LIII. A METHOD OF ESTIMATING PHENYLHYDRAZINE VOLUMETRICALLY AND ITS APPLICATION TO THE ESTIMATION OF PENTOSANS AND PENTOSE.

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THE well-known method of estimating furfural by precipitating it as phenylhydrazone and weighing the latter, first suggested by G. de Chalmot and B. Tollens [1891], has the disadvantage that the phenylhydrazone is difficult to dry, principally owing to the fact that its melting point is below 100°. The alternative method of Kröber [1901] in which the furfural is precipitated and weighed as phloroglucide, leaves little or nothing to be desired on the score of accuracy, but it requires considerable time and attention, in addition to which phloroglucinol is an expensive substance. Flohil [1910] devised a method in which the reducing power of furfural towards Fehling's solution is made use of as a quantitative method. This method however even after the modifications suggested by Eynon and Lane [1912], and by Baker and Hulton [1916] is less accurate than the phloroglucide method.

Now since the sole difficulty of the phenylhydrazone method is that of drying the hydrazone, we sought to remove this difficulty by attempting to estimate the excess of phenylhydrazine, required to precipitate the hydrazone, volumetrically.

A method of estimating phenylhydrazine volumetrically has recently been suggested by Menaul and Dowell [1919]. These workers refer to the work of Ebler [1905], who found that the oxidation of hydrazine salts by cuprammonium salts proceeds in accordance with the equation

Ebler suggests that on these principles a method of estimating copper or hydrazine may be based. Adan [1907] has shown that the reaction of phenylhydrazine with copper sulphate proceeds as follows:

He found however that the reaction is accompanied by others in presence of Cl-ions owing to the formation of *p*-chlorophenylhydrazine and a diazo-compound.

Menaul and Dowell describe a gasometric method of estimating pentosans and pentoses. The method consists in distilling the substance with dilute

sulphuric acid, precipitating with phenylhydrazine acetate in presence of sodium sulphate (instead of sodium chloride) to diminish the solubility of the hydrazone, adding a 10 % solution of ammoniacal copper sulphate, and collecting and measuring the liberated nitrogen. This method has been adopted by the U.S. Department of Agriculture (see *Bull.* 49), it being there recommended however to precipitate the hydrazone in presence of sodium chloride.

It occurred to us that it might be more convenient instead of the gasometric method of estimating phenylhydrazine, to employ a titration method, and accordingly attempts were made to elaborate an iodometric method.

The reaction between iodine and phenylhydrazine was first studied by Emil Fischer [1877] who showed that it occurred in accordance with the following equation:

the products being hydriodic acid, aniline, and diazobenzene-imide. E. von Meyer [1887] showed that the reaction discovered by Fischer only occurs in presence of an excess of phenylhydrazine. When excess of iodine (at least four equivalents to one molecule of phenylhydrazine) is present, the reaction proceeds in accordance with the equation

Our method for the estimation of pentoses or pentosans based on this reaction is carried out in the usual way so far as the distillation with acid is concerned.

In view of Menaul and Dowell's observation [1919], we carried out some experiments with sulphuric acid using a concentration of that acid equivalent to 12 % hydrochloric acid on the assumption that the ionisation of the sulphuric acid was 70 % of that of the hydrochloric acid. After eight hours' distillation however only 85 % of the possible furfural was obtained. It was therefore decided to use hydrochloric acid, and we found that the presence of sodium chloride and free acetic acid in no way affects the method.

After the accuracy of the method as compared with the phloroglucinol method had been established with solutions of furfural, it was applied to arabinose. A known weight of the pure sugar is distilled with 12 % hydrochloric acid in the usual manner until the distillate ceases to give the furfural reaction with aniline acetate paper. The distillation flask is heated in a sulphuric acid bath instead of by a direct flame, and the total distillate is made up to 250 cc. Of this 25 cc. is transferred to a 100 cc. flask, a drop of methyl orange solution added and the hydrochloric acid neutralised with 3*N* sodium hydroxide, care being taken during the neutralisation to avoid any rise of temperature. The solution is then acidified slightly with acetic acid, and 10 cc. of a standard aqueous solution of phenylhydrazine (approximately 2 %) added. The liquid is kept in a water bath at 50–55° for about twenty minutes when the precipitation of the hydrazone is complete. During

the precipitation the flask is closed with a cork, and the surface of the liquid reduced to a minimum by making it up with water to the neck of the flask. These precautions are taken in order to avoid oxidation of the phenylhydrazine by atmospheric oxygen. The solution is then cooled, its volume made up to 100 cc., and it is filtered through a hardened filter paper. The excess of phenylhydrazine is then determined in an aliquot portion of the filtrate. Into a flask is measured 10 cc. of $N/10$ iodine solution¹ and to it is added 10 cc. of the filtrate from the hydrazone. The liquid is then diluted with water to about 100 cc. and the excess of iodine is titrated with $N/20$ sodium thiosulphate, the volume in cc. being denoted by the symbol Y .

The titre of the original phenylhydrazine solution employed for the precipitation is ascertained in an exactly similar manner, and the number of cc. of $N/20$ sodium thiosulphate solution required is denoted by the symbol X . The number of cc. $N/20$ sodium thiosulphate equivalent to the furfural is $X - Y$.

The following are some results obtained with a sample of arabinose. It is seen that the results obtained by the new method agree closely with those obtained by the phloroglucinol method.

Weight of arabinose taken. g.	Weight of arabinose found by the phloroglucinol method. g.	Weight of arabinose found by the iodometric method. g.
0.250	0.248	0.250
0.250	0.249	0.250
0.232	—	0.2328

Some experiments were also carried out on the extract obtained by hydrolysing some Indian grasses with dilute sulphuric acid.

Extracts	Weight of pentoses found by the phloroglucinol method. g.	Weight of pentoses found by the iodometric method. g.
A	0.208	0.2095
B	0.152	0.1510
C	—	0.1860

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¹ The iodine solution we employed was 0.096 N .