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BY W. S. HENDRIXSON.

In the methods for the determination of chloric acid by reduction, metallic zinc in some form and ferrous sulphate have been the reducing agents most used, though sulphur dioxide and formaldehyde have also been employed. The conditions under which the two former reducing agents have been used have been much varied. Thus Thorpe and Eccles [*] used the zinc-copper couple, and determined with a solution of silver the chloride formed from the chlorate. Bothamley and Thompson [†] showed that the results by this method were too low unless sulphuric acid was added near the end of the reduction to dissolve any basic salts of zinc. By the same method Becker [‡] found the results too low and preferred to use zinc dust and a little copper sulphate. Fleissner [§] used zinc dust and boiled the neutral solution one hour, but Becker attained complete reduction only by using a large excess of zinc dust with sufficient sulphuric acid to dissolve it completely without the aid of heat.

Stelling [||] reduced chlorates by long boiling in an alkaline solution of ferrous sulphate, and determined the resulting chloride. Becker found that the reaction was very slow and incomplete, and recommended a neutral

[*] Jour. Chem. Soc. Lond., 11, 541; 14, 856.
[†] Jour. Chem. Soc. Lond., 53, 164.
[‡] Repert. d. Anal. Chem., 1, 377.
[§] Zeit. d. Anal. Chem., 20, 115.
[||] Zeit. d. Anal. Chem., 6, 32.

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solution of ferrous sulphate. Carnot * reduced the chlorates in bleaching powder by heating at 100° and in the presence of sulphuric acid with about twenty times the theoretical amount of ferrous ammonium sulphate. The amount of chloric acid was found either by titrating the resulting chloride by Volhard's method or by titrating the excess of ferrous sulphate with potassium permanganate. Rosenbaum † states that chlorine will be lost in this method of reduction if the acid and ferrous sulphate are added to a hot solution of the chlorate.

In the course of my own work on the action of chloric acid on metals, it was observed that metallic iron very readily reduces chloric acid even in very dilute solutions. At ordinary room temperature the solution of the metal is very rapid in moderately concentrated solutions, and in any case the iron goes at once into the ferric condition, as was proved by many tests while solution was going on. No gas is evolved, but the iron simply disappears and there results the yellowish-brown solution of a ferric salt, if the acid is in excess. Whether iron alone reduces chloric acid completely could not be determined owing to the large amount of iron oxide, and possibly insoluble basic salt, which were formed, and which made it impracticable to obtain a solution suitable for titration with silver without the use of a reducing agent and sulphuric acid. An approximation, however, showed that about 95 per cent of the chloric acid was reduced.

These facts suggested that the determination of chloric acid might be brought to a very simple form by using metallic iron as the chief reducing agent in the presence of an excess of sulphuric acid, which would prevent the formation of insoluble compounds, make the method applicable to chlorates by setting free the chloric acid, and form ferrous sulphate which is itself a reducing agent for chlorates, and which would already be present to serve when oxidized as the indicator in the titration of the chloride by the method of Volhard. It is evident, there-

* Comp. Rend., 122, 449 and 452
† Zeit. d. Angew. Chem. 1898, 80.

fore, that such a method would be a combination of the two already mentioned, the reduction of a chlorate by a metal and a more efficient one than zinc, and the reduction by ferrous sulphate.

To carry out the method a weighed amount of pure potassium chlorate or a measured amount of chloric acid was placed in a small flask with about 50 c.c. of pure sulphuric acid having a concentration of about 10 per cent, and an excess of "card teeth", used in most laboratories. In some of the experiments recorded below, the flask was fitted with a delivery tube, dipping into water, the purpose being to prevent the possible loss of hydrochloric acid, but this precaution was found to be wholly unnecessary. At first ferric salt is formed and the liquid becomes yellowish-brown, but the dissolved iron is soon reduced and the solution becomes colorless or slightly green. If all the chlorate is dissolved at the beginning, the disappearance of the yellow color may be taken to mark the end of the reduction, which requires at room temperature about one hour. No doubt the reduction could be hastened by heating, if precautions were taken to prevent the loss of any hydrochloric acid. As might naturally be expected the method serves quite as well for the determination of bromic acid and bromates as for chloric acid and chlorates, and two determinations of bromic acid in potassium bromate are given below.

After the reduction was completed, the solution was made up to a definite volume, and portions of it were titrated with $N/20$ silver nitrate. Usually, an excess of silver was added before the iron was oxidized to the ferric condition, to serve as the indicator, by the addition of an excess of nitric acid. There seems, however, to be little danger of the loss of chlorine, if the nitric acid is added before the silver.

The following are results obtained by the method described, the amount of silver required in the titrations being calculated to chloric or bromic acid:

1. 5 c.c. of a solution of chloric acid gave 1.0639. $HClO_3$.
2. 5 c.c. of chloric acid gave 1.0619 $HClO_3$.
   The same solution of pure chloric acid titrated with standard
   barium hydroxide gave in 5 c.c. 1.0665 $HClO_3$.

		CALCU-LATED
3.	0.4595 grams $KClO_3$ gave 0.3158 $HClO_3$.	.3165
4.	0.6709 grams $KClO_3$ gave 0.4628 $HClO_3$.	.4622
5.	0.8300 grams $KClO_3$ gave 0.5731 $HClO_3$.	.5718
6.	1.2744 grams $KClO_3$ gave 0.8778 $HClO_2$.	.8778
7.	0.3350 grams $KBrO_3$ gave 0.2605 $HBrO_3$.	.2585
8.	1.0983 grams $KBrO_3$ gave 0.8460 $HBrO_3$.	.8478

The method above described seems to have some advant-
ages. It is extremely simple. It can be carried out at
room temperature, avoiding the danger of loss of hydro-
chloric acid by heat. In the reduction and the prepara-
tion of the solution for titration are necessary only iron
and pure sulphuric acid and nitric acid which are always
at hand in every laboratory, and no filtering or other oper-
ations likely to occasion loss of chlorine or loss of time are
required.

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THE ACTION OF CHLORIC ACID ON METALS.

BY W. S. HENDRIXSON.

In the course of my work a year ago on Silver as a Re-
ducing Agent, in which the action of finely divided silver
on chloric, iodic and chromic acids was studied quantita-
tively, there was occasion to study the literature relating
to the action of chloric and related acids on other metals.
It soon appeared clear that the amount of information to
be gained about the action of chloric acid in particular, on
the metals was very meager, and it appeared also that there
were several errors, whose origin in most cases could not