VII.—*The Iodometric Estimation of Iron.*

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THE volumetric determination of iron by titration with sodium thiosulphate of the iodine liberated through the interaction of a soluble iodide and a ferric salt, which was first suggested by Mohr (*Annalen*, 1858, **105**, 53), is based upon the reaction $2HI+2FeCl_3=2HCl+I_2+2FeCl_2$. This reaction is known to be reversible, and the blue colour of the starch may return in spite of repeated discharge by thiosulphate. No explanation has been offered of the phenomenon, but various recommendations have been made, such as exclusion of air by a current of carbon dioxide, heating the solution to 60°, waiting 20 minutes before titration, and using very little hydrochloric acid, all of which are based upon a misconception of the nature of the reaction.

To realise the proper conditions necessary for carrying out the accurate estimation of iron by the above method, the process must be considered in two parts : (1) the liberation of iodine from hydriodic acid by the action of the ferric salt, and (2) the titration of the iodine. The conditions for the two operations are not the same.

(1) The first operation is essentially a mutual discharge of ferric and iodide ions and should be represented thus: $2Fe^{\cdot\cdot\cdot} + 2I' = 2Fe^{\cdot\cdot} + I_2$. The reaction therefore should depend merely on the effective concentration of these two ions. In the presence of water, however, the effective concentration of ferric ions is reduced owing to hydrolysis and formation of ferric hydroxide; this follows instantly upon dilution, increases with the time, and is vastly accelerated by the addition of hydroxyl ions, which appear, for example, on the decomposition of potassium iodide in water.

Therefore, the greater the amount of water employed, and the greater the amount of potassium iodide, the larger must be the addition of hydrogen ions. Thus, for the liberation of iodine, there must be a large excess both of iodide and of acid.

The preparation of a solution of iron in which the metal is actually in the soluble form and not colloidal is essential, and if the solution is to be kept stable it must contain acid of not less than about *N* concentration.

If a clear solution possessing the bright lemon-yellow colour of the ferric salt or ferric ions is treated with an equal volume of concentrated hydrochloric acid and sufficient potassium iodide (about 5·5 mols. of iodide to each atom of iron), the iodine will be liberated practically instantaneously, and may be immediately titrated with a theoretical result. In order to avoid this large excess of acid, it suffices to use *N*-acid, the reaction being then complete, whatever the concentration of iron, in 3 minutes at room temperature. No reversion is to be observed in these circumstances, and titration may be made at any later time.

(2) If the iron was truly in the state of a dissolved ferric salt when the iodide was added, the solution may be freely diluted with water after 3 minutes, and titrated with starch as indicator. The end-point should be sharp and there should be no return of blue colour. The reoxidation of ferrous iron by the air in these circumstances is negligible or non-existent, and precautions to avoid this are superfluous. The solution after titration by thiosulphate may be shaken violently with air for 2 hours without any return of the blue colour, even when the acidity is that of *N*-hydrochloric acid, and however dilute the iodide, but if hydrogen peroxide be added in a concentration corresponding to that of oxygen in saturated water, the appearance of free iodine is almost instantaneous: the oxidation by atmospheric oxygen, if it occurs at all, is about one million times slower than by hydrogen peroxide in equivalent oxygen concentration.

The above statements are true for pure solutions, provided that the iron was present as ferric ions when mixed with the iodide; but if not, the blue colour will return. In the presence of various impurities, hydrogen iodide will decompose at a rate proportional to the concentration of its ionised portion. This may be prevented either by raising the concentration of iodide ions or by lowering the concentration of hydrogen ions, as, *e.g.*, by the addition of sodium acetate. This addition is only necessary if impurities are present.

The factors which cause the return of the blue colour after thiosulphate titration by discharging iodide ions are: (1) colloidal ferric hydroxide or suspended oxide, which may be introduced with the reagents; (2) hydrogen acceptors (oxidising agents) such as chlorine or nitric acid; (3) copper. Oxidising agents present as impurities will give high results but will not cause a return of blue colour after titration unless they are added in the distilled water.

In the absence of colloidal ferric hydroxide (or oxide), therefore, the only cause of the returning blue colour is copper. In the analysis of the ash of plants and animals for iron, this metal will frequently be found, and may be recognised and even estimated with fair accuracy by the rate of return of the blue colour, other causes having been eliminated.

The effect is readily distinguishable from others in that it is catalytic; by means of the effect it is possible to distinguish 1—2 parts of copper in 2,000,000 parts of water. The presence of copper naturally leads to high results, and it must be removed if its effect is significant. With solutions of iron not weaker than $N/400$, this may be done readily by adding an excess of ammonium hydroxide, which leaves the copper entirely in solution.

The detailed procedure for successful use of the method is; therefore, as follows :

(*a*) Incinerate the material to remove organic matter, evaporate repeatedly with concentrated hydrochloric acid until any insoluble residue is colourless, and adjust the hydrochloric acid content of the final solution so that it is not less than 0·4 c.c. of concentrated acid in 10 c.c. (The total volume of acid employed should be noted, for a control may be necessary on the iron which it probably contains.) If the estimation is delayed, avoid diluting the acid ferric solution until immediately prior to the estimation, especially when the amount of iron is small.

(*b*) If copper is present, add excess of ammonium hydroxide, filter, wash, and redissolve the precipitate in acid.

(*c*) To 10 c.c. of the ferric chloride solution add 0·33 g. of potassium iodide dissolved in not more than 5 c.c. of water (= 2 c.c. of M-potassium iodide). The liberation of iodine is complete in 3 minutes at 15°.

(*d*) Dilute the above mixture with pure distilled water, add sodium acetate if desired, and titrate with thiosulphate of suitable strength. If very dilute thiosulphate is used, it must be freshly made each day. With $N/2000$-thiosulphate it is possible to estimate accurately quantities of the order of 0·05 mg. Fe.

The thiosulphate may be standardised on potassium dichromate, the procedure being the same as with the estimation of iron, except that hydrolysis does not interfere.

EXPERIMENTAL.

Numerous experiments have shown that 5·5 mols. of potassium iodide are required per atom of iron, and the concentration in the titrated liquid should be adjusted to about *M*/7·5, and the acid concentration should be *N*/3—3*N*. In such a case the liberation of iodine will be strictly proportional to the iron present within the limits 0·056—56 mg. of iron in 10—50 c.c. of liquid.

Any reagent causing lowering of hydrogen-ion concentration, *e.g.*, sodium acetate, thus favouring hydrolysis of ferric chloride, tends to produce recurrence of the blue colour. Old solutions of iron salts contain iron hydroxide, which dissolves slowly, and therefore they cause a slow recurrence of the blue colour. On the other hand, freshly made ferric chloride solutions, on dilution with water, contain hydroxide in a form which dissolves rapidly. Hence, in this case, the blue colour reappears rapidly and the total liberation of iodine comes to an end more quickly. This cause of the recurring blue colour is therefore quite distinct from the catalytic action of copper.

It will be noted that low hydrogen-ion concentration favours the recurrence of the colour due to the presence of ferric hydroxide, but also increases the stability of hydriodic acid in the presence of impurities.

The effect of copper is shown by the following results:

(N/40-$FeCl_3$ containing 0·4% HCl; M/7·KI solution.)

1. 10 c.c. Fe soln. + 2 c.c. KI + 3 c.c. water after 5 mins. = 10·16 c.c. N/40-$Na_2S_2O_3$.
2. 10 c.c. Fe soln. + 4 c.c. KI + 1 c.c. water after 5 mins. = 10·32 c.c. N/40-$Na_2S_2O_3$.
3. 10 c.c. Fe soln. + 2 c.c. KI + 3 c.c. M/200-$CuSO_4$ (= 0·96 mg. Cu) = 10·5 c.c. N/40-$Na_2S_2O_3$.

Less than 2 c.c. of *M*/200-copper sulphate does not immediately affect the liberation of iodine with this quantity of iron, but produces later the characteristic catalytic effect. No. 2 remained colourless for many hours, and No. 1 became coloured in 15 minutes owing to insufficient potassium iodide; No. 3 coloured rapidly, and in 12 minutes required an extra 0·43 c.c. of *N*/200-thiosulphate.

The power to cause recurrence of colour is possessed only by metallic ions which can change from higher to a lower valency, such as $Fe^{\cdot\cdot\cdot}$, $Cu^{\cdot\cdot}$, $Mn^{\cdot\cdot\cdot\cdot}$; all other basic ions tried, including $Na^{\cdot}$, $K^{\cdot}$, $Mg^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Ni^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Fe^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, were quite without influence upon the velocity of decomposition of hydrogen iodide, even when present in considerably more than equivalent concentration.

The catalytic activity of the cupric ion in discharging iodide ions is illustrated in the following table, which shows the amount of iodine liberated in one hour.

Copper added, mg.	Iodine liberated (c.c. of *N*/2000).	Mg. of Cu per c.c. *N*/2000-iodine (calc. 0·0032).
0·05	10·8	0·004
0·025	6·3	0·004
0·0125	4·2	0·003
0·0063	2·7	0·003
0·0031	1·96	0·002
0·0016	0·86	0·002

Small quantities of copper thus produce a marked catalytic effect. This gives a method of distinguishing 1—2 parts of Cu in 1,000,000 parts of water.

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