcohol. *G.M.* Factor = 3·518. Found: $Na_3Fe(CN)_6 = 88·4$, 88·1%. *V.M.* Found: $Na_3Fe(CN)_6 = 88·7$, 88·7% [$Na_3Fe(CN)_6,2H_2O$ requires $Na_3Fe(CN)_6$, 88·6%].

*Potassium ferricyanide* (standardisation). *V.M.* Found: $K_3Fe(CN)_6 = 100·0$, 100·2%.

As most ferricyanides are soluble in water, the method is almost generally applicable. In the case of insoluble ferricyanides the metal should be removed by some suitable reagent as outlined for insoluble ferrocyanides.

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