

Determination of Furfural

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IN STUDYING methods and procedures for the preparation of hemicellulose from plant material many obstacles are encountered. One difficulty is the possible loss of hemicellulose as the steps in the preparation are carried out. A means of determining any change in the hemicellulose content would aid considerably, as the procedure could be modified to prevent this loss. With certain types of material, furfural may be determined at the various stages of extraction and purification to indicate whether there is a change in the hemicellulose content. With this in mind methods for determining furfural were examined, seeking an accurate and rapid method which is easily manipulated.

The method of Tollens and Kröber for the determination of furfural (6) is the one most commonly used. The pentoses, pentosans, etc., are converted into furfural by distillation with 12 per cent hydrochloric acid solution according to a standard procedure. After precipitation with phloroglucinol the weight of furfural, pentose, or pentosan corresponding to a given weight of phloroglucide may be obtained by reference to Kröber's tables.

Pentoses do not usually yield the theoretical quantity of furfural upon distillation with acids. Xylose gives about 90 per cent and arabinose about 75 per cent of theoretical. This has been explained as being due to a partial destruction of furfural. Pervier and Gortner (3) and Youngburg (7) suggested distilling in a current of steam to lessen the opportunity for decomposition. Others (Iddles and Robbins, 2) found that passing steam into the solution during distillation gave little or no increase in furfural.

Instead of distilling pentoses or pentosans in the presence of hydrochloric acid, Youngburg (7) used phosphoric acid. The distillation was carried out in a stream of steam and the temperature in the flask was allowed to rise to 175° C. Good results were claimed when pure xylose or arabinose were distilled, but only approximations are obtained in the case of various complex materials yielding furfural.

Pervier and Gortner (3) found that furfural can be determined in acid solution by oxidation with bromate salts in the presence of bromides, determining the end point electrometrically. They also found that the Tollens-Kröber precipitation method was in considerable error when applied to dilute solutions of furfural. Powell and Whittaker (4) improved the method of determining the end point by using an excess of bromate, adding potassium iodide, and titrating back with thiosulfate. Each milliliter of 0.1 N bromate used is equivalent to 0.0024 gram of furfural. Hughes and Acree (1) carried out the reaction at 0° C. This procedure held the absorption to 1 mole of bromine per mole of furfural, and thus eliminated the error involved in the slow absorption of the second mole of bromine. Each milliliter of 0.1 N bromate used is equivalent to 0.0048 gram of furfural.

For the colorimetric estimation of furfural in the distillate such color reagents as benzidine, xylidine salts, and aniline salts have been used. Stillings and Browning (5) developed a method in which the furfural is allowed to react with aniline acetate in acetic acid solution and the intensity of color produced is measured photocalorimetrically.

Experimental

Since it was desired to select a suitable method for determining furfural in plant material, some of the available methods were compared. As the Tollens and Kröber method has been shown to be in considerable error, particularly when applied to low concentrations of furfural, attention was turned to a volumetric or colorimetric procedure.

A study of the colorimetric method of Stillings and Browning (5) showed that fairly consistent results are obtained when the temperature, concentration of reagents, and freedom from

light are carefully controlled. However, the method could be improved by reducing the time required for maximum color to develop and by stabilizing the color. With this in mind a number of substances were added to the furfural solutions prior to the addition of the color reagent. It was found that small amounts of a mixture of oxalic acid and disodium phosphate increased the rate of color development. In these trials 0.075 mg. of furfural, 25 ml. of glacial acetic acid containing 2.5 ml. of aniline, and varying amounts of the other reagents were used. The final volume was 50 ml. and the relative color intensities of the solutions were determined by means of a Kuder photoelectric colorimeter.

TABLE I. EFFECT OF OXALIC ACID AND DISODIUM PHOSPHATE ON COLOR OF FURFURAL SOLUTIONS

Sample No.	Treatment Grams		Kuder Readings ^a			
			30 min.	45 min.	1 hour	1.25 hours
1	1.0	NaCl	47.5	48.4	48.5	47.5
2	0.50	Na ₂ HPO ₄	48.7	48.8	47.5	46.0
3	0.25	Na ₂ HPO ₄	48.2	48.1	46.8	44.9
4	0.12	Na ₂ HPO ₄	48.4	48.2	46.8	44.6
5	{ 0.5 0.12	Na ₂ HPO ₄ Oxalic acid	49.1	50.2	50.1	49.4
6	0.25	Na ₂ HPO ₄	49.2	50.2	50.2	49.5
7	0.12	Na ₂ HPO ₄	48.5	50.2	50.1	49.8
8	{ 0.50 0.12 0.25	NaCl Oxalic acid Na ₂ HPO ₄	Cloudy			
9	0.12	Oxalic acid	48.9	50.0	50.7	50.2

^a All values represent means of from 2 to 4 determinations. Kuder readings are directly proportional to color intensity of solutions.

The results given in Table I show that the addition of 0.12 to 0.50 gram of disodium phosphate to the color reagents increases the rate of color development, but did not improve the stability of the color. The addition of a mixture of 0.12 gram of oxalic acid and 0.12 to 0.50 gram of disodium phosphate increased the intensity of color as compared to the sodium chloride treatment, and the solutions were more stable than those containing disodium phosphate alone. The addition of 0.25 gram of sodium chloride to this mixture had little or no effect on the color. A mixture of oxalic acid and sodium chloride gave a cloudy solution after standing 30 to 45 minutes.

Twelve per cent hydrochloric acid is commonly employed in the distillation of pentoses, pentosans, etc., for the separation of furfural. Since Youngburg recommended phosphoric acid, it was decided to compare phosphoric and different concentrations of hydrochloric acid.

A xylose solution containing 0.25 gram of xylose per 25 ml. was used, and 25-ml. aliquots were placed in 500-ml. two-necked, round-bottomed flasks. Samples of arabinose, sweet clover, alfalfa, and crude hemicellulose were also distilled. Acids to give the following concentrations were added to the flasks: phosphoric acid, 57 per cent; hydrochloric acid, 12, 18.5, and 24 per cent. A steam inlet tube, which extended almost to the bottom of the flask, was placed through one opening, and the flask was connected through the other opening to a condenser by means of an adapter, provided with thermometer. All connections were interchangeable ground-glass joints. A steady stream of steam was passed into the flask, under which a small flame was placed. A vigorous boil was maintained throughout the distillation. The distillate was collected in 1-liter

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TABLE II. DETERMINATION OF FURFURAL BY DISTILLING IN THE PRESENCE OF PHOSPHORIC AND HYDROCHLORIC ACIDS

Sample Material	Wt. of Sample Gram	Acid Used H ₃ PO ₄ %	HCl %	Temp. of Distn. °C.	Time of Distn. Hours	Furfural Found By titration %	Furfural Found Colorimetrically %
Xylose	0.25	57	..	98-105	3	57.4, 57.4, 57.7	49.5, 49.5, 51.1
l-Arabinose	0.25	57	..	110-12	2	55.3, 54.7	50.2, 51.0
Sweet clover	0.25	57	..	110-12	1	44.4, 44.1, 44.7	37.0, 36.3, 36.9
Alfalfa	0.20	57	..	110-12	1	8.2, 8.2	5.1, 5.1
Xylose	0.25	..	12	102-3	1	9.3, 9.1	6.1, 6.1
	0.25	..	18.5	105	2.5	60.6, 60.8	55.1, 55.8, 54.9
	0.25	..	24	105	2.5	60.8, 60.2	55.9, 54.8
Sweet clover	1.00	..	18.5	105	2.5	9.3, 9.0	6.0, 6.0, 5.9
Crude hemicellulose	0.10	..	18.5	105	2	33.2, 32.2	29.2, 29.2
Xylose	0.25	..	12	102-3	2	53.1	44.4
	0.25	..	12	102-3	3.5	58.0	51.1
	0.25	..	12	102-3	4.5	59.7	53.6
	0.25	..	12	102-3	6	60.8	54.9

volumetric flasks. The distillation is complete when several drops of the distillate placed in a test tube fail to give a color in 10 minutes when an equal volume of glacial acetic acid, containing 2.5 ml. of aniline per 25 ml., is added. The pH of the distillates was in the range of 3 to 5 and never failed to give a color test when furfural was present.

The furfural in the distillates was determined by both the titration procedure of Hughes and Acree (1) and the modified colorimetric method.

The results given in Table II show that higher furfural values were obtained when the distillations were carried out in the presence of hydrochloric acid as compared to phosphoric acid. Approximately equal values were obtained with 12, 18.5, and 24 per cent hydrochloric acid; however, 12 per cent hydrochloric acid required at least twice as long for the complete removal of furfural from the sample. The 18.5 and 24 per cent concentrations required about an equal length of time.

The titration procedure gave consistently higher values than the colorimetric procedure, but the reason for this was not clear. In an attempt to clarify this point it was decided to compare the results obtained by titration and colorimetrically when other sugars were distilled with 18.5 per cent hydrochloric acid. In addition, samples of xylose were reinforced with certain aldehydes and other compounds and distilled, and pure furfural was determined colorimetrically and by titration.

TABLE III. TITRATION AND COLORIMETRIC VALUES

[Distillates from rhamnose (methylpentose), levulose (hydroxymethylpentose), xylose, and xylose reinforced with 0.20 gram of aldehydes, etc.]

Substance Distilled	Wt. of Sample Gram	Results Calculated as Furfural	
		By titration %	Colorimetrically %
Rhamnose	0.17	29.6	0
Levulose	0.25	5.3	0
Xylose	0.25	58.3	55.6
Xylose + benzaldehyde	0.25	56.6	55.2
Xylose + vanillin	0.25	109.3	55.7
Xylose + quercitin	0.25	56.6	54.7
Xylose + salicylaldehyde	0.25	204.9	55.2
Furfural	1.000	98.7	98.7

Table III shows that methylpentose and hydroxymethylpentose gave a titration value but did not produce a color with the furfural color reagents. When xylose was reinforced with certain aldehydes the distillates gave higher titration values than xylose alone. The colorimetric procedure gave no higher values. Quercitin and benzaldehyde had no apparent effect on either the colorimetric or the titration procedure. Pure furfural gave almost theoretical values when titrated or measured colorimetrically. Samples of pure furfural (not shown) gave approximately 100 per cent recovery by steam-distillation. These results indicate that the colorimetric

method is more accurate for the determination of furfural. Since plant materials probably produce certain reducing substances on distillation with acids, these might interfere with the bromate titration method, as pointed out by other investigators.

To obtain evidence as to the effect of substances distilled from alfalfa and sweet clover on the colorimetric method, spectrophotometric curves of the color produced from the distillates of alfalfa and sweet clover were compared with similar curves plotted from pure furfural color solutions of equal concentration. Within experimental error all the curves were similar, which indicated that no appreciable interfering substances were present in the alfalfa or sweet clover distillates.

Procedure

A sample of pentose, pentosan, or plant material having a furfural content between 1 and 15 mg. is placed in a 500-ml. two-necked round-bottomed flask. Hydrochloric acid and water in sufficient amount to give between 200 and 225 ml. of about 18.5 per cent hydrochloric acid (approximately 1 to 1 by volume) is added to the sample. A steam tube extending almost to the bottom of the flask is inserted through one opening, and the flask is connected to a condenser through an adapter containing a thermometer. A steady stream of steam is passed into the solution and a flame is placed under the flask. When the contents of the flask begin to boil vigorously the flame is adjusted to hold the temperature between 105° and 106° C., measured at the opening into the condenser. The distillate is allowed to pass through a small filter, as it comes from the condenser, and then into a 1-liter volumetric flask. If the liquid in the distilling flask is reduced to approximately 75 ml., the steam inlet tube is removed and hydrochloric acid (1 + 1) is added to bring the volume back to 200 to 225 ml. The distillation is usually complete in 2 or 2.5 hours. This is determined when a few drops of the distillate fail to give a color in 10 minutes with an equal volume of glacial acetic acid containing 2.5 ml. of aniline per 25 ml. of acid.

The solution is diluted to the mark, and mixed, and 10-ml. aliquots are pipetted into 50-ml. volumetric flasks. The solutions are made just alkaline to phenolphthalein with sodium hydroxide, and 5 ml. of a solution containing approximately 0.12 gram of oxalic acid and 0.25 gram of disodium phosphate per 5 ml. are added. The solution is diluted to approximately 25 ml. with distilled water and 25 ml. of glacial acetic acid containing 2.5 ml. of freshly distilled aniline are added. The acetic acid and aniline should be mixed and allowed to come to room temperature just before using. It is then diluted to the 50-ml. mark, mixed, placed in a water bath at 20° C., and covered so that almost all the light is excluded. After 45 minutes to 1 hour it is read in a photoelectric colorimeter. The concentration of furfural corresponding to a given colorimeter reading is obtained by reference to a calibration curve made by plotting a series of known furfural solutions against colorimeter readings. If a photoelectric colorimeter is not available, the unknown solution may be compared to known standards in any type of colorimeter in general use.

Summary and Conclusions

The steam-distillation of pentoses and plant material with hydrochloric acid resulted in higher yields of furfural than steam-distillation with phosphoric acid. The use of 12 per cent hydrochloric acid required at least twice as long as 18.5 or 24 per cent hydrochloric acid to remove all the furfural. The yield of furfural from xylose was approximately the same when the three concentrations were used.

In the application of the aniline acetate colorimetric method, the addition of small amounts of oxalic acid and di-

sodium phosphate to the color reagents resulted in increased color intensity and shortened slightly the time required for maximum color to develop. The colorimetric method was not affected by methyl furfural or hydroxymethyl furfural. The distillates from alfalfa or sweet clover produced colored solutions very similar to that produced with pure furfural, as shown by spectrophotometric curves. The titration method of Hughes and Acree (1) gave consistently higher results than the colorimetric method when applied to the distillates from pure sugars, alfalfa, or sweet clover. This may be due to the presence of reducing substances other than furfural in the distillates. For these reasons it is thought that the colorimetric method may be more accurate.

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Determination of Total Sulfur in Rubber and Rubberlike Materials

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A modification is presented of the oxidation procedure employed in the standard method for the determination of total sulfur in rubber and similar materials. The method is especially valuable for the analysis of vulcanized synthetic rubberlike materials. It is likewise applicable to a wide variety of sulfur-containing organic compounds.

THE determination of total or combined sulfur in vulcanized rubber and materials of similar type involves numerous difficulties. This fact is attested by the very large number of methods which have been proposed (3).

The most important methods all involve oxidation of the sulfur, in whatever form it may be present, to sulfate and weighing the latter as barium sulfate. The only essential differences lie in the methods of oxidation employed.

The methods which seem to be the most popular at the present time are (a) oxidation of the sample in a Parr bomb with sodium peroxide, potassium chlorate, and sugar (5, 6, 8, 9); (b) oxidation with perchloric acid and nitric acid (12), sometimes with the additional use of bromine (4); (c) oxidation with nitric acid and bromine, followed by sodium carbonate-potassium nitrate fusion (1, 2, 11); and (d) oxidation with nitric acid-zinc oxide mixture, bromine, and potassium chloride (1, 2, 7).

Serious explosions have been known to occur with perchloric acid oxidations; hence this method is not so popular at present as the other three. The fusion methods are reliable, but they are time-consuming and therefore not convenient when large numbers of samples must be handled.

Methods (c) and (d) have been for a number of years the preferred procedures of the A. S. T. M. For several years the fusion method was the "recommended" one and method (d), commonly referred to as the "Kratz-Flower" method, was listed as the "alternate" method (1). In 1940 (2) the order of listing was reversed, with the Kratz-Flower method becoming the recommended and, at least inferentially, the preferred procedure.

This procedure involves a preliminary oxidation with nitric acid and bromine, following which the mixture is slowly evaporated to a foamy sirup. Then, if organic matter or carbon remains at this point, a few milliliters of fuming nitric acid and a

few crystals of potassium chlorate are added and the solution is evaporated at a boil. The operation is repeated until all carbon is gone and the solution is clear, colorless, or light yellow. It is then evaporated and nitrates are decomposed by one of two alternate methods.

The analyst is cautioned to use care during the addition of potassium chlorate. This is a standard precaution, to be found in all analytical textbooks. That it is well founded is proved by the fact that explosions frequently occur when the addition is carried out in this manner.

An additional disadvantage of this standard procedure is the fact that the seemingly drastic conditions of oxidation are still not sufficient to effect the oxidation of many samples. Carbon black is oxidized in some samples, but not in others. Some of the synthetic rubbers prove especially troublesome, as the solution reaches a dark, nearly black color which is not destroyed by repeated treatment.

A somewhat unorthodox modification of the above procedure has been found to take care of these difficulties and to yield a clear, light-colored solution with considerably less trouble. The writer does not claim to have originated the method; in its present form it is an adaptation of a general procedure with which he came in contact a number of years ago and the exact origin of which is not known. In the meantime, the method has been extensively tested, in the hands of both experienced analysts and students who were completely unfamiliar with the procedure. A number of variables affecting the procedure have thus been studied in some detail, and the operating details as indicated here are believed to be general in their application.

Modified Method

In the standard method as modified, the nitric acid-bromine oxidation is carried out as usual. Then the resulting solution is evaporated slowly until no more nitrogen oxide or bromine fumes are visible, diluted with 10 to 15 ml. of concentrated nitric acid, and heated to boiling. To the vigorously boiling solution are added successively several 0.5-gram portions of potassium chlorate.

Contrary to what one might expect, no explosion occurs. This procedure has been employed in hundreds of analyses of