Summary

A new cerimetric procedure has now been developed for the direct volumetric titration of mercury(I) to an iodine monochloride end point. This new method has the advantages, (1) it gives a direct titration, (2) the determination can be made at the room temperature and (3) the method does not involve any correction factors.

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References


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Cerimetric Determination of Thallium(I)

By

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The use of ceric sulphate as a volumetric oxidising agent for the determination of thallium(I) was first investigated by Berry¹ and Willard and Young² independently. Berry titrated thallous chloride with ceric sulphate to the iodine monochloride end point. He stated that ordinarily ceric sulphate does not react with thallous salts; and that even when iodine monochloride is present as catalyst the reaction does not proceed to completion. Willard and Young titrated thallium(I) in hydrochloric acid medium with ceric sulphate detecting the end point potentiometrically. The potentiometric titration is reported to give satisfactory results over a wide range of conditions (1) at the room temperature, if a large amount of hydrochloric acid (60 ml of cone. HCl per 200 ml) is present and if the thallium content is not too high, (2) at a higher temperature, if the volume of hydrochloric acid used is less or if the thallium content is large enough to cause much thallous chloride to be precipitated by the hydrochloric acid present. In many of the reactions the equilibrium reached rather slowly towards the end point. A sudden break in potential was followed by a slow increase for a minute or two. At temperatures below 60°C the end point break amounted to 200—250 mv per 0.02 ml of 0.1 N solution of ceric sulphate; but in the titrations made above 60°C the potential break amounted to only 40—100 mv. In the visual titrations, using the pale yellow colour of the ceric ions as the indicator, Willard and Young found that the results are satisfactory.
only when the temperature is between 75° and 98° C and a smaller volume of acid is used (20 ml of concentrated HCl for 200 ml total volume). WILLARD and YOUNG have also titrated thallous sulphate with a solution of ceric sulphate in 2 N hydrochloric acid medium at 50° C using 5 ml of 0.005 M iodine monochloride as catalyst. The end point is detected employing ferroin as indicator. They reported precise results. SWIFT and GARNER employed the iodine monochloride end point for the titration of thallium(I) in hydrochloric acid medium with ceric sulphate and found that the results are not precise. The positive error decreased on shaking during the titration. They have also shown experimentally that the high results are not entirely due either to the slow rate of reaction or to the oxidation of chloride ions.

In the present communication, the author has reported his observations in his investigation on the cerimetric titration of thallium(I).

**Experimental**

About 0.05 M thallium sulphate solution is prepared by dissolving an accurately weighed quantity of thallium carbonate (E. Merck) in dilute sulphuric acid. The solution is standardised by the iodate method of SWIFT and GARNER.

The ceric sulphate solution employed in this investigation is prepared from cerous oxalate supplied by May and Baker Company.

0.005 M iodine monochloride solution used in these experiments is prepared as described by WILLARD and YOUNG.

**Titrations to the Visual End Point**

Two series of experiments have been carried out at the room temperature in which the thallous solution is titrated directly with ceric sulphate in hydrochloric acid medium to a visual end point using ferroin as indicator. In the first series, the overall hydrochloric acid concentration and the amount of iodine monochloride are kept constant (5 ml of 0.005 M iodine monochloride and HCl to keep the overall acidity at 2 N) and the total volume is varied between 50 and 200 ml. It has been found that the speed of the reaction increased with a decrease in the total volume. But in no case the reaction is rapid enough to be recommended for a rapid direct titration at the room temperature. In the second series, the amount of iodine monochloride is varied from 1 to 5 ml (of 0.005 M) keeping the total volume constant at 50 ml and the overall hydrochloric acid concentration at 1 N. Here the speed of the reaction (as noticed by the change of color of the ferroin indicator) has been observed to increase with increasing amount of iodine monochloride. These two series of experiments indicate that iodine monochloride has a definite catalytic effect on the reaction between thallium(I) and ceric sulphate in hydrochloric acid medium. Nevertheless, the author has found that a rapid titration of thallium(I) is not possible at the room temperature whatever be the concentration of the catalyst employed.