QUICK ESTIMATION OF STARCH.

By P. L. Hibbard.

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THE accurate estimation of starch in presence of crude cellulose or similar substances containing other carbohydrates soluble in hot water or boiling dilute acids, has not yet been accomplished. Lintner's process of heating in closed vessels under high pressure, with water or a weak acid, like tartaric, *e. g.*, is good when soluble convertible carbohydrates other than starch are absent. Märcker's process of dissolving the starch out of the fiber by means of diastase is also fairly satisfactory. But both methods will bring into solution more or less of the various gums, etc., which are nearly always present in starch-bearing material. Entirely to avoid solution of these bodies is, so far, impossible; but it is certain that the less the material is heated with water, or especially with acid, the less will they be dissolved. Perhaps the best method published is Märcker's. The substance is boiled with water a few minutes to gelatinize starch, then cooled to 60° C., some diastase added, and the whole heated on the water-bath at 65° C. for one hour, to hydrolyze the starch. The solution is then filtered from the insoluble residue and converted by hydrochloric acid to dextrose, which is then determined by Fehling's solution. All the directions that I have seen, say the mixture must be heated with diastase for one hour, and then it must be heated two or three hours on a water-bath, with a reflux condenser. A modification of this method consists in heating the substance under pressure of three atmospheres, with lactic or tartaric acid, after the first treatment with diastase. The acid is then neutralized and the whole again warmed with diastase. The conversion to dextrose is as before stated. These methods are somewhat long and tedious, besides being liable to bring into solution other bodies than starch, which, by the subsequent process, will reduce Fehling solution.

Whole corn, soaked a few minutes, was stripped of its hulls. These hulls were carefully examined to see that they were free from starch and were not colored by solution of iodine. After boiling them a few minutes with water, the solution was filtered off and heated with acid a short time. It then reduced Fehling solution somewhat. This experiment shows that mere boiling with water brought into solution some body, which was converted by acid into a reducing sugar.

Having occasion to estimate starch in residues containing much of other soluble carbohydrates, I have modified the method using diastase, so that it is much shorter and easier, as well as fairly accurate. The method is satisfactory for factory work, where great accuracy is not so necessary as speed; and slightly modified is the most accurate method known.

Instead of taking trouble to prepare diastase by precipitating and washing with alcohol, I make a water extract of malt, which answers well. The coarsely pulverized dry malt is covered with water containing fifteen to twenty per cent. of alcohol. After a few hours the infusion is filtered off and is ready for use. The sugar in this must be determined by treating with acid as described below, in order to make the correction due to it when used to dissolve starch. The alcohol to some extent prevents action of the diastase on the starch of the malt, but is chiefly useful to preserve the malt extract, which would ferment very soon if some antiseptic were not present. Twenty per cent. of alcohol will preserve it for two weeks, even in very warm weather. I have found no effective preservative, except alcohol, that does not destroy the diastatic power of the malt extract.

The substance in which starch is to be determined should be finely pulverized, in order that the starch may be easily extracted without long boiling. Enough of the material to contain at least half a gram of starch is placed in a flask with about fifty cc. of water and one or two cc. of malt extract added. The mixture is at once heated to boiling, with frequent shaking to prevent formation of clots of starch. The addition of diastase before gelatinizing the starch, helps to prevent formation of insoluble clots, as it acts above the temperature at which starch becomes pasty. But if the material contains little starch in presence of much fibrous material, there is no particular gain in adding malt before heating to boiling, as most of the diastase is destroyed by the high temperature, before it has time to act on the starch. After boiling a minute the mixture is cooled to 50°-60° C., and two to three cc. malt extract added. Then it is heated slowly from ten to fifteen minutes till boiling, again partially cooled, and tested with iodine solution. If there is blue, the treatment with malt must be repeated. When all the starch is changed, the mixture is cooled, made up to definite volume, and filtered. I have found fine muslin or linen a very satisfactory filter for this purpose. Though it does not at first filter quite so clear as paper, it is more rapid, not being so easily clogged when the substance is albuminous. The cloth retains all the fibrous material, which might give rise to sugar in the subsequent treatment with acid. An aliquot part of the filtrate, sufficient to contain two or three-tenths of a gram of starch, is placed in a 100 cc. flask with five cc. HCl containing thirty per cent. of acid gas, and water to make about sixty cc. total. This is boiled moderately thirty minutes actual boiling, on a sand-bath. This gives complete conversion. I use a sand-bath and no condenser, as the amount evaporated from a narrow-necked flask in this time is not enough to make much difference. If a water-bath is used longer time is required. The solution is now cooled, nearly neutralized with sodium hydroxide, and the dextrose determined by Fehling solution. With pure starch the solutions obtained are almost colorless, but if the substance contains much albuminoid matter, which will be destroyed by the acid, the solution will be brownish. There is no apparent destruction of sugar in this length of time.

The action of various acids on starch has been investigated by F. Salomon, (*J. prakt. Chem.*, **28**, 82,) and it is concluded that hydrochloric is the best acid to use in the hydrolysis of starch. Less than an hour of moderate boiling with the strength of acid above given is sufficient to convert starch directly without previous solution with diastase. Much longer heating destroys sugar and the solution becomes brown.

The residue left after treatment of a good quality of starch by this method is little, but some of it is soluble in dilute acid, so that direct conversion with acid gives a little higher figures, but it seems probable that this is largely due to other bodies than starch. I have made many experiments to determine the proper time and best strength of solutions, and find the above given most satisfactory.

This method is simple, rapid, and fairly accurate. A determination of starch may be easily finished in less than two hours. Particular points are: prevention of insoluble clots by addition of malt before heating; the rapid heating prevents any lactic fermentation which may occur in the use of the older published methods; and the little boiling occasions a minimum solution of bodies other than starch, which could form reducing sugars. With nearly pure starch there is no occasion for use of this method. The process is valuable chiefly for estimating starch in presence of much other material which may give rise to reducing sugars by the action of acid, *e. g.*, fodders, cattle foods, and residues from starch manufacture. A sample of corn hulls, free from starch, gave only a trace of sugar by this method, but direct conversion with acid showed forty per cent. of reducing sugar.

The appended figures show the errors due to the acid method, and afford a comparison of the two:

		PER CENT. STARCH.	
Material.	Moisture in sample.	Malt method.	Acid direct.
Starch factory feed	10.0	10.0	40.9
Impure moist starch	12.0	81.3	82.3
Impure moist starch	...	79.5	80.9
Good starch	12.8	84.3	84.6
Purified dried starch	...	95.1	96.5
Corn, large white kernels	11.0	63.5	68.2
Wheat, hard red variety	10.0	60.5	65.0
Bran from same wheat	11.3	28.4	44.4
Middlings from same wheat	10.1	53.8	60.0
Low flour from same wheat	10.2	66.0	67.7
Good flour from same wheat	11.0	67.9	69.0
Wheat flour	10.0	70.7	73.6
Wheat bran	10.1	29.3	46.5

The method may be further improved and each chemist's needs will indicate to him useful modifications. Others may make it more perfect, and to them I commend it as the most promising method for determination of starch.

Most of the careful analytical work in the investigation of the method was done in the laboratory of the University of Nebraska, for the use of which I am indebted to the kindness of Professor H. H. Nicholson.

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ALKALI AND SULPHUROUS ACID PROCESSES USED IN THE MANUFACTURE OF STARCH FROM CORN.

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STARCH is produced from corn at the present time by two processes, known as the alkali and sulphurous acid. I am not aware, at this moment, of the existence of any published article showing the working of these processes, and I take pleasure in presenting two outlines, showing clearly, and at a glance, their essential points.

Alkali Process.—