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## THE SOURCES OF ERROR AND THE ELECTROLYTIC STANDARDIZATION OF THE CONDITIONS OF THE IODIDE METHOD OF COPPER ANALYSIS.

By AMOS W. PETERS.

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### I. Introduction.

This study of the iodide method had its origin in the necessity for very accurate volumetric determinations of the copper in the alkaline tartrates from sugar analyses. It is a preliminary to an examination and improvement of copper reduction methods of sugar analysis which will soon be published. When the results by the iodide method as at first applied were compared with electrolytic determinations on the same liquids discrepancies occurred which were greater than the supposed limits of error and whose underlying conditions were not understood. Further experiment then showed that the iodide method, even as previously described, could give erroneous results of varying and unknown amount, according to conditions which were accidental and unrecognized by the operator. An examination of the literature also showed that previous experiments were not planned advantageously to show what the liabilities to error are in the general application of the method. The special nature of the conditions under which accurate results were obtained in test analyses or the extent of their significance was only partially recognized. In the present work the point of view differs markedly in that the methods and conditions to be tested are regarded as procedures for obtaining the standard value of the thiosulfate solution which measures values in the iodide method. The other point of view by which a standard value obtained under certain conditions is accepted and then is inadvertently applied to any thiosulfate readings obscures the real sensitiveness of the iodide method to change of conditions. This leads to a false confidence in the results which is enhanced by the supposed electrolytic control. To this criticism it might be replied that an analysis should be made only under those conditions under which the standardization was made. To what extent this is feasible in view of the stand-

ard conditions which must be duplicated and in view of the conditions presented by unknown copper solutions to be estimated, will appear when the results of the experiments here presented have been considered. These observations seem to lead rather to the contrary very empirical and inconvenient but logical proposal that standardizations be made under those conditions under which the copper in each specific case is to be measured. This would lead to a multiplicity of standard values, and it was considered more advisable to determine how one fundamental standard value could be used by the adjustment of the conditions or by the quantitative compensation of the errors due to variable conditions.

The standards of accuracy adopted may be described as follows: It is assumed that in general such well developed methods of standardization, *e. g.*, as that of iodine for thiosulfate, readily permits of renewed standardization, certainly to within 0.1%, each standardization including not fewer than four concordant titrations. From this it follows that when the average values found by two different methods differ by more than the deviations of the individual titrations from their respective mean then some other factor than that of the unavoidable accidental errors of measurement is involved. In the present work there will be found sufficient duplication of values to enable the reader to determine by inspection whether the differences between the frequently occurring averages found in the tables are large enough to be significant. This is a very important criterion, for whether a difference is to be regarded as large or small primarily depends upon the sensitiveness of the method.

## 2. A Critique of Some Methods of Standardization of Thiosulfate Solutions.

From the standpoint of economy of time in making numerous estimations of copper a volumetric method must take precedence over any known gravimetric process. The iodide method of de Haën,<sup>1</sup> as subsequently developed by numerous analysts, gives, when certain conditions are observed, very accurate results with small expenditure of time. In this method the iodine which is liberated in equivalent amount from potassium iodide is estimated by a standardized sodium thiosulfate solution. The iodide method is properly controlled, as will be shown, by means of a standard copper solution whose value has been determined either by electrolytic deposition from a given volume or by weighing metallic copper of known purity and dissolving it to volume under certain conditions made necessary by the iodide method. In other words, the standardization of thiosulfate to be used for the measurement of copper can be correctly made only by means of standard copper or by other methods, if any, which give the same copper value for the thiosulfate. Now some other methods in common use for standardizing the

<sup>1</sup> *Ann.*, 91, 237 (1854).

thiosulfate do not give the same value as copper would, so that the actual copper value of a thiosulfate solution is not indicated by its normality, if the latter has been obtained by means of, *e. g.*, a standard iodine or a standard dichromate solution.

Thus Bray and MacKay<sup>1</sup> observed a discrepancy of over 0.2% between the standard values of the same thiosulfate solution as found by standard potassium iodide and by electrolytically controlled copper. They state (p. 1199) that "the conclusion was finally reached that the absolute accuracy of the copper standard is not quite so high as we had at first supposed." I have also standardized a thiosulfate solution by the iodide method of Bray and MacKay and have likewise obtained results discrepant with the copper standard. Bray and MacKay suggest that the failure of the copper standardization to agree with that by iodine may be due to adsorption or solution of some iodine by the precipitated cuprous iodide with the result of too low a titration value for the thiosulfate. These authors justly regard the method of standardization by means of iodine as the one of highest absolute accuracy. Bray and MacKay (p. 1198) also standardized thiosulfate by means of potassium permanganate (which in turn had been standardized against sodium oxalate) and observed a discrepancy of at least 0.15 to 0.20 % compared with the iodine method. The value obtained for the thiosulfate by the copper method was greater, and that by the permanganate method was lower, than the value by iodine. All these methods gave results concordant with themselves and their variations from each other exceed the limits of accidental error.

An illuminating comparison of the results by different substances that have been proposed and in some cases extensively used for the purpose of iodometric standardization is due to Julius Wagner.<sup>2</sup> He standardized thiosulfate solutions by means of potassium dichromate, potassium biniodate, potassium iodate, sodium iodate, potassium bromate, sodium bromate, and he also determined the conditions for the testing and purification of these substances. None of the other results could be made to agree with the dichromate standard, and the latter was found in error on account of the catalytic action of chromic acid on the liberation of iodine from potassium iodide. The conclusions of Wagner as they bear on the selection of a standardization of thiosulfate for absolute accuracy may be shown by brief quotations from the article cited as follows: p. 427: "Die Titerstellung der jodometrischen Lösungen gründet sich jetzt wohl allgemein auf die Erzeugung von Jod in angesäuerter Jodkaliumlösung." p. 451: "Praktisch ergibt sich der Schluss das man Kaliumbichromat als Mittel zur jodometrischen Titerstellung verwerfen muss.

<sup>1</sup> THIS JOURNAL, 32, 1193-1204 (1910).

<sup>2</sup> Z. anorg. Chem., 19, 427-453 (1899).

Allenfalls kann es zu Vergleichszwecken benutzt werden. Am meisten Empfehlung verdient das Kaliumbijodat und demnächst das Kaliumbromat, weil sie sich am leichtesten reinigen lassen." As to the magnitude of limits of error, p. 453: "Alle vorstehenden Titerstellungen und Vergleiche sind innerhalb einer Fehlergrenze von 1‰ bei mindestens drei Bestimmungen auszuführen." Thus the only standardizations of thiosulfate for absolute accuracy are those which give the same value as pure iodine would, and from the practical standpoint the iodine is best obtained from acidified solutions of iodides and iodates. I have made sufficiently numerous determinations which show that there is not agreement within limits of error between the iodide, biniodate, and iodate standards regarded as one group and the dichromate and pure copper standards as two other groups. The values within the first group were concordant. The question thus arises: What standardization of thiosulfate shall be used when copper is to be estimated by the iodide method? Evidently for this purpose only the empirical value of the thiosulfate as determined by copper of known purity can be used. This principle was not recognized by Gooch and Heath<sup>1</sup> in their examination of the iodide method, in which they controlled their copper solutions electrolytically but apparently standardized their thiosulfate according to the customary systematic normalities.

The facts above described lead to important conclusions regarding the accuracy of copper analyses which are especially significant when gravimetric and volumetric determinations are compared or used interchangeably. In sugar analysis by copper reduction methods the choice of gravimetric or volumetric determination almost always lies open, and these two procedures are assumed to give the same result in terms of copper. Thus, in the "Official and Provisional Methods of Analysis of the Association of Official Agricultural Chemists,"<sup>2</sup> pp. 51-53, are described six methods for the determination of reduced copper whose results are to be concordant and among these are a volumetric (permanganate) and electrolytic methods. Here again appears, p. 53, the discrepancy between the empirically determined copper value of a standard solution (here permanganate) and that calculated from its systematic normality.

E. Pflüger,<sup>3</sup> p. 436, in testing the sulfocyanide method for the volumetric estimation of copper, in this case also found a similar discrepancy and showed that if the atomic weight of copper was taken as 63.47 instead of 63.18, as used by him, the discrepancy would disappear. In the method of Pflüger-Allihn,<sup>4</sup> as described by Neubauer-Hup-

<sup>1</sup> *Am. J. Sci.*, 24, 65-74 (1907).

<sup>2</sup> U. S. Dept. of Agriculture, Bur. of Chem., *Bull.* 107 (1907).

<sup>3</sup> *Arch. ges. Phys.*, 69, 399-471 (1898).

<sup>4</sup> *Loc. cit.*

pert,<sup>1</sup> pp. 411-412, volumetric methods (iodide of de Haën and sulfocyanide of Volhard) are even used as controls for the gravimetric process when the precipitated copper may be contaminated. Finally the tabular values of the numerous published methods of sugar analysis by copper reduction are expressed quantitatively in terms of copper. The importance of proving the accuracy of any proposed method for volumetric copper determinations is hence evident. The necessity is still greater when a judgment is to be formed of the accuracy of any given tabular values by means of controls with pure sugar solutions. On account of the previously described discrepancies between different standardizations, this accuracy is attainable volumetrically only by the use of solutions whose value in copper has been obtained empirically and not calculated from their systematic normality or equivalence. The cause of this discrepancy affecting the equivalent value of copper solutions has never been satisfactorily determined. With the use of the modern atomic weight of Cu = 63.57 the discrepancy with the iodide method remains and the proposed theory of the absorption of iodine in this method has also been found untenable (see pp. 446-7). These facts have been emphasized here since accurate volumetric copper determination was adopted as the critical instrument of investigation for the problem of sugar analysis.

### 3. A Simple and Rapid Method of Electrolysis of Copper Solutions with a Tartrate Cyanide Electrolyte.

A method of electrolysis incidentally developed in connection with this work has the advantage of using the simplest of means and yielding results with a very moderate expenditure of time. It does not compete with the use of rotating electrodes but its simple appliances and satisfactory results may make it useful in those cases where special apparatus is not at hand and particularly for purposes of control in sugar analysis. No effort has been made to effect electrochemical separations by this procedure but simply to determine copper. In view of the fact that the preparation of solutions of copper for the application of the iodide method is always more or less circumstantial a very simple but effective method for this purpose will also be described. As the criticisms of conditions for the iodide method are dependent on the results of electrolysis, the latter process will be described first.

The special characteristics of this procedure for electrolysis are primarily (a) the composition of the electrolyte used and consequently (b) the comparatively high voltage and current density compatible with good deposits which this electrolyte permits, and (c) the rapid and continuous mixture of the liquid by both the evolution of gas and the external application of heat even to boiling. The attempt to electrolyze the alkaline

<sup>1</sup> Neubauer-Huppert, "Analyse des Harns," Wiesbaden, 1910.

tartrate solutions of copper from sugar analyses led to the observation that tartrates and citrates in either alkalin or citric acid solution are media in which the electric current deposits copper very rapidly. The observations made on a considerable number of other organic substances will not be reported. The character of the deposit, however, is not good from an analytical standpoint, exhibiting the sponginess, loose adherence, and sometimes carbonaceous appearance which are familiar difficulties in electrodeposition. No use could be made of this rapid rate of deposition until it was discovered that the addition of potassium cyanide in small amount was a means of completely controlling the character of the deposit. A dull metallic or bright copper color could be produced according to the amount of cyanide under the same current density and the deposit varied likewise from sufficient adherence for all necessary washing and handling to a hard coating that could not be rubbed off with the finger, even with pressure. It was observed, however, that alkalin cyanide had a solvent action upon the deposit and thus a retarding effect antagonistic to that of the tartrate and citrate. This influence made itself especially felt in the effort to deposit the final, small portions of the copper from a solution. The conditions here are exactly analogous to those with nitric acid in the customary sulfuric-nitric electrolytes. In the present method a peculiar use is made of cyanide in that its quantity is definitely limited to the least amount that will give a satisfactory hardness and color of deposit under a given set of conditions. The amount of cyanide used is always less than is required to decolorize the copper solution. The composition and use of the electrolyte finally adopted was as follows: An alkalin tartrate mixture is made containing in a final volume of 100 cc. 35 grams of pure sodium potassium tartrate (Rochelle salt) and 25 grams of potassium hydroxide, purified by alcohol. This is almost exactly the composition of Allihn's alkalin tartrate solution, which may also be used. Customarily a volume of 10 cc. of the copper solution, which may be slightly acid or alkalin, is placed in either the platinum dish or the glass beaker in which the electrolysis is to be made. An approximately equal volume of the alkalin tartrate solution is then added, but as much as two volumes may be used to one of the copper solution, especially when the latter contains some acid, which may be sulfuric or nitric. For larger volumes of electrolyte as for filling a test tube used as cathode vessel the rule is observed that one-half or more of the total volume should consist of the alkalin tartrate solution. In this connection it should be stated that when the alkalin tartrate has deteriorated by much exposure to the air it will cause much trouble by excessive foaming. A saturated aqueous solution of potassium cyanide is then added in quantities ranging from 0.4 to 1.0 cc. or more, depending upon the absolute amount of copper and

regulated by the character of the deposit. If the deposit is too soft or dark colored under a given set of conditions more cyanide is used, but it must be remembered that too much cyanide will lengthen the time required for complete deposition.

The anode in all cases is either a flat or a cylindrical spiral of platinum wire for use with a platinum dish or a narrow beaker, respectively. *Its distance from the cathode surface should be one centimeter or less.* For cathode a platinum dish may be used, which is set on a piece of sheet brass to which the cathode connection is made. The brass is more easily kept clean than copper sheet, as it oxidizes less in the air. This support for the cathode of platinum or for a glass beaker is used so that the electrolyte can be heated by a small Bunsen flame beneath and to one side of the vessel. The sheet metal is carried by a ring stand and the same stand by means of a clamp carries the anode coil. The anode is the only platinum necessary as a copper cathode will also give accurate results as will be shown subsequently. Sheet copper is cut in oblong form with a long, narrow strip extending at one end and at right angles to the length of the wider portion of the piece. This is coiled into the form of a cylinder and with its circumference not quite closed it is then placed in a narrow beaker of twice the height of the cylinder. The narrow strip is bent at right angles over the edge of the beaker for connection with the cathodic pole. The beaker here used had a capacity of 50 cc., a diameter of 3.5 cm., and a height of 7.0 cm. The height of the cylinder should be such that the volume of electrolyte to be used is sufficient to immerse it completely, except the extending strip. To secure large cathode surface with nearness of electrodes a long and wide test tube, *e. g.*, 20 × 2.5 cm. or larger, is substituted for the narrow beaker and the copper cathode is cut to this size as above described. The copper cathode should be cleaned with nitric acid followed by water, washed in alcohol and ether, dried while held by the hand over a source of heat, completely air-cooled and then weighed. The amount of copper deposited on such an electrode is, of course, found by taking the difference between the initial and final weight for each determination. The initial weight will vary after each preparation of the electrode by cleaning with nitric acid, washing and drying. It was, however, necessary to test whether the copper electrode will remain of constant weight like a platinum cathode through the process of preparation, omitting the acid treatment but including washing, drying, exposure to air, etc., by which, at the close of electrolysis, it must be prepared for weighing. Repetitions of this procedure gave the following results:

After first preparation = 17.7801 grams. After second preparation = 17.7799 grams. After third preparation = 17.7801 grams. After fourth preparation including standing in alcohol for 5 minutes = 17.7801 grams. After standing on balance pan for 1 hour = 17.7802 grams. After fifth preparation = 17.7801 grams.

These results are sufficient to show the constancy of the copper cathode. The principal conditions for accuracy are that it be freshly cleaned immediately before use (even in immediately succeeding electrolyses), that it be thoroughly air-cooled before weighing, and that it be handled with the fingers only at the edge of the extending strip. The same cathode may be used many times, but it should be weighed each time immediately before and immediately after use. If unused for some time it should be freshly cleaned, washed, heated and air-dried before renewed use. These precautions are important for accurate results with the copper cathode, but have less significance with platinum.

In all cases the anode wire must extend well out of the platinum dish or the glass beaker so that these vessels can be covered with split watch glasses to prevent loss by spraying. The ring stand carrying the whole apparatus is best set in or near a sink so that at the close of the electrolysis the current can be interrupted by running a stream of water from a rubber tubing attached to the tap into the cathode vessel until the illumination of the resistance lamp completely disappears. By this method no solution of copper can occur. The cathode is then prepared for weighing as before described, avoiding any heat greater than that of warmth to the hand.

Among the various factors upon which the rate of electrodeposition depends it is well known that one of the most important is the rapid change of fresh portions of electrolyte upon the surface of the electrodes. In the present method this change is made continuous and rapid both by an abundant evolution of gas and by the continuous application of heat from a small Bunsen burner, placed under the brass plate and at some distance to one side of the position of the cathode vessel. With the test tube arrangement a wire gauze is interposed between the test tube and a small Bunsen flame beneath. As previously explained, the total volume of mixed electrolyte which was customarily used was about 25 cc. with the platinum dish or the beaker and 70 cc. with the test tube. The capacity of the platinum evaporating dish used as cathode was about 40 cc. and its dimensions were approximately 50 mm. in diameter and 25 mm. in depth. The 25 cc. of electrolyte covered a platinum surface of approximately 40 sq. cm. The copper electrode used for the beaker was approximately 10 cm. long and 2.7 cm. wide. Three triangular notches were cut out of its lower edge to facilitate the passage of liquid, as the copper cylinder stood on the bottom of the glass beaker. The total area of this copper cathode was approximately 50 sq. cm. The test tube cathode of copper measured  $15 \times 6$  cm. when flat.

The direct 110 volt current, the same as that of the lighting system, was used, with the ordinary lamp resistance in circuit. A resistance of three thirty-two candle-power lamps in parallel was customarily inter-



posed in the circuit. The amount of current was sufficient to heat the electrolyte and to give rise to an abundant evolution of gas, by means of which the liquid was kept well mixed. When the three thirty-two candle-power lamps and the electrolyte as above described were in circuit the voltage measured 2.6 and the amperage 2.85. Thus the density  $ND_{100}$  for the platinum cathode was 1.14.

To test for the completion of the deposition a modification of the exceedingly delicate hydrobromic acid test for cupric copper of Endemann and Prochazka<sup>1</sup> was used. One volume of concentrated sulfuric acid is diluted with two to three volumes of distilled water. About 1 cc. of this diluted acid is placed in a narrow test tube, a few crystals of potassium bromide are added and the whole is heated to boiling. If to the hot mixture one drop of a solution containing as little as 0.007 mg. of copper is added, a red color will develop. The color is best seen by placing the test tube in the hollow of a white porcelain evaporating dish held by the observer on a level with his eye while his back is turned toward the source of daylight. One or two drops of the alkaline electrolyte here used when added to the above hot hydrobromic acid mixture will at once become acidified and show the presence of a very small amount of copper. The electrolyte loses its blue color as the electrodeposition proceeds and the test for copper should not be made until some time after the liquid has lost its blue color.

By the above method repeated determinations have been made on the same solution of pure copper sulfate delivered in approximately 10 cc. volumes by an automatic pipet of constant delivery as shown by weighing repeated deliveries as in calibration. The results were often identical but differed at most by only one or sometimes two-tenths of a milligram of copper on a total of about 177 milligrams. This amount was fully deposited in less than thirty minutes with the platinum dish and beaker cathodes and in less than fifteen minutes with the test tube arrangement. On account of the similarity of composition of the electrolyte and of the alkaline copper solutions much used for sugar analysis this method is well adapted for the accurate control of these methods by the determination of copper.

#### 4. A Method for the Preparation of Nitric Acid Solutions of Copper or of Its Compounds for the Iodide Method.

As nitric acid is the most available acid for the solution of copper and of its compounds for analytical purposes, much attention has been given to methods for the removal of the lower oxides of nitrogen in preparation for the iodide method. Evaporation with sulfuric acid nearly to dryness and to the evolution of white fumes is a well known but inconvenient method. The preparation of the nitric acid solution by boiling,

<sup>1</sup> Endemann and Prochazka, *Chem. News*, 42, 8 (1880).

followed by a treatment with ammonia, then heating again and then adding acetic acid and again boiling, as described by Low,<sup>1</sup> pp. 84-85, is most frequently used. In former editions Low<sup>2</sup> included a treatment with bromine in the procedure just described "to insure complete destruction or removal of the red fumes." The last boiling (with acetic acid, etc.) he emphasizes as important "as it effects the neutralization or expulsion of any remaining oxidizing compounds that would cause a return of the blue color after titration." A method that avoids boiling is due to Kendall,<sup>3</sup> sodium hypochlorite and phenol with subsequent neutralization being used. The very simple method here proposed which serves in the determination of unknown copper also consists in vigorously boiling the nitric acid solution of copper for 5-10 minutes with a little pure talcum powder in the presence or the absence of sulfuric acid. It was observed that a sulfuric-nitric acid solution of metallic copper, which had been freed from brown fumes by boiling, evolved an additional quantity of brown fumes upon the addition of powdered talcum to the hot liquid. The vigorous ebullition which occurs under these conditions greatly accelerates the removal of lower oxides of nitrogen, including nitrous acid. No bumping or spurting occurs. The copper or its compound is dissolved in an Erlenmeyer flask in the least required volume of concentrated nitric acid, to which one-half its volume of water has been added. Five to 10 cc. of this diluted acid should be used for 0.5 g. or less of copper. After solution with the free use of heat until brown fumes are no longer apparent to the eye 15 to 25 cc. of distilled water and a little pure powdered talcum are added. The mixture is then kept in vigorous ebullition for five to ten minutes. The escaping vapors, when not too strongly acid, may be tested for nitrous acid with moist starch-iodide filter paper and the result of this test speedily becomes negative. Ebullition under these conditions is so effective that in preparations for the iodide method evaporation need not be continued to dryness. After cooling, enough distilled water is added to make the volume here required, including reagents, about 120 cc. at the end of titration (see pp. 442-6). In general, a smaller volume would be desirable.

This method has been subjected to numerous tests, of which the following show its accuracy. If the method is accurate, then its simplicity gives it an advantage over all other methods. In one experiment a sample of the purest obtainable metallic copper foil was used. 1.2499 grams were weighed and treated by the nitric acid-talcum procedure, as above described, by adapting the amounts of reagents to this weight of copper.

<sup>1</sup> Low, A. A., "Technical Methods of Ore Analysis," 5th Ed., New York, 1911.

<sup>2</sup> *Ibid.*, 1st Ed., 1905.

<sup>3</sup> THIS JOURNAL, 33, 1947-1952 (1911).

The solution was then made to a volume of 100 cc. and placed in a calibrated buret. Electrolysis by the method previously described gave for two determinations on 10 cc. each, 125.0 and 125.0 mg. of copper. Three titrations of this same solution of 10 cc. each were made by the iodide method as subsequently described by means of a thiosulfate solution, whose standard copper value was to be determined in this way. The thiosulfate volumes thus found were 9.85, 9.85, and 9.87 cc., *i. e.*, an average of 9.86 cc. Hence,  $\frac{0.12499}{9.86} = 12.676$  mg. Cu. per cc. of thio-

sulfate. To test the consistency of the method two independent titrations on amounts of copper appropriate for one titration each were made with the same thiosulfate. Weights of copper of 0.3268 and 0.3252 g. required 25.76 and 25.63 cc. of thiosulfate. These titrations gave standard values of the thiosulfate as 12.686 and 12.688 mg. Cu per cc., respectively, which is good agreement with the previous results. The same thiosulfate was now standardized by means of Kahlbaum's purest analyzed copper sulfate of the brand "Zur Analyse mit Garantieschein" described as containing in 10 grams 0.75 mg. of iron oxide and 1.50 mg. of alkali salts, etc., and *no* other metals. An aqueous solution was made in the proportions required for Fehling's solution and placed in a calibrated buret. Electrolysis on two samples of 10 cc. each by the method previously described gave 175.6 and 175.6 mg. of copper. Two titrations by the iodide method were made as subsequently described on 20 cc. each of this copper solution, requiring 27.71 and 27.70 cc., respectively, of the above thiosulfate solution. These values give  $\frac{175.6 \times 2}{27.71} =$

12.674 and  $\frac{175.6 \times 2}{27.70} = 12.679$  mg. Cu per cc. of thiosulfate. These

values obtained on pure copper sulfate without the nitric acid-talcum procedure compare well with the above values obtained by means of that procedure. This procedure was now applied to two 20 cc. portions of this same copper sulfate solution by the addition of nitric acid containing nitrous acid for the purpose of determining whether the process itself would leave the above values unaltered. The titration results were again 27.71 and 27.70 cc. From all these results it follows that the nitric acid-talcum procedure effectively removes all the decomposition products of nitric acid that would interfere with the accuracy of the iodide method. It was now shown that the method of Low, involving the additional use of ammonia and acetic acid, gave no different results than the above when applied to the same metallic copper, copper sulfate, and thiosulfate. By the metallic copper the standard value of the thiosulfate was found by Low's method as 12.699, 12.679 and 12.700 mg. of Cu per cc., *i. e.*, an average of 12.693. On the copper sulfate solution the titra-

tion results with Low's method were 27.72, 27.71, 27.70 cc. of thiosulfate, *i. e.*, an average of 27.71, which gives  $\frac{175.6 \times 2}{27.71} = 12.674$  mg. Cu per cc. of thiosulfate. The average of all the results by Low's method is 12.683 and that by the nitric acid-talcum method is 12.681.

In view of the above comparisons of results the following criticisms appear to be justified. The efficiency of both of these methods is due to the same cause, which is simply the boiling process. In other words, the ammonia and acetic acid treatments in the Low method are superfluous for the purpose of removing nitrous acid, although they may facilitate evaporation by boiling. It may be noted here that Low has now found it feasible to omit the bromine formerly constituting an additional reagent of this method. The reasons given by Low for the use of these reagents have been quoted above.

The method of Kendall<sup>1</sup> is more complicated than either of the methods above discussed and involves the accumulation of salts in the titration liquid. As is shown subsequently in this paper, the results by the iodide method under these conditions may easily deviate from the highest standard of accuracy (see pp. 434, 438). The plan of the test analyses of Kendall would not result in positive evidence on this question. Whether the concentration of the salts by this method is sufficient to affect the results was not tested but seems worthy of consideration, in view of the other data here developed.

#### 5. The Conditions for the Standardization of Thiosulfate Solutions by means of Copper and of Iodine and the Application of the Iodide Method to Alkaline Tartrate Solutions from Sugar Analyses.

(1) *Introduction.*—The most accurate of all methods for the estimation of copper is admittedly the electrolytic. For accuracy, with the advantages of simplicity and speed, no other method is as good as the iodide. The extensive use of the latter method for both scientific and technical purposes gives value to any additional determination of its conditions of accuracy. Owing to the fact that this method depends upon the following well known equilibrium reaction,  $2\text{CuSO}_4 + 4\text{KI} \longrightarrow 2\text{K}_2\text{SO}_4 + \text{Cu}_2\text{I}_2 + \text{I}_2$ , it seems necessary to judge from this standpoint the application of the method to any concrete case. Whether the results obtained by the iodide method represent the copper with quantitative accuracy depends wholly upon the observance of conditions which are somewhat narrowly defined for concrete cases. This circumstance explains why the history of the method shows authoritative analysts among both its advocates and its opponents. These conditions, except certain details that need emphasis, have been much studied, so that further investigation is in danger of dealing with repetitions. Therefore the substance

<sup>1</sup> *Loc. cit.*

of the propositions here to be demonstrated will be at once stated as follows:

A. There is an irreconcilable difference with the use of well known methods between the standard values of a thiosulfate solution as determined by standard iodine (*e. g.*, from potassium iodate, etc.) and by means of pure copper. This difference, when at a minimum, is several times as great as the limits of error of each method of standardization by itself. For accurate copper determination the copper standardization alone can be used and this only when determined under proved conditions.

B. The necessity under the conditions of most frequent occurrence for a definitely regulated concentration of acid in order to attain the highest accuracy and consistency with the iodide method will be shown. This condition has not been sufficiently recognized by some investigators of the method and has been denied by others. For the frequently occurring practical cases where acids and salts are present, which latter depress the ionization of the acid, the influence of this condition becomes of critical importance. This is especially the case in the determination of copper in the filtrates from such analytical processes as sugar reduction methods. The influence of salts on the reaction by which iodine is developed has not been heretofore recognized.

C. The equilibrium reaction above given, upon which the iodide method depends, is much influenced by changes of temperature so that perceptibly more free iodine will be developed at 30° than at 15°. Since, for reasons of expediency, sulfuric acid more or less concentrated is used, this error, designated as the "temperature error," may easily occur on account of insufficient or of excessive cooling. Recognition of this source of error leads to its easy prevention and the details of experiments made on this point will therefore not be presented.

D. The opinion of many, *e. g.*, Kendall,<sup>1</sup> p. 1949, that this equilibrium reaction runs to completion only in small volumes and that consequently small volumes for titration are necessary for accurate results with the iodide method is erroneous. The logically related statement of Moser,<sup>2</sup> p. 597 and others, that the results of the iodide method are influenced by the concentration of the copper in the titration liquid is also erroneous. For our present knowledge of other factors the experiments of Moser<sup>3</sup> p. 598, are inconclusive. It will be shown that the iodide method is exceedingly accurate with quite large as well as quite small amounts of copper, provided its conditions are regulated. The estimations of larger and smaller amounts are strictly proportional even when titrated in the same volume.

<sup>1</sup> THIS JOURNAL, 33, 1947-1952 (1911)

<sup>2</sup> Z. anal. Chem., 43, 597-608 (1904).

<sup>3</sup> Loc. cit.

E. The theory was suggested by Bray and MacKay,<sup>1</sup> p. 1199, that the discrepancy between iodide and copper standardizations described above under A is due to absorption of iodine by solid cuprous iodide. Meidinger and Carl Mohr<sup>2</sup> showed the possibility of such absorption. Since the absorption might vary under different conditions of dilution, etc., its occurrence has been regarded as a source of error. The theory of absorption as a source of error or as an explanation of the discrepancy of standards is not tenable. This will be shown by determinations in which the cuprous iodide enters wholly into solution before titration.

F. The iodide method is a procedure of empirical character from the standpoint of its conditions of accuracy. The easy variability of its results by acids, salts, temperature, and by the application of the same standard value of thiosulfate to different conditions of titration are not recognized in practice. In these experiments it will be shown how these factors can be either adjusted to accuracy or can be quantitatively compensated.

(2) *The Standard Copper Solution and its Measurement.*—A critical estimation of any given procedure for the iodide method is best obtained by attempting to standardize the thiosulfate by the same procedure and by comparing the quantitative results of different procedures and of different methods of standardization. All the conditions necessary for subsequent analyses may thus be determined.

Standard copper solutions which were to be used for the determination of conditions for the iodide method were prepared by two different procedures, which gave the same quantitative results. The first and preferred method consisted in dissolving the purest crystallized copper sulfate obtainable to an approximately known concentration. The exact concentration of the element copper cannot be calculated with reliability by the formula  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Numerous experiences in making Fehling's copper sulfate solution from the purest as well as the commercial salt led to this conclusion. The results were always low to the extent of a considerable fraction of 1%, even when the salt was pulverized and well air-dried on filter paper. Drying by other means is not permissible. Thus a solution made from the purest obtainable crystallized copper sulfate, which was specially prepared for analytical purposes, when pulverized, air-dried, weighed and made into solution and electrolyzed, was found to contain 0.51% less than the calculated amount of metallic copper. The low result was due presumably to persistently adherent moisture. The standard value of the solutions of pure copper sulfate here used was therefore determined electrolytically as previously described. The second method consisted in the solution by nitric acid

<sup>1</sup> THIS JOURNAL, 32, 1193-1204 (1910).

<sup>2</sup> Mohr-Classen, "Titriermethode," 7 Aufl., S. 350 (1896).

and by the procedure previously described of the purest metallic copper obtainable and then making a control determination of copper by electrolysis.

For obtaining known quantities of copper there was used a constant volume of copper solution taken from an automatic pipet of approximately 10 cc. delivery. This and other pipets of the same construction were obtained from Bleckmann & Burger, Berlin, and were described as "genau justirt." The exact volume delivered was not of consequence for the present purpose, but its reliability for delivering a constant volume of copper solution was very important. The use of this apparatus was found highly advantageous from both standpoints of accuracy and of economy of time. Its constancy had been tested at various times with very satisfactory results by weighing the quantity of liquid delivered. Two successive deliveries of the stock solution of copper sulfate used below weighed, respectively, 9.4123 and 9.4124 grams.

The reservoir of this pipet contained about one liter of solution and a thermometer was kept in the liquid showing a temperature of 25° when the above deliveries were made. Two successive electrolytic determinations made with the tartrate-cyanide electrolyte on a platinum dish cathode gave 176.9 mg. and 176.9 mg., respectively, of copper. No copper determinable by the hydrobromic acid test remained in solution. For the following experiments we have hence relied upon the pipet to deliver 176.9 mg. of copper so long as the temperature of the liquid remained constant. The ten liters of stock solution from which the automatic pipet was periodically filled was regarded as the standardized copper solution. It was made from the purest purchasable, guaranteed and analyzed copper sulfate, dissolved in pure distilled water.

(3) *The Standardization of Thiosulfate by Iodine from Potassium Iodate.*—For the iodometric standardization of thiosulfate there is here selected, in accordance with preceding discussion (pp. 423–5) of this subject, one of the methods in which iodine is liberated from an acidified solution of iodide and iodate. Repeated determinations made in an earlier stage of this work gave concordant results with the methods that use (a) resublimed iodine, (b) pure potassium iodide and iodate in acetic acid solution, (c) the iodide method of Bray and MacKay.<sup>1</sup> I abstained from the use of biniodate upon finding that the determined acidity of a supposed pure specimen was discrepant with that which is calculated from its formula,  $KIO_3 \cdot HIO_3$ .<sup>2</sup> The standardizations described below were made by the use of potassium iodide and iodate in acetic acid solution. For the purpose of comparison with the conditions of copper stand-

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Krauch, C., "The Testing of Chemical Reagents for Purity," 3rd Ed., New York, 1902. See p. 219.

ardization some results obtained with sulfuric acid are also given. Potassium iodate, Merck's Blue Label Reagent and Kahlbaum's purest potassium iodide were used. Their degree of purity and fitness for the purpose here used can be judged from the following experiment: Pure distilled water was boiled and while still warm crystallized iodide and iodate were added and dissolved. After 15 minutes in bright diffuse daylight a tinge of color due to free iodine had developed, but so slight as to be beyond titrimetric measurement with ordinary concentrations. After 30 minutes, the color still being very pale, solution of soluble starch was added. It was then found that one drop of a thiosulfate solution of approximately 0.07 *N* was in excess of the amount needed to discharge the blue color. The mixture stood, still colorless, for seven hours from the first mixture of the salts.

TABLE I.—STANDARDIZATION OF THIOSULFATE BY IODATE.

No.	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> . Cc.	Conc. acetic. Cc.	KI. Grams.	Vol. Cc.
1.....	20.90	} 10	} 2.8	} 60
2.....	20.92			
3.....	20.93			
4.....	20.87			
5.....	20.93			
6.....	20.92			
7.....	20.92	} 5	} 2.8	} 63
8.....	20.89			
9.....	20.88	} 3	} 2.8	} 63
10.....	20.93			
		Conc. H <sub>2</sub> SO <sub>4</sub> .		
11.....	21.04	} 1	} 2.8	} 65
12.....	21.00			
13.....	21.00			
14.....	21.04	} 2	} 2.8	} 61
15.....	21.04			
16.....	21.05			
17.....	21.05			
		Conc. acetic.		
18.....	20.90	} 10	} 5.5	} 60
19.....	20.92			

A large stock solution of thiosulfate, approximately 0.2 *N*, had been prepared about one week when the following standardizations were made: Calibrated burets were used, deliveries being made according to the time and manner specified by the German Imperial Commission.<sup>1</sup> All solutions, however, were used at the same room temperature which introduces no error into the comparative values on the iodometric and

<sup>1</sup> Schloesser, W., "Beiträge zur Prüfung maasanalytischen Messgeräte." *Z. anal. Chem.*, 46, 392-414 (1907) and references. Also various reports of the German Imperial Commission in *Z. angew. Chem.*, 1893, p. 557; 1897, p. 643; 1904, p. 1746. Also Schloesser, *ibid.*, 1903, p. 953ff.



the copper standards. The potassium iodate was dried in an oven, cooled in a desiccator and a weight of 14.8302 g. was dissolved to a volume of two liters. This standard solution had therefore a value of 0.20786 N. From this solution, in a buret, 20 cc. volumes were delivered into 200 cc. Erlenmeyer flasks. Distilled water 20 cc., concentrated acetic acid 10 cc., and then crystallized potassium iodide about 2.8 g. were added in the order named. The free iodine was titrated with the thiosulfate, using soluble starch indicator at the end. Experiments with sulfuric acid were also made on the same plan as with acetic. The results are tabulated in Table I.

The accuracy and consistency of the data obtained with acetic acid are highly satisfactory. Since the normality of the potassium iodate solution was 0.20786 that of the thiosulfate =  $\frac{20.00}{20.91} \times 0.20786 = 0.19880$  N. Since a normal solution of copper is equivalent to 63.57 grams per liter, the value of the thiosulfate solution in terms of copper, *calculated according to the theory of normalities* =  $\frac{20.00}{20.91} \times 0.20786 \times 63.57 = 12.633$  grams of Cu per liter, *i. e.*, the standard value of the thiosulfate is 12.633 mg. of copper per cubic centimeter. This value is attended by a very small limit of error, as shown by the deviations from the mean and is at least 0.6% less than the lowest values calculated from the copper standardizations given below.

With reference to the conditions of this standardization it should be noted that these were the same for all the titrations except the acidity. Acetic acid permits of a wide range in the amount of acid present without variation in the results. Sulfuric acid causes the liberation of more iodine as the concentration of acid increases. Since its concentration markedly influences the results it is evidently not as well adapted to this purpose as acetic. Furthermore, the titration results with acetic acid are lower and consequently it gives a higher normality than would sulfuric acid. If the values with the latter acid were adopted the copper value of the thiosulfate as determined by iodine (from iodate) would differ still more than has been above stated from the copper value as determined by means of copper.

(4) *The Influence of the Concentration of Acids and of Salts on the Results of the Iodide Method.*—Before making direct experiments on the standardization of thiosulfate by copper, the results of the following experiments will be given which show the influence, not simply of acid but of an excess of acid adjusted to the conditions if correct results are to be obtained by the iodide method. This influence is especially evident in solutions which contain a quantity of ionizing salts and particularly in the neutralized alkaline tartrate solutions or filtrates occurring

in sugar analysis. This is especially the place where the iodide method should serve on account of its possibilities of accuracy and rapidity. Moreover, since Gooch and Heath<sup>1</sup> set a maximum limit of about 0.3 g. of copper for a titration under the conditions which they investigated it was important to determine whether the method could be extended with accuracy to the larger amounts which occur in some methods of sugar analysis.

In a method of sugar analysis here tested, a published report of which will shortly follow, the total volume for reduction was always 60 cc. This consisted of 20 cc. of Allihn's alkaline tartrate solution + 20 cc. of Fehling's copper sulfate solution + 20 cc. either of water as in a blank determination or of an aqueous sugar solution. After reduction with sugar (under conditions subsequently to be described) the mixture, while still quite hot, is filtered free from cuprous oxide through a suitable filter. After washing, the filtrate (alkaline copper solution) has a volume of 70-75 cc.

The question of how to acidify this solution properly for the iodide method was approached through the following preliminary tests on the degree of acidity. To 20 cc. of the alkaline tartrate solution were added 40 cc. of water and some phenolphthalein. Concentrated sulfuric acid was added by drops from a graduated pipet. With 2.65 cc. of acid the solution became acid to phenolphthalein, but was neutral to litmus. With 2.75 cc. distinct acidity to litmus occurred. In another test with methyl orange, acidity occurred with 3.35 cc. These data indicate, of course, the conversion of alkali to acid salt shown by phenolphthalein and litmus with 2.75 cc. of acid and to neutral salt shown by methyl orange with 3.35 cc. of acid. They afford an excellent basis for testing the influence of acids and salts upon the results of copper measurement by the iodide method, since they exhibit gradual variations of both constituents. The 70-75 cc. of alkaline tartrate and copper above described were now treated in separate samples with 2.7, 3.0, 3.4, 4.0, and 5.0 cc. of concentrated sulfuric acid. With the temperature of these liquids at approximately 20°, 10 cc. of a saturated solution of potassium iodide were added and then they were titrated with the same stock of sodium thiosulfate. With 2.7 cc. of acid the evolution of iodine was imperfect and the mixture became of a dirty green color. The end-point was so slow and uncertain as to be practically useless for accuracy. Both with 2.7 cc. and with 3.0 cc. of acid the annoying phenomenon of false end-points occurred frequently before the final and slowly obtained end-point was reached. Evidently simple acidity to litmus is not sufficient for accuracy when a quantity of salts is present. It may be noted in passing that with less than 2.45 cc. of acid there was a considerable

<sup>1</sup> *Loc. cit.*, p. 74.

precipitation of salts upon cooling, which ceased to occur with 4.0 and 5.0 cc. of acid. With additions of 3.45 cc. or more of acid the evolution of iodine was always good and the end-point very sharp, as the close agreement of duplicates in the following table shows:

TABLE II.—INFLUENCE OF ACID ON THE RESULTS BY THE IODIDE METHOD IN THE PRESENCE OF MUCH TARTRATE AND SULFATE.

Conc. H <sub>2</sub> SO <sub>4</sub> . Cc.	Acid/Vol.	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> . Cc.	Conc. H <sub>2</sub> SO <sub>4</sub> . Cc.	Acid/Vol.	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> . Cc.
3.....	1/40	27.60	4.....	1/30	27.85
3.....	1/40	27.41	4.....	1/30	27.85
3.....	1/40	27.34	4.....	1/30	27.84
3.....	1/40	27.35			
	Average,	27.40		Average,	27.85
3.45.....	1/29	27.87	5.....	1/24	27.92
3.45.....	1/29	27.82	5.....	1/24	27.94
3.45.....	1/29	27.73	5.....	1/24	27.92
3.45.....	1/29	27.69			
	Average,	27.78		Average,	27.93

It is highly important that the reagents be mixed in the order above mentioned, especially that the concentrated acid be not added until the dilution with the amount of water to be used has been made. Salts are thus held in solution which would otherwise precipitate, thus causing different or irregular titration values dependent on salt concentration, as shown in Table III. The results will also be different if the potassium iodide be first added to the alkaline liquid and the acid subsequently, even though the acid is previously diluted. It should also be noted that such conditions are sought as will bring the reaction to a close quickly, so that titration may follow at once after the addition of potassium iodide and thorough mixing.

In the experiments recorded in the following table the volume at the end of titration was always approximately 120 cc. and 10 cc. of saturated solution of pure potassium iodide were uniformly used. Each titration also was made on two deliveries of the electrolytically standardized solution of copper sulfate taken by means of two deliveries of the automatic pipet.

The data above tabulated show clearly that the values obtained by the iodide method are easily influenced by the amount of acidity or of a salt in which the evolution of iodine occurs. The potassium iodide here used was the same as that which was tested as described on p. 437. If a way cannot be found of using the iodide method satisfactorily with this high grade of reagents then the method must be pronounced impracticable where accuracy is required. However, impurity of reagents would

scarcely account for the gradation of results shown by the table. There is a discrepancy of 4 parts in 279, or about 1.4% between the highest and lowest values. Even if we start from the methyl orange neutral point at about 3.35 cc. of acid there is an increase in the evolution of iodine with increasing acidity. Now by electrolytic determination each of the analyses of this table represents two deliveries of 176.9 milligrams of copper = 353.8 milligrams of copper. The question arises, which of these averages, if any, correctly represents the copper, or *vice versa*, if the thiosulfate were to be standardized for the measurement of copper, which of these averages should be used as a divisor for the 353.8 milligrams of copper. Evidently there is need of a criterion by which to judge not only of the accuracy of the standardization in the iodide method but also of the accuracy of its indications in those numerous cases where varying acidity and salt content occur.

In order to test further the influence of salts a series of experiments was made in which slightly more of a given salt than would dissolve was added to each titration liquid after acidification. The only exception is ammonium nitrate, of which 4 grams were used in a final volume of 120 cc. Potassium iodide was then added (temperature about 20°) and titration followed. These were estimations of pure solutions of copper without the presence of the alkali or the tartrate of the preceding series. The acidities were such as succeeding data discussed on pp. 442ff. will show to be capable of giving correct results on pure solutions of copper when these salts are absent. Two deliveries of copper sulfate from the automatic pipet =  $2 \times 176.9 = 353.8$  mg. of copper were used in each titration. The ratio of added acid to final volume Acid/Vol. is calculated uniformly on an approximate volume of 120 cc.

The table includes, among others, those salts which different authors have either added to the titration liquids for the iodide method in their special procedures or which have been formed in the processes used. In pure solutions as a control test these salts did not act upon potassium iodide.

The above data show that even when the amount of acid and all other conditions except salt content are kept constant the results of the iodide method are affected by the presence of salts. In those cases where sodium acetate without added acid was used the development of iodine was so imperfect as to affect the certainty of the end-point, which resulted in the poor agreement of the duplicates. By comparison with the first four titrations where results are given with neutral reaction and with acetic acid, but without addition of salts, it is seen to what extent the titrations in the presence of these salts varied from this standard.

All the preceding data lead to the conclusion that the condition of acidity or of salt content, as well as both combined, as in the copper

liquids of sugar analyses, and in other practical cases, may affect the accuracy of the results of the iodide method.

TABLE III.—INFLUENCE OF SALTS AND ACID ON THE RESULTS BY THE IODIDE METHOD.

Salt added.	Acid added.	Acid/Vol.	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> . Cc.	Vol. Cc.
None	Neutral	0/120	27.86	117
"	"	0/120	27.84	119
"	20 cc. conc. acetic	1/6	27.86	120
"	20 cc. "	1/6	27.85	118
Na <sub>2</sub> (C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> )	None	0/120	27.88	125
"	"	0/120	27.67	123
"	20 cc. conc. acetic	1/6	27.96	124
"	20 cc. "	1/6	27.95	124
"	2 cc. conc. H <sub>2</sub> SO <sub>4</sub>	1/60	27.94	126
"	2 cc. "	1/60	27.95	126
NH <sub>4</sub> (C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> )	20 cc. conc. acetic	1/6	27.87	120
"	20 cc. "	1/6	27.99	123
"	20 cc. "	1/6	27.97	100
Zn(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	None	0/120	26.68	118
"	"	0/120	26.51	119
"	20 cc. conc. acetic	1/6	27.97	118
"	20 cc. "	1/6	27.98	119
"	2 cc. conc. H <sub>2</sub> SO <sub>4</sub>	1/60	27.98	123
"	2 cc. "	1/60	27.94	122
Na <sub>2</sub> SO <sub>4</sub>	20 cc. conc. acetic	1/6	27.55	120
"	20 cc. "	1/6	27.59	120
K <sub>2</sub> SO <sub>4</sub>	2 cc. conc. H <sub>2</sub> SO <sub>4</sub>	1/60	27.91	120
"	2 cc. "	1/60	27.98	120
NH <sub>4</sub> NO <sub>3</sub>	20 cc. "	1/6	27.78	118
"	20 cc. "	1/6	27.74	118
KCl	2 cc. conc. H <sub>2</sub> SO <sub>4</sub>	1/60	28.11	120
Pure sucrose	20 cc. conc. acetic	1/6	27.86	120
"	20 cc. "	1/6	27.83	120
"	20 cc. "	1/6	27.85	120

(5) *The Standardization of Thiosulfate by Copper and the Influence of Varying Concentrations and Volumes.*—The next series of experiments was made for the purpose of standardizing the same thiosulfate solution heretofore used by means of electrolytically standardized copper solutions. Excess of salts other than reagents is excluded, but varying conditions of acidity were tested. The results of this series, together with those which precede, were expected to provide the basis for the selection of standard conditions for accuracy.

The following results show the disturbing effect of varying acidity even when the titration liquids are free from excess of salts. As in preceding experiments, they uniformly show an increasing development of iodine with increasing acidity. If, again, the results under conditions of neutrality be made the basis of comparison it appears that a small concentration of sulfuric acid does not cause variation from this basal value.

TABLE IV.—STANDARDIZATION OF THIOSULFATE BY COPPER.

Acid added.	Acid/Vol.	CuSO <sub>4</sub> . Del.	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> . Cc.	Aver. Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> . Cc.	Sat. KI. Cc.	Vol. Cc.
Neutral.....	0/120	2	28.82	27.83	10	120
Neutral.....	0/120	2	27.85			
10 cc. acetic . . . .	1/6	1	13.90	13.92 (27.84)	5	60
10 cc. acetic . . . .	1/6	1	13.93			
20 cc. acetic . . . .	1/6	2	27.83	27.85	10	120
20 cc. acetic . . . .	1/6	2	27.86			
2 cc. H <sub>2</sub> SO <sub>4</sub> . . . .	1/60	2	27.85	27.83	10	120
2 cc. acetic . . . .	1/60	2	27.82			
2 cc. H <sub>2</sub> SO <sub>4</sub> . . . .	1/30	1	13.95	13.94 (27.88)	5	60
2 cc. H <sub>2</sub> SO <sub>4</sub> . . . .	1/30	1	13.93			
2 cc. H <sub>2</sub> SO <sub>4</sub> . . . .	1/30	1	13.94	13.95 (27.90)	5	60
2 cc. H <sub>2</sub> SO <sub>4</sub> . . . .	1/30	1	13.95			
5 cc. H <sub>2</sub> SO <sub>4</sub> . . . .	1/24	2	27.89	27.88	10	120
5 cc. H <sub>2</sub> SO <sub>4</sub> . . . .	1/24	2	27.87			
6 cc. H <sub>2</sub> SO <sub>4</sub> . . . .	1/25	2	27.85	27.85	10	150
10 cc. H <sub>2</sub> SO <sub>4</sub> . . . .	1/15	2	27.89	27.89	10	150

TABLE V.—STANDARDIZATION OF THIOSULFATE BY COPPER.

Acid added.	Acid/Vol.	CuSO <sub>4</sub> . Del.	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> . Cc.	Aver. Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> . Cc.	Sat. KI. Cc.	Vol. Cc.
Neutral.....	0/120	2	27.84	27.85	10	120
Neutral.....	0/120	2	27.85			
2 cc. H <sub>2</sub> SO <sub>4</sub> . . . .	1/60	2	27.81	27.83	10	120
2 cc. H <sub>2</sub> SO <sub>4</sub> . . . .	1/60	2	27.85			
2 cc. H <sub>2</sub> SO <sub>4</sub> . . . .	1/70	2	27.79	27.80	10	140
2 cc. H <sub>2</sub> SO <sub>4</sub> . . . .	1/60	2	27.80			
2 cc. H <sub>2</sub> SO <sub>4</sub> . . . .	1/30	1	13.95	13.94 (27.88)	5	60
2 cc. H <sub>2</sub> SO <sub>4</sub> . . . .	1/30	1	13.93			
5 cc. H <sub>2</sub> SO <sub>4</sub> . . . .	1/28	2	27.89	27.91	10	140
5 cc. H <sub>2</sub> SO <sub>4</sub> . . . .	1/28	2	27.92			
5 cc. H <sub>2</sub> SO <sub>4</sub> . . . .	1/24	2	27.86	27.87	10	120
5 cc. H <sub>2</sub> SO <sub>4</sub> . . . .	1/24	2	27.88			
5 cc. H <sub>2</sub> SO <sub>4</sub> . . . .	1/12	1	14.00	14.01 (28.02)	5	60
5 cc. H <sub>2</sub> SO <sub>4</sub> . . . .	1/12	1	14.02			

This concentration seems to be in the vicinity of 1/60 of the total volume at the end of titration. As before, a high concentration of acetic acid, *e. g.*, 1/6 of the final volume, does not affect the values obtained. These results, pertaining to small concentrations of sulfuric acid and large concentrations of acetic acid, agree with the findings of Gooch and Heath.<sup>1</sup> These authors set a maximum limit of 2 cc. of concentrated acid in 50 cc. of liquid, *i. e.*, a proportion of 1/25. Bray and MacKay<sup>2</sup> considered the proportions used by Gooch and Heath too large, as they found the development

<sup>1</sup> *Loc. cit.*, p. 71.

<sup>2</sup> *Ibid.*, p. 1199.

of iodine under the influence of the reagents above to be large enough to be easily measurable. Bray and MacKay<sup>1</sup> also found that acetic acid had practically no influence on the results compared with mineral acids. The method pursued in obtaining the above tabular values, *viz.*, that of performing titrations with varying amounts of acid, show the influence of the acid under exactly the conditions of analysis. These data show that the maximum proportion of 1/25 set by Gooch and Heath is distinctly too large, and these authors state as follows (p. 74) with reference to acid: "We find no ground for the inference of Moser<sup>2</sup> that the presence of acid, best sulfuric acid, is necessary to the attainment of good results at all volumes excepting the most concentrated; and there appears to be no reason why the addition of small amounts of acid should increase the amount of iodine liberated, if the potassium iodide is free from iodate or other oxidizer. We are wholly unable to offer any explanation for Moser's extraordinary observation, quite contrary to our own, that variation in the amounts of  $\frac{10N}{I} H_2SO_4$ , from 1<sup>cm</sup><sup>3</sup> to 100<sup>cm</sup><sup>3</sup> (0.49 gram to 49 gram) for 50<sup>cm</sup><sup>3</sup> of a solution of copper sulfate, is practically without effect in the treatment by potassium iodide."

All these accounts taken together indicate that possibly no acid is necessary, *i. e.*, that a neutral reaction is always adequate for the iodide reaction, and that in any case a low concentration of mineral acid is permissible. But since the tabular results here presented show the variety of values that may be obtained, there is wanting a delimitation of conditions that would result in invariable accuracy. In order to obtain a basis for the correct standardization of these conditions it is here proposed that the results obtained with neutral solutions and with moderate proportions of acetic acid (*e. g.*, 1 volume in 6) and in the practical absence of salts be regarded as the correct standard. These two conditions have been found in agreement by other experimenters. In the above tables they have the following values, for neutral titration liquids: 27.86, 27.84, 27.84, 27.85, 27.82, 27.85 = average of 27.84 cc. with an average deviation from the mean of 0.01 cc. For acetic acid titrations with a proportion of 1 to 6: 27.86, 27.85, 27.80, 27.86, 27.83, 27.86 = average of 27.84 cc. with an average deviation from the mean of 0.02 cc. Under these standard conditions then 27.84 cc. of thiosulfate =  $2 \times 176.9 = 353.8$  mg. of copper. Therefore the thiosulfate has a value of 12.708 mg. of copper, per cc. The value 12.708 is to be compared with 12.633 by iodine (from iodate) found on p. 438. This is a discrepancy of 75 parts in 1270 = 0.6%. The results with sulfuric acid in the concentration of 1 to 60 and in the practical absence of salts may now be examined and

<sup>1</sup> *Loc. cit.*, p. 1199.

<sup>2</sup> *Z. anal. Chem.*, 43, 597 (1904).

they have the following values: 27.85, 27.82, 27.81, 27.85, 27.79, 27.80 = average of 27.82 cc. with an average deviation from the mean of 0.02 cc. This agrees well with the results under the above standard conditions with neutrality or with acetic acid. All the other values with sulfuric acid would give different results. If now the results with sulfuric acid in the absence of tartrate and sulfate be examined, it is found that when 4 cc. of sulfuric acid were used the result, 27.85 cc., was the same as under the standard neutral or acetic acid conditions. Hence with this amount of acid the alkalin tartrate solution of copper can be correctly estimated by the iodide method, so that the results essentially agree with those of electrolysis. All the other concentrations of sulfuric acid that were tried would result in erroneous values.

The principle here involved is that the copper measurements by the thiosulfate must give the same values in the presence of salts and acids as in their absence and that these results must in all cases be the same as those of electrolysis. Where the salt mixture can be obtained separate from the copper to be estimated as with the alkalin tartrate solutions of sugar analysis, this end is easily reached by standardizing the thiosulfate with and without the salt or acid to be tested. The amount of acid is adjusted to give the same result as the control standardization. When the amount of acid and salt, even though mixed and unknown, are constant for routine analyses, electrolytic controls once made suffice to show the measuring power of the thiosulfate in comparison with the standard conditions with neutrality or with acetic acid.

When the conditions presented are those of unknown and miscellaneous samples, accuracy can still be attained by a method of quantitative compensation described on p. 448.

Finally, with reference to the discrepancy between the standard values by iodine (from iodate) and by copper the following considerations should be made. If the standardizations were made under the use of mineral acids the development of iodine would be greater in both cases, as shown by all the tables, and consequently the standard values of both in terms of copper would be correspondingly depressed but their relation would not be materially altered. The discrepancy then is due in the first instance to the development of too little iodine by the copper method, thus giving a comparatively high result for the value of the thiosulfate. Bray and MacKay<sup>1</sup> have suggested as the cause of this difference, the absorption of iodine by the cuprous iodide precipitate, thus withdrawing it from the action of thiosulfate. Some of the experiments tabulated below show the result when the amount of potassium iodide is sufficient to dissolve all the precipitated cuprous iodide, thus removing the possibility of absorption.

<sup>1</sup> *Loc. cit.*, p. 1199.



TABLE VI.—INFLUENCE OF THE CONCENTRATION OF COPPER ON THE RESULTS OF THE IODIDE METHOD.

No.	CuSO <sub>4</sub> .	Cu. Mg.	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> . Cc.	Aver. Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> . Cc.	Vol. Cc.	Sat. KI. Cc.	Conc. acetic acid. Cc.	Calc. Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> . Cc.	Diff. Cc.
1	2 Del. . . . .	353.8	28.85	27.86	120	10.0	20	(27.86)	. . . .
2	2 Del. . . . .		27.86						
3	2 Del. . . . .	353.8	27.85						
4	2 Del. . . . .		27.84	27.85	120	10.0	20	(27.85)	. . . .
5	2 Del. . . . .		27.85						
6	40/100 of 4 Del. . . . .	283.0	22.28						
7	40/100 of 4 Del. . . . .	283.0	22.29	22.29	120	10.0	20	22.29	0
8	30/100 of 4 Del. . . . .	212.8	16.73						
9	30/100 of 4 Del. . . . .	212.8	16.72						
10	20/100 of 4 Del. . . . .	141.5	11.15	11.16	120	10.0	20	11.14	+0.02
11	20/100 of 4 Del. . . . .	141.5	11.16						
12	10/100 of 4 Del. . . . .	70.8	5.60						
13	10/100 of 4 Del. . . . .	70.8	5.59	5.60	121	10.0	20	5.57	+0.03
14	10/100 of 4 Del. . . . .	70.8	5.60						
15	12/100 of 4 Del. . . . .	84.9	6.74						
16	12/100 of 4 Del. . . . .	84.9	6.70	6.71	118	10.0	20	6.68	+0.03
17	12/100 of 4 Del. . . . .	84.9	6.68						
18	10/100 of 4 Del. . . . .	70.8	5.56						
19	10/100 of 4 Del. . . . .	70.8	5.58	5.57	{ 118 } 116	10.0	20	5.57	0
20	10/100 of 4 Del. . . . .	70.8	5.60						
21	10/100 of 4 Del. . . . .	70.8	5.59						
22	10/100 of 4 Del. . . . .	70.8	5.58	5.57	23	2.5	4	5.57	0
23	10/100 of 4 Del. . . . .	70.8	5.55						
24	8/100 of 4 Del. . . . .	56.6	4.43						
25	8/100 of 4 Del. . . . .	56.6	4.45	4.44	119	10.0	20	4.46	-0.02
26	8/100 of 4 Del. . . . .	56.6	4.46						
27	8/100 of 4 Del. . . . .	56.6	4.44						
28	6/100 of 4 Del. . . . .	42.5	3.36	3.36	124	20.0	20	3.34	+0.02
29	6/100 of 4 Del. . . . .	42.5	3.35						
30	5/100 of 4 Del. . . . .	35.4	2.76						
31	5/100 of 4 Del. . . . .	35.4	2.80	3.78	{ 116 } 118 118	10.0	20	2.79	-0.01
32	5/100 of 4 Del. . . . .	35.4	2.79						
33	5/100 of 4 Del. . . . .	35.4	2.78						
34	5/100 of 4 Del. . . . .	35.4	2.79	2.79	117	10.0	20	2.79	0
35	4/100 of 4 Del. . . . .	28.3	2.28						
36	4/100 of 4 Del. . . . .	28.3	2.24						
37	4/100 of 4 Del. . . . .	28.3	2.24	2.25	117	10.0	20	2.23	+0.02
38	4/100 of 4 Del. . . . .	28.3	2.24						

Here also are tabulated the results of experiments so planned as to show to what extent the evolution of iodine in the iodide method is affected by the relative concentrations of copper or by the relative volumes in which the reaction occurs. In most of the experiments four deliveries

of the standardized pure copper sulfate (176.9 mg. Cu each) were run into a 100 cc. volumetric flask and made to the mark with distilled water. This solution was then placed in a buret from which the proportions shown by column 2 were taken. Each portion was then estimated by the iodide method as indicated by the table.

The basis of comparison for all the above results is the largest titration of copper made under constant conditions on the constant volume of approximately 120 cc. This amount is 27.86 cc. and has been verified by other titrations. The calculated titrations of column 9 were obtained on the supposition that aliquot volumes would give strictly proportional titrations. The differences of column 10 show the variation of the experimentally found values of column 5 from those calculated in column 9. The results clearly show that such proportionality does exist and that the results obtained by the iodide method under controlled condition of reagents are strictly comparable for large and small amounts of copper.

The concentration of copper expressed as  $\frac{\text{Cu. mg.}}{\text{Vol. cc.}}$  for the determinations

in 120 cc. vary from  $\frac{354}{120}$  to  $\frac{28}{120}$ , *i. e.*, from 2.95 to 0.23. The limits of error, especially with the smaller amounts of copper, are surprisingly small when the unfavorable conditions of large volume and concentrated thiosulfate solution compared to the small amount of copper to be estimated are considered. For other reasons small amounts of copper should, of course, be measured with dilute thiosulfate in a small volume. The severest test for the present proposition was to maintain the same large volume and comparatively concentrated thiosulfate for widely varying amounts of copper.

The results above tabulated also permit the following observations on absorption of iodine by cuprous iodide. In experiments Nos. 1-25 the concentration of potassium iodide, as shown by the table, was not sufficient to hold all of the cuprous iodide in solution. In experiments 26-38 complete solution occurred. Although the amounts of copper here determined were small and the conditions unfavorable, as above described, the results found and calculated agree very closely. However, the basis of calculation was the value 27.85 cc. obtained with the large amount of copper of 353.8 milligrams where solid cuprous iodide occurred in abundance and could have permitted absorption of iodine. The exact proportionality of the results show that such absorption did not occur in any of these determinations, even when abundance of solid cuprous iodide was present. Hence this possible source of error does not exist in the method as here followed and the factor of absorption does not explain the discrepancy between the iodine and the copper standardiza-

tions of thiosulfate. The possibility that cuprous iodide may absorb some iodine under certain conditions is, of course, not denied.

(6) *General Conclusions on the Iodide Method.*—A salient characteristic of the iodide method from the standpoint of accurate, electrolytically controlled copper measurement is its sensitiveness to change of conditions. This fact finds its explanation in the dependence of the method upon a sensitive equilibrium reaction. The ready variability of values by the iodide method according to concentration of acid and of salts, and according to the selection of the standard values of the thiosulfate, etc., renders it difficult to guarantee its accuracy without full knowledge of the special conditions involved in each analysis. This latter necessity ranks the iodide method below the electrolytic method in general applicability, when a high degree of accuracy is required.

Very accurate measurements of copper can be made by the iodide method with the procedure previously described and under the following provisions: (1) The conditions of the analyses to be made can frequently be so adjusted that the same values for thiosulfate hold as for the special conditions of the original standardization of the thiosulfate. The copper of the alkaline tartrate solutions from sugar analyses can thus be accurately determined by adjusting once for all the degree of acidity. (2) The thiosulfate is empirically standardized for the special conditions of a series of analyses by the electrolysis of a sample of the frequently recurring routine solutions which present a repetition of the same conditions. (3) The influence of varying conditions which may not be in harmony with those of the original standardization of the thiosulfate can be tested and quantitatively compensated by the following method: The maximum amount of the unknown copper solution is first titrated and secondly, to half of this amount is added an equal and exactly known amount of pure standard solution of copper and another titration is then made with the same final volume and reagents. The divergence from the first titration and its sign are then noted and twice this amount is applied as a correction to the first value. The corrected thiosulfate value thus found may now with accuracy be multiplied by the standard value of the thiosulfate obtained under standard conditions. When the amount of copper is small a smaller volume, *e. g.*, 50 cc. and a more dilute thiosulfate, *e. g.*, of a value of about 3 mg. of copper per cubic centimeter, provides corresponding conditions for the above procedure.

The iodide method can be made to give exceedingly accurate results, comparable within limits of error, with those of electrolysis. It requires, however, rigid control of pure copper or by electrolysis, which control must be extended to the detailed conditions of its application in order to obtain results concordant with the theory.

## 6. Summary of the Conditions of the Iodide Method for the Greatest Accuracy and Sensitivity Especially in the Analysis of Alkaline Tartrate Solutions.

(1) *Introduction.*—A highly valuable experimental study of the conditions for the iodide method was made by Gooch and Heath<sup>1</sup> where also the principal developments of the preceding literature are taken into consideration. The earlier paper of Moser<sup>2</sup> is also a valuable contribution on the iodide method. From these accounts, as well as from the results of numerous copper determinations made by myself, the desirable conditions for the iodide method may be summarized as follows:

(2) *The Concentration of Potassium Iodide.*—The concentration of the potassium iodide should be high in comparison to the equivalent (see equation) of copper present, regardless of whether the absolute amount of copper be small or large. The reaction between copper sulfate and potassium iodide does not run to completeness unless there is present a considerable excess of the iodide. The most important point is that the concentration of iodide be high in relation to the final volume at the end of titration and not simply with reference to the absolute amount of copper present. This is a condition of great importance, which was well developed by Gooch and Heath.<sup>3</sup>

I use a solution of potassium iodide which is in saturated condition when the solution has reached room temperature. It has been found that when this solution is kept in the dark instead of on the laboratory table, and when stoppered, it liberates iodine much less rapidly. Free iodine should be removed with dilute thiosulfate solution. Ten cubic centimeters of such a saturated solution weighed 17.120 g. and after evaporation to dryness left a residue of 10.840 g. Hence 1 cc. represents about 1.1 g. of the iodide. Since comparatively large quantities must be used, the titrated liquids, if numerous determinations are made, should be saved for the recovery of iodine as described below.<sup>4</sup> In this

<sup>1</sup> *Am. J. Sci.*, 24, 65-74 (1907).

<sup>2</sup> *Z. anal. Chem.*, 43, 597-608 (1904).

<sup>3</sup> *Loc. cit.*

<sup>4</sup> The following method for the recovery or rough evaluation of waste titration liquids containing iodine was found efficient and convenient. The titrated liquids including the cuprous iodide are distilled from a tubulated retort carrying a safety tube. The open end of the retort is immersed in cold water. Upon boiling the liquid with manganese dioxide and sulfuric acid, free iodine passes over and is collected in the water, some also adhering to the neck of the retort. The whole distillate is filtered through glass wool and the iodine is dried on a porous plate. The iodine may be converted to hydriodic acid by the method of Winkler, as follows: It is dissolved in a quantity of carbon tetrachloride which is covered with a layer of water. Hydrogen sulfide is passed and as the iodine is removed by the accumulation of hydriodic acid in the watery layer, more iodine is added to the tetrachloride. The action is slow at first, but the process works very satisfactorily. When the quantity of these waste titration liquids is large it may be advisable to sell the evaluated material.

work approximately 120 cc. at the end of titration was the most frequently used volume, and for this 6–10 cc. of the iodide solution were taken. For titrations in a volume of 60 cc. or less, 5 cc. of iodide solution were generally used. Beyond a certain limit included within the above amounts, an increase in potassium iodide no longer affects the results, but a very great excess should be avoided as liable to produce the same effect as high salt concentration (see Table III, p. 442). Occasionally when the amount of copper was small the resulting cuprous iodide was completely dissolved by the iodide, but this does not vitiate the results.

These titrations were made with an approximately uniform volume of 120 cc. at the end of titration and with 5 cc. of concentrated sulfuric acid. They were all made on the same amount of copper sulfate solution, *viz.*, one delivery of the automatic pipet:

TABLE VII.—INFLUENCE OF THE CONCENTRATION OF POTASSIUM IODIDE ON THE RESULTS OF THE IODIDE METHOD.

Sat. KI. Cc.	KI/Vol.	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> titrat. Cc.	Sat. KI. Cc.	KI/Vol.	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> titrat. Cc.
6	1/20	13.98	2	1/60	13.94
5	1/24	13.98	1	1/120	13.91
3	1/40	13.94	0.5	1/240	9.66
			4	1/30	13.97

(3) *The Degree of Acidity.*—A second desirable condition is the presence of a limited but indefinit concentration of hydrogen ion. Nitric or even hydrochloric acid<sup>1</sup> is undesirable for this purpose. When no considerable amount of electrolytes is present, acetic acid within a wide range of concentration may be used, or sulfuric acid in relatively small amount. Sulfuric and not acetic acid should be used for acidifying the alkaline reduction mixtures occurring in sugar analyses. These also contain a considerable concentration of Rochelle salt which, together with the salt formed by acidification, tend to depress the ionization of the excess of acid. With acetic acid this depression, especially when the volume is small, is so great that the liberation of iodine is not free and rapid. Under these circumstances a premature end-point may occur with the thiosulfate, more iodine being liberated soon after the apparent end-point, or the whole reaction and titration may proceed so slowly as to be uncertain. Sulfuric acid should be used in small but sufficient excess to give a prompt and complete evolution of iodine. The result is due to its greater ionization than that of acetic acid.

In any case prompt evolution of iodine, a yellow to brown, not a greenish color of the reaction mixture, and a rapidly attained end-point with thiosulfate are evidences of sufficient excess of acid. Too great an ex-

<sup>1</sup> See Moser, *Loc. cit.*, p. 600.

cess of acid would, as Gooch and Heath<sup>1</sup> and Bray and MacKay<sup>2</sup> observed, liberate iodine from potassium iodide in the presence of air. Possibly this source of error always occurs in the iodide method, but its amount should be negligibly small during the time consumed in a titration. That iodine develops in a longer period of time and redevelops after the titrations are finished has but little practical significance.

(4) *The Loss of Iodine by Volatilization.*—Another condition for the accuracy of any iodine titrations is that they be performed in narrow-necked Erlenmeyer flasks of the smallest convenient volume, *e. g.*, of 100 to 300 cc. and, it need scarcely be added, the temperature should not exceed that of the room. It was not found necessary to stopper the vessels used under these conditions, especially when the liberation and the titration of the iodine altogether occupied only a few minutes.

(5) *The Volume of the Titration Mixture.*—The practical question arises as to what is the most favorable concentration of sodium thiosulfate with which to titrate the liberated iodine under any conditions of dilution. The answer depends primarily upon the volume of liquid in which *at the end of the titration* one drop of thiosulfate of any proposed concentration will still produce a definitely perceptible change of color called the end-point of the titration. Thus the conditions for the greatest accuracy are summarized as follows: The largest amount of substance (copper) to be estimated, contained in the smallest volume, should be titrated with the most dilute thiosulfate that gives a good end-point. When any one of these three conditions is determined, the other two can be adjusted for the maximum accuracy which the determined condition permits.

One of the most frequent and least perceived of the errors made by the iodide method is the failure to use sufficient potassium iodide and acid when volumes above 100 cc. are obtained at the end of titration. Only by observing this condition can comparable results be obtained for the same amount of copper in large and in small volumes.

(6) *The Starch-iodine End-point in the Presence of Suspended Cuprous Iodide.*—A comparison of the relative usefulness of various concentrations of thiosulfate involves a consideration of the nature of the end-point in the iodide method. The presence of a greater or less quantity of the precipitated slightly yellowish white cuprous iodide considerably modifies this end-point from that of a simple iodine titration where the final change from blue to colorless is very easily determined. In the presence of cuprous iodide and starch the mixture, shortly before the end of the titration, assumes a chocolate-brown color, which changes to a light cream-white as the last necessary drop of thiosulfate is added. The end-

<sup>1</sup> *Loc. cit.*, pp. 70-71.

<sup>2</sup> *Ibid.*, p. 1199.

point *has already occurred* when another drop of thiosulfate does not diminish the prevalent very light shade of the mixture. The recognition of the end-point must be learned by some practice. It can be satisfactorily obtained in good diffuse daylight, as well as by artificial light, by working over a white surface. It is by no means uncertain or indefinite, as the very close agreement of repeated titrations by several observers shows. Bray and MacKay<sup>1</sup> found that the change of color of the particles of suspended precipitate was a good indication of this end-point. In these experiments the phenomenon of colored particles was not observed when fresh soluble starch was used, but only with an indicator of common boiled starch (used only for trial) and of older solutions of soluble starch. The "spot test," contrary to the opinion of Moser,<sup>1</sup> seems to be the best of all direct indications of the end-point. So long as a drop of thiosulfate falling upon the quiet surface of the titration liquid produces a perceptible white area the end-point has not yet been reached. Practically all the titrations here reported were made with this end-point.

It is strongly urged that another buret be constantly kept at hand containing an iodine solution of practically equivalent concentration to the standard thiosulfate. This scheme is highly useful when the conditions of illumination are not favorable, or in the presence of sufficient coloring matter to disturb or when overtitation is suspected, and for the inexperienced. When the end-point is supposed to have been reached the liquid is back-titrated with the iodine to the first definitely recognizable darkening due to iodide of starch. The appearance of a color constitutes in general a better end-point for a titration than the disappearance of a color. In the former case overtitation has better defined limits. This back-titration must be done within a few minutes after the thiosulfate titration and before the liquid has stood exposed to the air long enough<sup>2</sup> to redevelop some iodine. The thiosulfate end-point is thus confirmed or corrected if necessary. For accuracy it is important to remember that all volumetric end-points are slight overtitrations and that hence the mean between the direct thiosulfate and the back-titration with iodine is more nearly correct than either alone. This error is, however, practically eliminated when, as in the residual method of sugar analysis, the quantity of reduced copper to be determined is found by taking the difference between two thiosulfate titrations, the first of which is a blank determination.

It must not be inferred from the above details and refinements that the end-point in the iodide method is not practically useful or involves any formidable difficulties.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> See Bray and McKay, *Loc. cit.*, p. 1199.

### 7. Summary of Results.

(1) The different methods for the standardization of thiosulfate solutions may be classified into groups each of which gives values at variance with the others, but very constant with itself. The differences between the group values far exceed the limits of error of the individual groups. Of these groups, that which gives the same result as pure iodine must be regarded as correct for the purpose of measuring iodine *per se*. The standard value of thiosulfate determined by copper under electrolytic control is discrepant with the results of the iodine group much beyond the limits of error of either method. For accurate copper measurement by the iodide method only the empirically determined value of the thiosulfate by means of copper can be used. The copper value of the thiosulfate which can be *calculated* from the normality of the thiosulfate by iodine is therefore not applicable in the iodide method for the determination of copper.

(2) A tartrate-cyanide electrolyte for the deposition of copper has been described which permits the use of high voltage, high current density and boiling temperature compatible with a deposit of good quality. The proportion of cyanide is limited. A copper cathode may be used instead of platinum. Rapid deposition is due to the composition of the electrolyte and its continued mixture by abundant evolution of gas and from heating.

(3) A rapid method has been described for preparing solutions of copper or of its compounds for the iodide method. Solution is made in an Erlenmeyer flask by means of heat with the least necessary amount of slightly diluted nitric acid. After additions of water and powdered talcum the mixture is boiled vigorously for 5 to 10 minutes. The rapid ebullition occurring under these conditions quickly removes nitrous acid. Upon cooling and diluting, the iodide method may be applied. Sulfuric acid may be added to the nitric acid solution when a sulfate solution is desired.

(4) The accuracy of the results obtained by the iodide method is affected by (a) varying concentrations of mineral acid, (b) by the presence of salts both independently of and in conjunction with acetic or mineral acid. The results obtained in neutral and in acetic acid solutions, both of which are free from excess of salts, are concordant and thus constitute the standard of correctness. When much salt is present or when the alkaline copper solutions from sugar analyses are to be estimated, sulfuric acid rather than acetic should be used in order to obtain prompt evolution of iodine and a good end-point.

(5) It has been shown that when the conditions of the iodide method are under control: (a) the results are independent of the concentration of the copper titrated or of the volume in which the titration is made;



(b) the results on large and on small amounts of copper in the same or in different volumes are strictly comparable.

(6) It has been shown that absorption of iodine by precipitated cuprous iodide as a perceptible source of error does not occur in the iodide method as here performed. Hence this explanation of the discrepancy between the iodide and the copper standardizations of thiosulfate solutions is untenable.

(7) The ease with which the results of the iodide method are affected by a variety of conditions has been shown. Procedures have been described for testing the presence of these influences and for adjusting the conditions or quantitatively compensating them. These procedures have a general application, so that even for a high degree of accuracy the iodide method need not be limited to the special conditions of the original test analyses. The iodide method, only under control of conditions it must be emphasized, has the decided advantages of exceeding accuracy combined with rapidity.

I am under much obligation to Professor F. G. Benedict for advice and valuable criticism throughout this work. I was also ably assisted in obtaining the experimental data and in their re-examination by Mr. Richard I. Carney and Mr. Wm. F. O'Hara, of the staff of this laboratory.

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## THE PROPERTIES OF SALT SOLUTIONS IN RELATION TO THE IONIC THEORY. III. ELECTRICAL CONDUCTANCE.

BY A. A. NOYES AND K. G. FALK.

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CONTENTS.—11. Theoretical Considerations. 12. The Conductance and Viscosity Data. 13. Ionization Values at 18°. 14. Discussion of the Ionization Values at 18°. 15. Comparison of the Ionization Values at 0° and 18°. 16. Equivalent Conductance of the Separate Ions. 17. Change of the Equivalent Conductance with the Concentration.

### 11. Theoretical Considerations.

This article is devoted to the consideration of the electrical conductance of solutions of single salts.

The conductance of a solution may be explicitly defined in terms of the ordinary units as the number of coulombs of electricity that pass through it per second when a potential-difference of one volt exists at the electrodes. The specific conductance ( $L$ ) of a solution is the conductance of one centimeter cube of it between electrodes one centimeter apart.

The conductance of aqueous solutions of salts, acids and bases (hereafter referred to by the single word "salt") seems to be almost wholly