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Vanadametry*

Determination of Thallium(I)

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The oxidation-reduction potential of the thallous-thallic couple has been found to vary with the nature of the acid employed. NOYES and GARNER⁵ measured the oxidation potential in nitric acid solution and gave 1.230 volts for the E_0 value. PARTINGTON and STONEHILL⁶ determined the potential in sulphuric acid solution to be 1.2207 at 25°C. Working in perchloric acid medium, SHERILL and HAAS⁷ obtained the value of 1.25 volts. But HUGHES and GARNER³ determined the E_0 value in hydrochloric acid medium to be 0.75 volt only.

From this potential data, it will be evident that the oxidation of thallium(I), in any acid medium other than hydrochloric acid, is thermodynamically possible only with an oxidising agent like potassium permanganate, or a salt of quadrivalent cerium. But in practice it has not been found possible to titrate thallium(I) in sulphuric acid medium even with these oxidants. On the other hand, in hydrochloric acid medium, the titration of thallium(I) has been found possible with potassium iodate (SWIFT and GARNER⁸) potassium bromate (KOLTHOFF⁴, ZINTL and RIENÄCKER¹⁰) potassium permanganate (SWIFT and GARNER⁸, BEALE and coworkers¹) and ceric sulphate (BERRY², WILLARD and YOUNG⁹, and SWIFT and GARNER⁸). The ease of reaction in hydrochloric acid medium

^{*} See also: Z. analyt. Chem. 156, 181 (1957); 157, 178 (1957).

is no doubt due to the considerable lowering of the thallous-thallic potential in hydrochloric acid medium by complexation of thallium(III) with the chloride ion.

From a survey of the literature, it appears that no one has investigated the use of sodium vanadate for the volumetric estimation of thallium(I). In the present investigation, we have found that sodium vanadate can be employed for the determination of thallium(I) under the conditions prescribed.

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 GARNER⁸.

Approximately 0.05 M sodium vanadate solution is prepared from analar grade ammonium vanadate and sodium carbonate. The strength of the vanadate solution is determined by titration with a standard solution of iron(II) sulphate prepared from B. D. H. analar iron wire. A 0.02 M solution of iodine monochloride is employed as the catalyst.

We have found that sodium vanadate and thallium(I) sulphate do not react in sulphuric acid medium at the room temperature. The reaction does not take place even when the mixture is heated to 98-100°C. However, the reaction has been found to take place, even at the room temperature, if it is carried out in hydrochloric acid medium. When a solution of sodium vanadate is added to a suspension of thallous chloride in hydrochloric acid, the precipitate of thallous chloride dissolves gradually, as thallium(I) gets oxidised to thallium(III). From a number of such experiments of a qualitative nature it has been found that (1) the speed of reaction between thallium(I) and sodium vanadate in hydrochloric acid medium increases with an increase in the concentration of hydrochloric acid and (2) the reaction is accelerated by iodine monochloride. We have also observed that the speed of oxidation of thallium(I) with sodium vanadate is very rapid, when iodine monochloride is used in conjunction with a high concentration of hydrochloric acid (above 5 N). Under these conditions, a direct titration is possible if a suitable indicator can be found to detect the end point. Diphenyl benzidine and N-phenyl anthranilic acid have not been found suitable, because they get destroyed during the titration in the presence of iodine monochloride and a high concentration of hydrochloric acid. The potentiometric method has also proved unsatisfactory, because of insufficient break of potential at the end point. Hence, the author has employed the so called iodine monochloride end point using carbon tetrachloride layer as the indicator. Experiments have shown that the concentration of hydrochloric acid must be at least 7.5 N at the end point.

The procedure adopted is as follows: An aliquot volume of the thallium(I) solution is pipetted out into an iodine flask followed by the addition of 5 ml of 0.02 M

iodine monochloride solution and requisite amounts of concentrated hydrochloric acid and water. The flask is then cooled, and 5 ml of carbon tetrachloride are added. Then the titration is started with a standard solution of sodium vanadate. As the oxidant is added the solution becomes pale-green and the organic layer acquires a purple colour. The purple colour of the organic layer gradually increases in intensity as the oxidant is added, until the first stage in the reduction is completed. With further addition of sodium vanadate, the intensity of the purple colour of the organic layer decreases, indicating the start of the second stage of the reaction i.e. the oxidation of iodine to iodine monochloride. The reaction speed is slow in the second stage and requires sufficient acid concentration (at least 7.5 N at the end point) for quantitative completion. The completion of the titration is indicated by the disappearance of the purple colour of the organic layer. Moreover, efficient shaking is required. The titration is found to give positive errors, if the hydrochloric acid concentration near the end point is below 7.5 N or if the shaking is poor, during the second stage of the titration. A large number of determinations of thallium(I) have been made under these conditions now developed by us. A selection of some results is given in the Table 1.

Amount of thallium(I) taken in millimoles	Amount of thallium(I) found in millimoles
0.0685	0.0683
0.0813	0.0815
0.1075	0.1071
0.2136	0.2132
0.2408	0.2413
0.2614	0.2620
0.2956	0.2945

Table 1. Vanadametric Estimation of Thallium(I)

Summary

A vanadametric procedure has now been developed for the direct volumetric titration of thallium(I), to an iodine monochloride end point. The concentration of hydrochloric acid must be at least 7.5 N at the end point.

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