60. *The Standardisation of Sodium Thiosulphate with Potassium Dichromate.*

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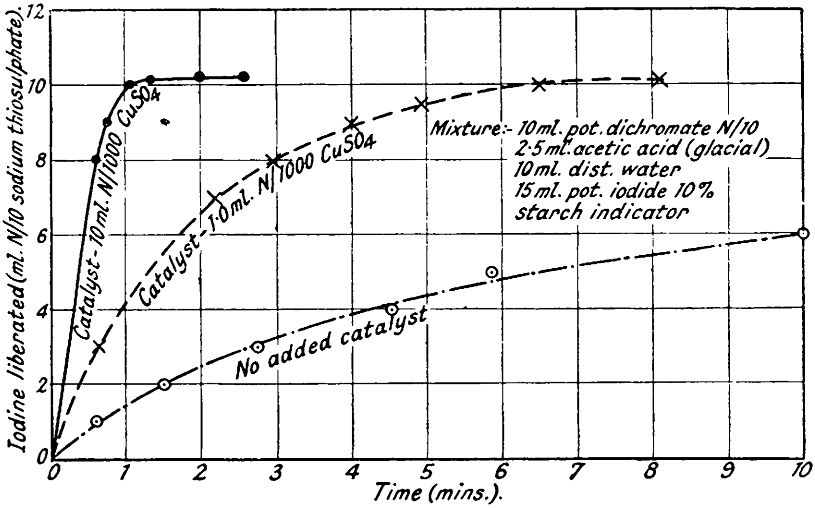
Copper is shown to be a powerful catalyst for the reaction between potassium dichromate and potassium iodide. A new method of standardising sodium thiosulphate based on this fact avoids the use of a mineral acid with potassium iodide and is both more rapid and more accurate than the customary procedure.

Potassium dichromate is readily obtainable in a high state of purity and is very stable in solution. It is therefore a desirable reference substance for the standardisation of thiosulphate solution. The reaction between potassium dichromate and potassium iodide liberates iodine very slowly unless the p_H of the solution is low: in the usual method 25 ml. of N/10-potassium dichromate, 30 ml. of 10% potassium iodide, and 6 ml. of concentrated hydrochloric acid are allowed to react in the dark for about 15 mins., during which the reaction is supposed to run to completion, and the iodine liberated is titrated with sodium thiosulphate with starch as indicator. The final solution is green owing to chromium salts, and in order to make the end-point more distinct it is customary to dilute the solution before titration.

The end-point is always quite sharp, but the reaction is not always quantitative, and variations of ½% are easily obtained. Snethlage (*Rec. Trav. chim.*, 1934, **53**, 567) showed that the amount of iodine liberated is influenced by the rate of addition of potassium iodide, the concentration of acid, and even by the degree of illumination. It was further found that reproducible results are not obtainable except in dilute solution, and that sulphuric gives better results than hydrochloric acid.

It is well known that atmospheric oxygen liberates iodine from potassium iodide in the presence of a strong mineral acid, and hence it is preferable to work with a weaker acid, so the effect of acetic acid was investigated. 10·00 Ml. of N/10-potassium dichromate were acidified with 2·5 ml. of glacial acetic acid and diluted with 10 ml. of water. At zero time 15 ml. of a 10% solution of potassium iodide were added, and the liberated iodine was titrated immediately, the thiosulphate being added in quantities of 1 ml., and the time taken for the reappearance of the blue colour was noted with a stop-watch. The results obtained are shown in the Figure.



The reaction was still not quite complete after one hour, so an attempt was made to catalyse it by addition of various salts. Iron and manganese had no appreciable action, but the effect of copper in very small amounts was remarkable: addition of 1 ml. of M/1000-copper sulphate solution liberated 90% of the iodine in 4 mins., and 10 ml. of the same solution afforded 90% of the iodine in 45 secs. Without a catalyst this degree of reaction requires 30 mins.

The reaction rate varies with the concentration, and to obtain the best results it is essential to avoid excessive dilution; for instance, 10·00 ml. of N/10-potassium dichromate, 2·5 ml. of glacial acetic acid, 10 ml. of M/1000-copper sulphate, and 15 ml. of 10% potassium iodide in 400 ml. of water liberated less than the equivalent of 0·1 ml. of N/10-sodium thiosulphate in 5 mins.; there was little increase in rate on adding 10·0 ml. of glacial acetic acid, and even on adding 1·0 ml. of concentrated hydrochloric acid the reaction was only 50% complete in 7½ mins. It is clearly inadvisable to dilute the solution until all the iodine has been liberated. Boiled-out water is necessary if mineral acids are used in the presence of potassium iodide.

From the foregoing considerations the following procedure is recommended. To 20·00 ml. of N/10-potassium dichromate in a 250-ml. conical flask add 5·0 ml. each of glacial acetic acid and N/1000-copper sulphate solution, the sides of the flask being washed down with 20·0 ml. of distilled water. Add 20·0 ml. of 15% potassium iodide and titrate the iodine as it is liberated with N/10-sodium thiosulphate solution, a little freshly made starch solution being added towards the end. The temperature should be about 20° and should not exceed about 25° in order to minimise the liberation of iodine by the action of atmospheric oxygen. The titration is complete in 3—4 mins. after addition of the iodide. The end-point when once reached is stable for a long time, the colour being that of a complex chromium acetate, and no difficulty is experienced in working to a fraction of a drop if a second flask containing the previous titration with an excess of sodium thiosulphate is used for comparison. 0·05 Ml. must be subtracted from the titration reading to allow for the iodine liberated by the copper sulphate catalyst. Individual titrations by different observers did not vary by more than 0·1%, and the mean value so obtained was 0·1% lower than that obtained by standardisation against copper wire.

For this standardisation the following method was used: it differs slightly from published methods in so far as it avoids formation of an excess of sodium acetate, the buffering effect of which results in a sluggish end-point. Polish a length of copper wire weighing approx. 1·4 g. with a little kieselguhr and water, dry it, wind it into a flat spiral, and weigh it. Transfer the spiral to a beaker, cover it with distilled water, add concentrated nitric acid very slowly until the copper just starts to dissolve, then allow it to stand without warming until dissolution is complete. Heat it slowly and remove nitrous fumes by short boiling. After cooling, neutralise the excess of nitric acid with concentrated sodium or potassium carbonate solution until a slight precipitate is formed. This is dissolved immediately with a slight excess of N-hydrochloric acid, and the solution diluted to 200 ml. at 20°. 20·00 Ml. of this solution are measured into a conical flask, 0·5 g. of urea is added, and the solution boiled gently for 5 mins., then cooled and neutralised to turbidity with N-sodium hydroxide, avoiding excess. Add immediately 5·0 ml. of glacial acetic acid, dilute to 100 ml., and add 20 ml. of 15% potassium iodide. Titrate the liberated iodine with the sodium thiosulphate to be standardised. When near the end-point add 4 ml. of a 50% w./w. ammonium thiocyanate solution (Foote, *J. Amer. Chem. Soc.*, 1938, **60**, 1349). Complete the titration, using starch as indicator. The end-point should be stable for 5—10 mins.

The remarkable influence of such minute traces of copper on the reaction between potassium dichromate and potassium iodide makes it possible that in the past some investigators have fortuitously achieved good results owing to the presence of copper as an impurity in their reagents : 1 p.p.m. of copper in the titration solution accelerates the reaction about six-fold.

Copper has previously been used as a catalyst for many oxidation reactions but usually no quantitative data are given. The present reaction may be compared with the copper-catalysed reaction between ferric salts and sodium thiosulphate which, according to Feigl (" Qualitative Analysis by Spot Tests," Nordemann Publishing Co., 1939, p. 37), can be used to detect one part of copper in 2,500,000 parts. Steigmann (*Phot. Korr.*, 1934, **70**, 54) has shown that copper acts as a powerful catalyst for the formation of molybdenum-blue in a solution of ammonium molybdate and sodium thiosulphate stabilised by formaldehyde, and Brode (*Z. physikal. Chem.*, 1901, **37**, 257) made a quantitative study of the oxidation of the iodide ion by hydrogen peroxide catalysed by iron and copper. The latter found that iron is more effective than copper, and that the combined effect of both is greater than that to be expected from the influence of each metal separately.

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