THE USE OF CERIC SULFATE FOR THE DETERMINATION OF CUPROUS OXIDE OBTAINED BY THE ACTION OF REDUCING SUGARS ON FEHLING'S SOLUTION

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Existing methods for the volumetric determination of cuprous oxide, especially as applied to standard procedures for the estimation of reducing sugars, fall quite generally into two classes—iodometric and manganimetric. All fail to fulfill the essential requirements of convenience, accuracy, and low costs. Iodometric methods are based upon an equilibrium which, under correctly controlled conditions, can be made to proceed in either direction (*5*). While good results can be obtained, accuracy is usually sacrificed by modifications tending to lower the cost of the procedures. Manganimetric methods (*1, 2, 3*) have proved rather unsatisfactory, due to the high oxidation potential of permanganate which causes it to oxidize adsorbed organic material, as well as to the difficulty of detecting the permanganate end-point in a blue copper solution.

Ceric sulfate (*6*) offers advantages which adapt it to the determination of cuprous oxide. It is exceptionally stable, even in the presence of quite variable concentrations of sulfuric acid. It can be used in the presence of hydrochloric acid, which is often suggested to assist in the solution of cuprous oxide. The valence change is simple and there is no danger of the cerous sulfate formed being reoxidized by exposure to the air. Its oxidation potential is less than that of permanganate, which minimizes its effect upon the adsorbed organic matter. It can be obtained commercially or easily prepared at low cost. Its former disadvantage, the lack of a suitable indicator has now been overcome by the introduction of orthophenanthroline ferrous complex, a reversible indicator (*7*).

A stoichiometric relationship is found to exist between Ce++++ and Cu+. This is made use of by separation of the cuprous oxide from the reducing solution, solution in a known amount of standard ceric sulfate solution, and titration of the excess ceric sulfate with ferrous sulfate, using orthophenanthroline ferrous complex as indicator. The color change at the end-point (orange-red to blue-green) is easily distinguished. The method can be applied to all reducing sugar determinations involving separation of the cuprous oxide from the reducing solution. Good results are obtained over a variety of conditions.

A comparison of the method with similar methods involving permanganate and dichromate was made, dichromate having been suggested and used by Jackson and Mathews (*4*), whose procedure, however, required an electrometric end-point. The permanganate method selected was that of Bertrand (*1*), modified by the application of orthophenanthroline ferrous complex as an aid in detecting the end-point. Dichromate was used in the same manner as ceric sulfate, using barium diphenylamine sulfonate as internal indicator. Ceric sulfate proved superior to both, permanganate giving consistently high results, in spite of the fact that the use of orthophenanthroline ferrous complex reduced the error, while dichromate, using indi-

cators now available, necessitates the application of an end-point correction which varies with the volume of solution used.

The procedure for the determination of cuprous oxide using ceric sulfate as outlined appears to offer advantages which should permit its wide application to reducing sugar determinations.

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