The alkalies, alkaline earths, salts of cadmium, manganese, nickel, and cobalt are alkaline to erythrosine. The oxygen salts of iron, aluminum, and chromium behave like free acids to this indicator. It is not suitable for the titration of organic acids ; and even oxalic acid cannot be used. Ammonia, however, may be titrated with it. Erythrosine may be used with fairly turbid waters and also with colored waters. In this respect it is much better than lacmoid or phenacetolin, both of which tend to give too high results with such waters.

LABORATORY OF " COMMISSIONERS OF WATER WORKS,"
CINCINNATI, OHIO, January 10, 1899.

SOME NOTES ON THE ESTIMATION OF CARBOHY-DRATES.

BY F. W. TRAPHAGEN AND W. M. COBLEIGH.

IN common with agricultural chemists in many parts of the country we have been interested in the direct determination of the carbohydrates of grains, foods, etc., in place of the method of subtracting from one hundred all other constituents and calling the remainder " nitrogen-free extract."

It seemed to us, as it was necessary to take advantage of the cupric reducing power for the estimation of the carbohydrates or their hydrolyzed products, that the first matter of importance in studying these methods was a determination of the simplest means for estimating the quantity of copper precipitated.

For the determination of copper electrolytically, if many determinations are to be made at a time, the platinum apparatus becomes very expensive. If for this method, which when properly conducted gives excellent results, we can substitute a volumetric method giving equally good results, it would seem desirable to do so. A volumetric method for the estimation of the precipitated cuprous oxide is much to be preferred to any gravimetric method, provided that it gives results of the same degree of accuracy. We offer the following method which in our hands has given excellent results :

100 cc. of Fehling's solution are diluted with 100 cc. of water and heated in a boiling water-bath. A known amount of sucrose or starch contained in carefully analyzed samples which are as nearly as possible like the substance under analysis, is inverted.

These solutions are used with similar solutions containing approximately known amounts of sucrose or starch. The amounts taken in each case are such that the precipitated cuprous oxide is nearly identical in weight. The precipitated cuprous oxide is collected on a Hirsch funnel covered with asbestos felt. After washing thoroughly with water the top layer of the asbestos carrying most of the cuprous oxide is transferred with a platinum spatula to the beaker in which the precipitation was made. The remaining asbestos is moistened and the cuprous oxide adhering to the side of the funnel is easily rubbed off. Water is added and the mass thoroughly stirred. Fifty cc. of a saturated solution of ferric sulphate in twenty per cent. sulphuric acid is added. After the cuprous oxide is dissolved, filter on the same funnel, thus leaving it ready for another filtration. The solution is then ready for titration with potassium permanganate. The end-reaction is clear and definite.

The possible objections to be urged against the use of a volumetric method are : First, the possibility of oxidation of the cuprous oxide ; second, the possible re-solution of the oxide. This is equally an objection to any gravimetric method, should it occur, but our investigations proved that no such re-solution occurs. A third objection may be made that the results are not strictly comparative. The experiments made bear directly upon these points.

As to the oxidation of cuprous oxide, six lots containing equal quantities of invert sugar were treated as usual. Three of these lots were filtered, washed, dissolved, and titrated at once with permanganate. 47.00, 47.10, and 47.15 cc. were required, an average of 47.10 cc. The remaining three lots were treated as above, except that instead of being dissolved at once they were allowed to remain for three hours on the filter, then removed and kept under water over night. The next day they were dissolved and titrated, requiring 47.15, 47.10, and 47.00 cc. respectively, an average identical with the results obtained where every possible precaution was taken against oxidation.

When the precipitated cuprous oxide was allowed to stand in the alkaline solution from which it was precipitated, instead of filtering immediately, the following results were obtained :

In the case of immediate filtration and titration, 41.4, 41.4,

and 41.5 cc., being an average of 41.43 cc. of permanganate solution, were required, while for the oxide which stood twenty-four hours in the alkaline solution from which it was precipitated before it was filtered, there was required 41.5, 41.7, and 41.3 cc. permanganate, the average of which, 41.5 cc., is almost identical with the preceding value. This indicates clearly that no re-solution takes place. While in ordinary work it is not necessary to allow these precipitates to stand more than twenty-four hours before treatment, it might occasionally be necessary, however, to allow them to stand over night ; this could be done with safety.

The following results will show that under proper manipulation, it is possible to get figures which are perfectly harmonious among themselves. Sugar solutions were made which would contain, on inversion, the starch or invert sugar equivalent of 0.38 gram of sucrose. This solution required, when the cuprous oxide was precipitated by Allihn's method, an average of 41.3 cc. of potassium permanganate solution, while the average obtained by precipitating the oxide in a boiling water-bath for one-half hour was 41.47 cc. Three different solutions, inverted independently, were used. These required for the first method 41.1 cc. ; 41.3, 41.2 cc. ; and 41.4, 41.5 cc., respectively, while for the water-bath precipitation 41.4, 41.5 cc. ; 41.4, 41.7 cc. ; and 41.5, 41.3 cc. were required. With a commercial starch the results were, by Allihn's method of precipitation, 34.5, 34.7, and 34.6 cc. ; and by the water-bath 34.8 and 35 cc.

It will be noticed that these results are remarkably close together, that while the water-bath precipitation gives somewhat higher results, that as a whole these figures are as consistent and harmonious as analytical results generally are, and that the extreme error is very slight.

The constant checking of results in compounds of unknown carbohydrate content against those obtained from substances of known composition, places each chemist, after he has become familiar with the manipulation, where he is entirely independent of the possible influences of local climatic conditions. Our own work shows that one can constantly obtain the same percentages with the same reducing solutions. Of course we appreciate the fact that it is difficult to constantly obtain, from complex carbo-

hydrates, solutions having constant reducing power, and on this account we have taken substances which were easily hydrolyzed to a constant reducing power.

Our purpose has been to deal in this paper only with the determination of the reduced copper. The amount of dextrose calculated to copper according to the ratio $5Cu_2O : 2C_6H_{12}O_6$ is 1 mg. $Cu = 0.5678$.

An inspection of Allihn's tables will show that, while the values given at the beginning of the table for weights not far from ten milligrams of copper is higher than that calculated from the reaction, that it soon begins to drop and for 100 milligrams it reaches its lowest point, namely, 0.509 milligram of dextrose for one of copper, which is much lower than the calculated weight; from this point the ratio steadily rises until at the highest point in copper weight the table reaches, 463, the dextrose equivalent 249.9 gives a ratio of 1 : 0.539.

A calculation of the amount of dextrose or its equivalent in unknown mixtures corresponding to potassium permanganate as given by the ratios $2C_6H_{12}O_6 : 5Cu_2O$; $10Fe : K_2Mn_2O_8$ gives, as would be expected, results entirely too high.

Our method for overcoming this difficulty is to take a known amount of pure cane-sugar as a standard for sucrose and for starch a commercial starch which has been very carefully analyzed, and treat this under exactly similar conditions with the substances containing approximately known amounts of sugar or starch. Thus we always get nearly the same weights of suboxid in all cases, and inasmuch as we determine each time our sucrose or dextrose ratio, any variation of climatic condition can hardly affect results. In this connection it has seemed to us that the variation in boiling-point due to the locations of laboratories at different altitudes might seriously affect the direct use of Allihn's tables. Unfortunately our weights of cuprous oxide were so high (they were made so intentionally to avoid multiplying errors), that we could not make this comparison by use of results now in our possession, but we shall make it a point as early in the future as possible, to investigate this matter. Our laboratory is over 4800 feet above sea-level, the average barometric pressure 637 millimeters, and the boiling-point close to 95°. This difference of 5° in the boiling-point may be well supposed to have its effect.

Another point has occurred to us : our results by permanganate have led us to suspect that all the copper may not be present in the precipitate as cuprous oxide. We are satisfied that after precipitation, and until acted upon by the ferric sulphate solution, no oxidation of the precipitate takes place, yet we find more copper by the electrolytic method than by the permanganate. The ratio is 1 : 0.9905. It may be urged that this represents the error due to the determination of the cuprous oxide by the permanganate method, but we are unwilling to concede this.

However, even were this granted, the admission would not affect the accuracy of the method we offer, for correct results depend only upon the permanganate factor, and not upon the absolute amount of copper.

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THE ATOMIC MASS OF TUNGSTEN AND THE PREPARATION OF SODIUM PERTUNGSTATE BY MEANS OF THE ELECTRIC CURRENT.[1]

BY GEORGE EDWARD THOMAS.

I. THE ATOMIC MASS OF TUNGSTEN.

THERE have been numerous determinations of the atomic mass of tungsten made in this laboratory; but as there were noted discrepancies in the results obtained, it was deemed advisable to pursue further investigation, as there appeared to be a probability that an examination of the trioxide of tungsten from different sources might reveal the cause of the disagreement mentioned.

Scheelite from Schlackenwald, Bohemia, and wolframite from Monroe county, Connecticut, were treated independently as follows: The finely divided minerals were digested for several days with *aqua regia*, and the insoluble residue washed repeatedly with water, and subsequently treated with ammonium hydroxide. These solutions were then evaporated and the crystals obtained were ignited, and to remove any molybdenum which might be

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[1] From the author's thesis for the degree of Doctor of Philosophy.