LXXXIX.—*Estimation of Furfuraldehyde.*

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THE most reliable method for estimating this aldehyde is that of Flint and Tollens (*Landw. Versuchs-Station*, 1893, 42, 381), which is based on the production and gravimetric estimation of the phenylhydrazone. Their method, however, involves the use of a factor, which must be determined for the special conditions under which the estimation is carried out, as it varies with the concentration of the solution, amount of substance, &c. Further, since the phenylhydrazone cannot be heated above 60°, the time required to dry it to constant weight may amount to from one to three days, according to the means and apparatus available. The following method dispenses with the use of a factor, and can be carried out in half an hour with a much

smaller quantity of substance than is necessary for the successful application of the phenylhydrazone process.

The method is based on the oxidation of furfuraldehyde to pyromucic acid by means of an ammoniacal solution of silver oxide, the reaction being represented by the equation

Under the conditions given, this reaction takes place quantitatively, so that the estimation of furfuraldehyde may be reduced to the volumetric estimation of silver.

A solution of ammoniacal silver oxide is prepared by precipitating a known weight of silver nitrate by means of caustic soda solution, thoroughly washing the silver oxide with water, and dissolving it in the minimum quantity of ammonia solution. The solution is then diluted to decinormal strength and standardised according to Volhard's method by means of decinormal ammonium thiocyanate.

The following results were obtained with a solution of pure furfuraldehyde which contained 2.50 grams of furfural in the litre. In each case, 10 c.c. of the furfuraldehyde solution containing 0.0250 gram of furfuraldehyde were added to 10 c.c. of the silver solution, and the mixture warmed at 25° for the times given in the subjoined table. The precipitated silver was then removed by filtration through asbestos, the filtrate acidified with nitric acid, and titrated with decinormal ammonium thiocyanate solution :

Time of heating.	AmSCN required.	Ag ₂ O reduced.	Furfuraldehyde found.
13 min.	5.0 c.c.	5.0 c.c.	0.0240 gram.
19	4.9	5.1	0.0245
26	4.8	5.2	0.0250
32	4.8	5.2	0.0250
39	4.8	5.2	0.0250
45	4.8	5.2	0.0250

From this table, it is apparent that after the furfuraldehyde has been oxidised there is no further action on the silver solution, so that the time of heating is immaterial so long as it is sufficient to permit complete oxidation. At 25°, half an hour is necessary, but at 70° only a few minutes are required.

The filtrate from the precipitated silver gave, on acidification and treatment with ether, an ethereal extract, which, after evaporation of the ether, left a crystalline residue possessing the melting point and other properties of pyromucic acid.

An ammoniacal solution of silver nitrate, such as was employed by Henderson in the estimation of sugars (Trans., 1896, 69, 145), cannot

be substituted for the ammoniacal solution of silver oxide in the estimation of furfuraldehyde.

Application of the Method to Furfuraldehyde Solutions obtained from Textile Fibres, Sugars, &c.—The vegetable substance is distilled with 10 per cent. hydrochloric acid until furfuraldehyde no longer passes over in the distillate (Flint and Tollens, *loc. cit.*; Cross and Bevan, *Cellulose*, p. 99). The volume of the distillate is measured, and the whole, or a known fraction of it, neutralised with solid sodium carbonate. A small quantity of oxalic acid is then added, and the solution distilled with steam. The distilling flask must be provided with a trap bulb, otherwise chlorides pass over into the distillate. The distillation is continued until a drop of the distillate no longer gives a red coloration with a solution of aniline acetate. Excess of ammoniacal silver solution is now added to the distillate, and the mixture heated to 60—70°. The form in which the reduced silver separates varies according to the strength of the furfuraldehyde solution. A mirror is frequently formed on the walls of the containing vessel, but occasionally the silver remains suspended in the colloidal condition, and cannot be filtered off. In such a case, it is necessary to cool the reduced solution and then add a few c.c. of 25 per cent. solution of caustic potash to induce coagulation. The caustic potash used must of course be free from chlorides. The silver is then filtered off and the filtrate acidified and titrated with ammonium thiocyanate as before.

The following results were obtained by this method:

A sample of jute (distilled under special conditions so as to obtain the maximum yield of furfuraldehyde) yielded 500 c.c. of distillate. Of this distillate, 400 c.c. were treated by the phenylhydrazine method of Flint and Tollens, and 100 c.c. by the silver method as above described.

Phenylhydrazine method ...furfuraldehyde = 10·9 per cent.

Silver method..... „ = 10·7 „

By the phenylhydrazine method, Smith (*Trans.*, 1894, 65, 479) found the percentage of furfuraldehyde from oat-straw cellulose to be 14·5. Two samples treated by the silver method gave respectively 14·4 and 14·8 per cent.

The silver method, then, with pure solutions of furfuraldehyde gives accurate results, and also results for celluloses, &c., which are comparable with those obtained by the phenylhydrazine method. The advantages it possesses over this method are that a much smaller quantity of material need be used for the estimation, and that the time required in the actual determination of furfuraldehyde in a hydrochloric acid distillate is reduced from a day to half an hour.