[Contribution from the Chemistry Department, University of Oregon]

THE ELECTROMETRIC TITRATION OF REDUCING SUGARS

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It is a well-known fact that the quantitative determination of reducing sugars by means of Fehling solution, either gravimetrically or volumetrically, is open to numerous objections. Results are affected by such factors as time of heating, temperature attained, auto-reduction, etc. Many experiments have been carried out for the purpose of establishing a set of conditions which, if used consistently in standardization and analysis will give comparable results.[1]

The usual gravimetric methods require a comparatively great amount of time, while in volumetric methods the exact determination of the end-point is difficult in the presence of the colored precipitate. Since the volumetric methods are more rapid than the gravimetric, it would seem desirable to have some means by which the end-point could be determined more satisfactorily than is usually the case. The recently developed electrometric methods having given highly satisfactory results when applied to oxidation and reduction reactions, it seemed worth while to try the method in the determination of reducing sugars.

Various simplified and elaborated forms of apparatus have been devised and placed on the market. Some of these are described by Hostetter and Roberts,[2] and by Kelley[3] and others. The simple form, described by Hildebrand,[4] and essentially by Roberts,[5] is easily assembled from the equipment of the average laboratory. In the present work a normal calomel electrode, a common type of adjustable resistance for the main circuit, a miniature millivoltmeter, a commercial type of galvanometer and a motor-driven stirrer were used. Since this work was of a preliminary nature, no effort was made to regulate conditions as carefully as was done by Peters[1a] and other workers, yet similiar conditions were observed in all experiments.

A few preliminary experiments were carried out to determine whether an end-point could be obtained. In the preliminary runs, the sugar solution was added slowly to the boiling Fehling solution and the voltage read after each addition of sugar, and characteristic curves were obtained.

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[1] (a) Peters, This Journal, **34**, 928 (1912). (b) Quisumbing and Thomas, *ibid.*, **43**, 1503 (1921).

[2] Hostetter and Roberts, This Journal, **41**, 1337 (1919).

[3] Kelley and others, *J. Ind. Eng. Chem.*, **9**, 780 (1917).

[4] Hildebrand, This Journal, **35**, 850 (1913).

[5] Roberts, *ibid.*, **41**, 1358 (1919).

Preparation and Standardization of Solutions

The Fehling solution was made up according to Leach,[6] but it was found that a more satisfactory end-point resulted by using only half the amount of sodium hydroxide there recommended. All further "B" solutions were, therefore, made up using only 50 g. of sodium hydroxide per liter. Solution A and Solution B refer to the two solutions from which Fehling solution is made up; A, the copper sulfate solution, and B, the alkaline tartrate solution. Solution A was standardized electrolytically, using both stationary and rotating electrodes. The results of the two methods were in agreement and gave the value of 0.01745 g. of copper per cc. A sample of pure dextrose from the United States Bureau of Standards was used for the sugar solution; 0.9991 g. was dissolved in 100 cc. of water, giving a solution containing 0.00999 g. per cc. It was found that 10 cc. of Solution A required 10.05 cc. of sugar solution for complete reduction, so that 1 cc. of "A" is equivalent to 0.01004 g. of dextrose.

Procedure

The procedure in all cases was as follows. To exactly 10 cc. of Solution A, drawn from a calibrated buret, an equal amount of Solution B and 50 cc. of distilled water were added. The mixture was brought to boiling and the sugar solution was added rapidly until the end-point was reached. In these determinations, the progress of the reaction is followed by noting the deflections of the galvanometer which is in circuit with the titrating vessel. Upon the first additions of the sugar solution, these deflections are small and somewhat irregular, and the galvanometer reading may be kept very nearly at zero by continual slight changes of the adjustable resistance. At the end-point, 1 drop of sugar solution produces a large deflection, and a large change of the resistance is required to bring it again to zero. Further additions of sugar produce relatively small deflections. This method of determining the end-point allows the titration to be carried out rapidly after the solution has been brought to boiling, thus greatly reducing the errors introduced by extended heating, auto-reduction, etc. When the conditions are uniformly observed, results are comparable, except as affected by daily changes in the barometric pressure. Quisumbing and Thomas[7] give figures showing the magnitude of the error which may thus be introduced.

The method was next tried using a sample of crude glucose of unknown purity. During the course of this investigation a large number of determinations were made; only a few representative examples are given here. 10.9472 g. of glucose was dissolved in 625 cc. of water, giving a solution containing 0.0175 g. per cc.

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[6] Leach, "Food Inspection and Analysis," John Wiley and Sons, 1st ed., **1905**, p. 486.

[7] Ref. 1b, p. 1505.

Expt.	"A" Cc.	Glucose Cc.	Ratio
1	10.02	8.56	1.171
2	11.11	9.54	1.165
3	10.01	8.56	1.169
			Av. 1.168
		Maximum variation from av.	0.26%

Using the dextrose value of the Fehling solution as above determined, the percentage of reducing sugar in the sample may be readily calculated, giving for Expt. 3 above, 67.09% of dextrose.

Since this method depends upon the complete precipitation of the copper as cuprous oxide, it seemed advisable to check these results gravimetrically. This was done by filtering on a Gooch crucible the precipitate from Expt. 3, drying and weighing it. The weight of the cuprous oxide thus found was 0.1969 g. Since the amount of cuprous oxide theoretically obtainable from 10.01 cc. of Fehling solution containing 0.01745 g. of copper per cc. is 0.1966 g., the difference between the two weights, 0.3 mg., shows that the end-point had been determined in a satisfactory manner.

Summary

A rapid method has been described for the volumetric determination of reducing sugars by means of Fehling solution, using the electrometric method for ascertaining the end-point. The uncertain personal element in determining the end-point is thus eliminated.

The method, as checked gravimetrically, is found to be accurate.

No work has yet been done on the determination of very small amounts of reducing sugars, or upon the effect of the presence of large quantities of other sugars such as sucrose.

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THE REACTION OF NITROSYL CHLORIDE ON TOLUENE

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Some time ago one of us found[1] that nitrosyl chloride will readily react with normal heptane in the sunlight to produce a blue material which easily changes to a colorless oil. The blue compound was later shown[2] to be nitroso-dipropylmethane and the rearranged oil, dipropyl-ketone oxime. It was also demonstrated that this reaction is probably general for all of the paraffin hydrocarbons, a conclusion reached mainly because

[1] Lynn, This Journal, **41**, 368 (1919).

[2] Lynn and Hilton, *ibid.*, **44**, 646 (1922).