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A comparative study of the official method for determining furfural and pentosans and a colorimetric method

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A COMPARATIVE STUDY OF THE OFFICIAL METHOD FOR DETERMINING FURFURAL AND PENTOSANS AND A COLORIMETRIC METHOD

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INTRODUCTION

Of all the methods used for the quantitative determination of furfural that of its precipitation as furfural phloroglucid by means of phloroglucinol is still in vogue as manifested by its widespread application in pentosan work.

Whatever the merits and demerits of the method, it has, in the opinion of the "Association of Official Agricultural Chemists", fewer disadvantages than other procedures.

However, the loss of time in the formation of the phloroglucid precipitate and its subsequent filtration, drying and weighing; the indefinite nature of the phloroglucid and the empiricism of the calculation of the amount of furfural from the amount of phloroglucid, are all inherent difficulties and sources of error in the Official Method. On account of these facts the present investigation was undertaken with the purpose of finding another method free from the above mentioned difficulties and errors.

While essentially a study of methods for the determination of pentosans the investigation really involves only the determination of furfural, for it is assumed, for the time being, that the boiling of pentosans with dilute hydrochloric acid, according to the Official Method, quantitatively converts pentoses or pentosans into furfural.

After a careful review of the literature it was decided to limit the present study to the colorimetric determination of furfural as in general suggested by DeChalmot[1], referred to later in the review of literature.

REVIEW OF LITERATURE

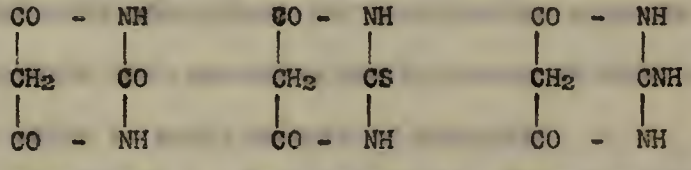
The earliest method used for the quantitative determination of furfural, yielded by pentoses and pentosans, was one suggested by Tollens and Stone[2]. It involved the distillation of furfural with 12 per cent hydrochloric acid (sp. gr. 1.06), and subsequent precipitation by means of ammonia as hydrofurfuralamide. The results obtained, however, did not warrant further use of the method, due to incomplete precipitation of the furfural.

Günther and Tollens[3] attempted to estimate furfural by titrating it with a standardized phenylhydrazine solution in acetic acid, using aniline acetate paper as indicator. Later Flint and Tollens[4] pointed out that this titration method was inaccurate on account of the levulinic acid arising from hexoses and the instability of standard phenylhydrazine acetate solution.

However, when furfural was precipitated by phenylhydrazine acetate solution as furfural hydrazine, there was laid the basis of a new gravimetric method which was declared by Tollens and DeChalmot to be the best of all phenylhydrazine methods. Favorable though the verdict, yet the defects were quite serious as it was found difficult to dry furfuralhydrazine properly, and the conversion factors had to be determined experimentally.

Kerp and Unger[5] precipitated furfural by means of semioxamizide as furfursemioxamazone which was found to be insoluble in ordinary solvents. The results obtained, however, were too low, hence the method was considered impracticable.

Conrad and Reinbach[6] found that furfural and barbituric acid condensed in the presence of dilute hydrochloric acid. Later, Unger and Jäger[7] applied this reaction to the quantitative determination of furfural. They found that six to eight times as much barbituric acid as the theory required was needed to give the calculated value for furfural. The product obtained, as the result of condensation, had the advantage of being only very slightly soluble in hydrochloric acid (1.22 mg. per 100 c.c.). The reaction consisted in the condensation of one molecule of furfural and one molecule of barbituric acid, through the aldehyde group of the former and the methylene group of the latter, with the splitting out of one molecule of water. Arthur W. Box and G. P. Plaisance[8] carried parallel determinations using barbituric acid (malonylurea), thiobarbituric acid (malonylthiourea) and malonylguanidine as precipitants for furfural. The three precipitants are analogous in many respects, as will be seen by a glance at the structural formulas:



Barbituric acid | Thio barbituric acid | Malonylguanidine

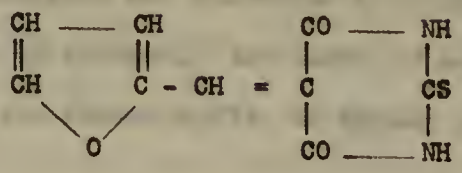
Their aim was to find out whether these compounds would all react with furfural in a similar manner, and possibly give a more complete

precipitation. They prepared a stock solution of pure, freshly distilled furfural of exactly one per cent strength, and 5 cc. aliquot portions were taken for each determination. The furfural was diluted with 12 per cent hydrochloric acid and solutions of the different precipitants in 12 per cent hydrochloric acid added. The total volume of the reaction mixture being 400 cc., conditions were similar to those obtained in pentosan determinations. The precipitate was allowed to stand over night, filtered on a Gooch crucible and dryed to constant weight at 100°. The results obtained showed plainly that with barbituric acid the per cent of furfural recovered was very low. It was further observed that with barbituric acid and furfural in molecular proportion of sixteen to one, the result was nearly quantitative thus confirming the view of Unger and Jäger, that eight times the theoretical amount of barbituric acid was necessary for complete recovery of the furfural. With thiobarbituric acid, the precipitation was quantitative without using a large excess of the reagent.

The condensation of furfural with malonylguanidine was not quantitative as results showed that only a trifle more than half the theoretical amount of furfural was recovered. Leaving molanylguanidine out as an undesirable precipitant for quantitative purposes the next problem was to ascertain the respective sensitiveness of barbituric and thiobarbituric acids to small amounts of furfural.

It was found that barbituric acid method was inapplicable to the determination of small amounts of furfural while thiobarbituric acid method gave quantitative results. With thiobarbituric acid and furfural

the condensation product was represented by the structural formula given below:



This was a brilliant lemon-yellow precipitate practically insoluble in cold dilute mineral acids, and in several ordinary solvents. The accuracy of determinations depended, however, on the absolute purity of thiobarbituric acid used, as impure samples of the same caused only a partial precipitation of furfural, only 90 to 95 per cent of the original amount being recovered.

J. T. Flohil[9] in 1911 described a method dealing with the estimation of pentoses and pentosans involving the use of Fehling's solution. Furfural yielded by the substance to be analyzed was distilled over with 12 per cent hydrochloric acid until 400 cc. of distillate was collected. Of this volume 50 cc. were withdrawn, neutralized with NaOH, and 20 cc. of Fehling's solution added. The total volume was made up with water to 100 cc. and then the liquid boiled under a reflux condenser for thirty-five minutes. The reduced cuprous oxide was determined gravimetrically or the unreduced cupric salt was titrated iodometrically. It was necessary, however, to carry out a blank determination containing the same amount of sodium chloride as the acid in the aliquot portion, from total distillate, would yield when neutralized with caustic soda. This step was deemed necessary because Fehling's solution tended

to undergo spontaneous reduction in presence of sodium chloride. Under these conditions Flohil found that 1 cc. of N/10 sodium thiosulphate solution was equivalent to 0.0063 gms. of copper or 0.0024 gms. of furfural. The weight of metallic copper multiplied by the factor 0.3775, he stated, would give the weight of furfural.

L. Eynon and J. H. Lane[10] made use of this method and studied carefully the action of furfural solution of different concentration upon Fehling's solution, also the effect of varying quantities of sodium chloride, resulting from the neutralization of hydrochloric acid with caustic soda, upon the amount of reduced copper oxide.

J. L. Baker and H. E. Holton[11] compared the values found by Eynon and Lane for the copper oxide equivalent of pure furfural, but did not agree with their figures for copper oxide yields from 20 cc. of Fehling's solution when heated with salt alone. The determination of this value was of prime importance and should be employed as a "blank" since, when the quantity of furfural present was small, a considerable percentage of total copper obtained was due to the action of sodium chloride on Fehling's solution. The two sets of values obtained by these investigators agreed pretty closely for lower quantities of salt, yet they diverged considerably when the amount of salt present was that usually obtained by the neutralization of the acid distillate, as will be seen from the comparison of different values given below:

	Salt (NaCl) in gms.											
	0	4	5	6	7	8	9	10	11	12	13	14
CuO in mgms.	6	9.3	10	10.6	11.3	11.7	12.2	12.7	13.3	13.8	14.2	14.8+
	9	10	10.5	11	12.5	14	16	20	20	20	21	22++

These estimations made by Eynon and Lane were obtained by diluting aqueous solutions of pure furfural to varying degrees, and then boiling them with Fehling's solution with various known amounts of salt. When the furfural solution was obtained by distilling a material with hydrochloric acid, the acidity of the distillate had to be estimated. This was done by taking a 10 cc. aliquot portion of the total distillate and neutralizing it with N/2 caustic soda, the usual percentage of acid found being between 8 and 12 per cent. From this relationship they calculated the amount of sodium chloride that would result after neutralization. The calculated amount represented the weight of salt to be taken for blank determination. The final reduction product of Fehling's solution, after filtering in a Gooch crucible and drying at 100°, was usually weighed as Cu_2O, but Eynon and Lane preferred to reduce it to copper while Baker and Hulton ignited the product in a current of air and weighed it as CuO, 3 mgms. of CuO representing approximately 1 mgm. of furfural.

Baker and Hulton were of the opinion that the method was capable of improvement and suggested that a larger volume of Fehling's solution be employed, in order that a considerably larger portion of

+ Eynon and Lane.
++ Baker and Hulton.

the total distillate may be treated with the reagent, thus increasing the weight of CuO obtained, and consequently decreasing possibility of error while proceeding otherwise.

Secondly, they suggested that the flask with its contents of furfural and Fehling's solution be immersed in a water bath and heated to boiling for the required length of time instead of using a burner to accomplish the same purpose. By so doing, they thought to reduce the weight of copper oxide obtained from salt and Fehling's solution alone (the "blank"). Their view was justified by the results which successive determinations gave as will be seen from the table given below:

	Mgs. CuO		
Gms. Salt	Eynon & Lane	Baker & Hulton	Water bath method
0	6	9	2
7	11.3	12.5	3
10	13	20	4

They claimed that water bath method was advantageous because of the reduction obtained in the "blank" correction.

Stenhouse obtained a dyestuff from aniline, aniline hydrochloride and furfural, of the composition $(C_6H_6N)_2.C_6H_4O.HCl.H_2O$. This dyestuff was always obtained provided above substances were present. But when an excess of mineral acid was unavoidable all the aniline was used in combining with the acid and the characteristic color failed to appear. Behavior of acetic acid, however, was found to be quite different for a red color immediately appeared as soon as

aniline and furfural were added to an alcoholic solution of acetic acid, provided the acid was concentrated enough. The reaction was very intense, and the pink color could be detected in very weak solutions of furfural.

DeChalmot[12] made use of this fact and determined furfural in solutions of different concentration. He treated 1 cc. of weak solution of furfural in 5 per cent acetic acid in a long tube with 1 cc. of a 1 per cent solution of aniline in 95 per cent alcohol. The tube was then sealed up, shaken, and placed in the dark. Another tube containing a solution of furfural (1 part in 10,000) was prepared in the same way, and the two compared after 20 minutes. If the colors did not match each other, he diluted the stronger until they matched. He calculated the amount of furfural present in solution as follows:

A. - If the solution of unknown strength be the stronger.

$$H = \frac{a + 2}{2} \times \frac{1}{10000}$$

B. - If the standard solution be the stronger.

$$H = \frac{2}{a + 2} \times \frac{1}{10000}$$

Where H = value sought, and a = number of cubic centimeters used.

Sensitive though the test was, yet he observed that the color reaction of furfural, if present 0.000008 gms. per cubic centimeter of solution, could not be detected.

R. A. Gortner and N. C. Pervier[13] in their quest for an improved method for the determination of furfural tried several volumetric procedures, of which potassium bromate method proved to be the most successful, and hence worthy of our consideration. From

preliminary tests, they concluded that sodium hypoiodite would yield enough free iodine to react with furfural quantitatively. But subsequent tests showed very plainly that the desired reaction was effected only in alkaline solutions, and that the amount of iodine taken up by furfural was in direct proportion to the alkalinity, while in strongly alkaline solutions satisfactory checks were difficult to obtain.

Acid permanganate was tried next only to be abandoned soon due to the reduction of large and indefinite quantities of permanganate to manganese dioxide by small amounts of furfural.

While attempts were being made to oxidize cystine, Okuda suggested the use of potassium bromate which later was proved to react with acidified potassium bromide solution in a manner shown in the following equation.

$$KBrO_3 + 5KBr + 6HCl \text{ ----- } 3Br_2 + 6KCl + 3H_2O$$

Wedekind (1901) was of the opinion that furfural in aqueous solutions, could both be oxidized and brominated. Thus incidentally he laid the basis of potassium bromate method that Gortner and Pervier later made use of. The method called for an indicator to mark the end point. To this effect Okuda suggested the yellow color of free bromine while in a preliminary test Gortner and Pervier found that a simplified electrometric apparatus would serve the purpose equally well if not more accurately. This apparatus consisted of a galvanometer, a tapping key, and two platinum wires, one of which was immersed in an acidified solution of potassium bromide containing a trace of bromine. The second wire was immersed in the solution to be titrated, a small electric stirrer keeping the

unknown solution thoroughly mixed. The potential of platinum wires depended upon the concentration of free bromine in the unknown solution, an excess causing a vigorous deflection of galvanometer needle in the opposite direction. If no diflection was observed, it was concluded that the bromine concentration in both solutions was identical and the end point reached.

The chemicals used in these determinations were of standard purity. An analysis of "chemically pure" potassium bromate gave 99.99 per cent $KBrO_3$ of which N/10 solution was used, while 20 per cent of pure, bromate free, potassium bromide solution was found to satisfy all requirements. The procedure was to measure 10 cc. volumes of furfural solution, then adding to each 10 cc. of 20 per cent potassium bromide solution followed by (after diluting to 100 cc.) the addition of various amounts of hydrochloric acid. In each case, titration with potassium bromate showed that the degree of oxidation of furfural was in direct proportion to the acidity of the solution. At low acidities (1.4 to 4.3 per cent hydrochloric acid) the reaction almost came to a stop, further action of bromine on furfural being effected only at an exceedingly slow rate. An accurate study of this point proved that best results could be obtained when the acidity was 4 per cent as at this concentration of hydrochloric acid, bromine was liberated promptly, thus shortening the time required for titration also.

The effect of potassium bromide concentration on results obtained was studied. This, however, did not seem to have any influence at all. Neither did the concentration of furfural have any effect on the ultimate results.

In order to get concordant results it was necessary, towards the end of the titration, to add the bromate solution very slowly and in small increments (0.25 cc.). This precaution was due to the fact that oxidation of furfural by bromine proceeded at a very low rate as the reaction approached completion.

The factor which was necessary to convert the volume of N/10 potassium bromate used to grams of furfural was obtained by dividing the weight of furfural taken by the total volume of the bromate solution used. The average experimental factor calculated was 0.004792, a figure closely approaching the theoretical factor (0.004803), which in its turn was obtained from molecular ratio of potassium bromate to furfural of 1 : 3.

The phloroglucinol method is the one most generally used at present for quantitative estimations of furfural. Phloroglucinol was first applied by Wheeler and Tollens (1889) as a color test, but credit goes to Councler[14], who adapted the test for gravimetric estimations thus originating the present method. Defects, however, were not wanting and the whole system needed amplification, and what was more important, perfection. Kröber[15] improved the whole pentose procedure and by actual experiments calculated factors and tables for the conversion of various weights of phloroglucinol precipitates into the corresponding weights of arabinose, xylose, pentoses and pentosans. The method, although extensively used, is decidedly empirical in nature as the views concerning phloroglucinol - furfural reaction are very complicating. Goodwin and Tollens (1904) claimed that one molecule of water

is eliminated in the reaction the exact mechanism of which they represented as follows:

$$C_6H_6O_3 + 2C_5H_4O_2 - H_2O \longrightarrow C_{16}H_{12}O_6$$

Phloroglucinol — Furfural

They further maintained that at 80°C. three molecules of water were lost, while Kröber worked out his formulas and tables on the assumption that two molecules of water were eliminated as will be evident from the following reaction:

$$C_5H_4O_2 + C_6H_6O_3 - 2H_2O \longrightarrow C_{11}H_8O_3$$

Furfural — Phloroglucinol — Phloroglucid

96 126 186

He based his conclusions on the fact that 0.1926 gms. of phloroglucid were obtained from 0.1 gm. of furfural and consequently 96 gms. (molecular weight of furfural) would yield 184.89 gms of phloroglucid which value closely agreed with the theoretical figure calculated from the above equation.

Aside from the difficulty encountered in giving the so-called "phloroglucid" a definite chemical formula, the product was found to be hygroscopic with a tendency to undergo oxidation when exposed to light. The consensus of opinion as held by the Association of Official Agricultural Chemists, however, seemed to endorse Kröber's views in their entirety. His method, after slight modifications in distillation procedure, was adopted as the official method. It reads as follows:(16)

"Place a quantity of the material, 2 - 5 grams, chosen so that the weight of phloroglucid obtained shall not exceed 0.300 gram, in a 300 cc. distillation flask, together with 100 cc. of 12 per cent

hydrochloric acid (sp. gr. 1.06) and several pieces of recently heated pumice stone. Place the flask on a wire gauze, connect with a condenser, and heat, rather gently at first, and regulate so as to distil over 30 cc. in about 10 minutes, the distillate passing through a small filter paper. Replace the 30 cc. distilled by a like quantity of the dilute acid, added by means of a separatory funnel in such a manner as to wash down the particles adhering to the sides of the flask, and continue the process until the distillate amounts to 360 cc. To the total distillate add gradually a quantity of phloroglucin dissolved in 12 per cent hydrochloric acid, and stir thoroughly the resulting mixture. The amount of phloroglucin used should be about double that of the furfural expected. The solution turns first yellow, then green, and very soon an amorphous greenish precipitate appears, which grows darker rapidly, till it becomes finally almost black. Make the solution up to 400 cc. with 12 per cent hydrochloric acid, and allow to stand over night.

Filter the amorphous black precipitate in a tared Gooch crucible, having an asbestos mat, wash carefully with 150 cc. of water in such a way that the water is not entirely removed from the crucible until the very last, then dry for four hours at the temperature of boiling water, cool and weigh in a weighing bottle, the increase in weight being reckoned as furfural phloroglucid. To calculate the furfural, pentose, or pentosan from the phloroglucid, use the following formulas given by Kröber.

(1) For a weight of phloroglucid, designated by "a" in the following formulas, under 0.03 gram.

Furfural = (a + 0.0052) x 0.5170
Pentoses = (a + 0.0052) x 1.0170
Pentosans = (a + 0.0052) x 0.8949 "

In the above and also in the following formulas, the factor, 0.0052 represents the weight of phloroglucid which remains dissolved in the 400 cc. of acid solution.

" (2) For a weight of phloroglucid "a" between 0.03 and 0.300 gram, use Kröber's table XXX, Table 2, on the following formulas:

Furfural = (a + 0.0052) x 0.5185
Pentoses = (a + 0.0052) x 1.0075
Pentosans = (a + 0.0052) x 0.8866

(3) For a weight of phloroglucid "a" over 0.300 gram,

Furfural = (a + 0.0052) x 0.5180
Pentoses = (a + 0.0052) x 1.0026
Pentosans = (a + 0.0052) x 0.8824 "

The modifications introduced into the process of distillation are two. Namely, reduction of the volume of total distillate to 360 cc. and the discard of the use of aniline acetate paper to detect the presence of furfural in the final dropsof distillate. Tollens, in his work with pentosan determinations, had recommended 400 cc. as the total volume of distillate to collect and had made use of the pink color due to reaction between furfural and aniline acetate to mark the completion of distillation.

The factor, 0.0052, used in Kröber's system for solubility corrections, was obtained by comparing different amounts of phloroglucid yielded by varying quantities of furfural and phloroglucinol.(17)

The derivation was made purely on empirical and mathematical grounds, as will be seen from Kröber's aggument given below. Assuming molecular weight of phloroglucid to be 186, he maintained that the theoretical yield of phloroglucid that could possibly be obtained from a given quantity of furfural or phloroglucinol, might be calculated from the following equation which essentially was the one he used to demonstrate the mechanism of furfural - phloroglucinol condensation:

$C_5H_4O_2$	+	$C_6H_6O_3$ -----	$C_{11}H_6O_3$ + $2H_2O$
Furfural		Phloroglucinol	Phloroglucid
96		126	186

As his chief concern was to get a definite factor for solubility corrections, he treated a fixed amount of furfural with varying volumes of phloroglucinol solution of the same concentration, and compared actual phloroglucid obtained with the theoretical weight of the same, calculated from the above equation.

The following table represents a detailed resume of his work at this juncture:

	Furfural solution 1.032 gms. per 1000 cc.	Phloroglucinol solution, 0.7 gm per 1000 cc.	Phloroglucid	Phloroglucid + 0.0052 gm.
1.	50 cc. = .0516 gms.	50 cc. .0350 gm.	.0470 gm.	.0522
2.	50 cc. = .0516	50 cc. .0350	.0466	.0518
3.	50 cc. = .0516	100 cc. .0700	.0933	.0985
4.	50 cc. = .0516	100 cc. .0700	.0936	.0988
5.	50 cc. = .0516	200 cc. .1400	.0936	.0988
6.	50 cc. = .0516	200 cc. .1400	.0937	.0989

In the first two cases above, the proportion of phloroglucinol to furfural was 1/2 mol. to 1 mol. respectively, which naturally meant that phloroglucinal available would be inadequate to react with the total furfural present. Calculating from the equation, he found that .0350 gms. of phloroglucinol would theoretically yield 0.0516 gm. of phloroglucid while he actually obtained an average weight of .0468. Difference between the two figures approached .0052 very closely.

In the experiments 3 and 4, the phloroglucinal - furfural proportion was 1 : 1 while in 5 and 6 it was 2 : 1, respectively. The results, however, were identical and when compared with calculated theoretical amounts, the difference seemed to approach .0052. Hence the average weight of phloroglucid dissolved in 400 cc. of solution was accepted to be .0052 gram.

At this time it would not be out of place to mention a procedure for the direct determination of pentose sugars. The method was first divised by H. A. Spoehr (18), and later modified by Rosa.

In its simplest form it calls for the hydrolysis of carbohydrate material into pentose and hexose sugars. This is accomplished by boiling with dilute hydrochloric acid (8 cc. conc. hydrochloric acid in 150 cc. water).

The mixed solution of pentose and hexose sugars is then subjected to fermentation by means of yeast. The hexose sugars being thus fermented, the remaining solution contains only the pentoses. The solution is then filtered and the pentose sugars determined by means of Fehling's solution.

EXPERIMENTAL PART

I. Preliminary Tests of Various Amines

The first problem to be attacked experimentally was the finding of a suitable aromatic amine. Such an amine should give a distinct color with furfural and this color should also sufficiently vary in depth or tint, with change in concentration of furfural, so that small differences in amounts of furfural can be determined.

Toluidine: A 10 per cent solution of toluidine in 95 per cent alcohol was prepared, and a small portion of it was tested with an equal volume of furfural solution in 12 per cent hydrochloric acid. An intense yellow color with a slightly reddish tinge manifested itself, but though the color itself was satisfactory, it was found that changes in the concentration of furfural made insufficient changes in color intensity to allow the use of toluidine.

Xylidine: Xylidine was tested in the same manner with no better results. A trifle stronger red tinge was produced in this case but still it was not strong enough to warrant its satisfactory usage for quantitative purposes.

Aniline: The use of aniline as a test for furfural has long been known and used qualitatively, as referred to in connection with the work of Stenhouse and DeChalmot[1]. The latter was the first to make use of this color reaction for quantitative purposes. The reaction occurs

when furfural solution or vapor is brought in contact with a solution of aniline, a brilliant cherry-red color being produced. DeChalmot, found, however, that the presence of hydrochloric acid, usually in excess, interfered with the color reaction. He found, furthermore, that when acetic acid was used even if present in excess, the color reaction was satisfactory. However, as by the Official Method for the determination of pentosans, the furfural is distilled over with 12 per cent hydrochloric acid, it would be necessary in following DeChalmot's colorimetric method, to neutralize the hydrochloric acid with sodium hydroxide or carbonate, and then acidify the solution with acetic acid. Such a procedure was found to make the color tests very questionable in accuracy due probably to the presence of the resulting sodium chloride. It was decided, therefore, to follow the Official Method and a procedure was devised as described later, by which the use of hydrochloric acid did not interfere with the quantitative application of the color reaction.

II. Preparation and Testing of Standard Furfural Solution

The next problem was the preparation of a standard stable furfural solution. As a medium of measuring the relative concentrations of furfural solutions, it was absolutely essential that the standard should always keep its furfural value. On account of the tendency of furfural to polymerize, the concentration of a solution is liable to change thus necessitating restandardization at frequent intervals.

In the process of standardization the Official Method was made use of. Furfural amounting to 5.5190 gms. was dissolved in 2000 cc. of 12 per cent hydrochloric acid (sp. gr. 1.06). Simultaneously 5 gms. of phloroglucinol were dissolved in 1500 cc. of hydrochloric acid of the same strength and specific gravity as above. Five samples of 40 cc. each of the furfural solution, were measured and treated with varying volumes of the phloroglucinol solution, ranging from 50 cc. to 70 cc. Nothwithstanding the differences in the amount of phloroglucinol used, the furfural value per cubic centimeter solution, as calculated from the different amounts of phloroglucid obtained, using Kröber's formulas, was the same.

Table I shows the results of the foregoing determinations, together with those of two other samples.

TABLE I

Standard Furfural Solution

Serial No.	Furfural Solution (taken) cc.	Phloroglucinol Solution (used) cc.	Phloroglucid (obtained) gms.	Furfural (calculated from phloroglucid) gms.	Furfural (per cc.) gms.
1	40 cc.	50 cc.	0.1980	0.10536	0.002634
2	40	60	0.1950	0.10380	0.002595
3	40	70	0.1980	0.10536	0.002634
4	40	50	0.2060	0.10951	0.002738
5	40	50	0.1970	0.10484	0.002621
6	20	25	0.0980	0.05351	0.002675
7	20	25	0.1000	0.05455	0.002727
				average	0.00266

From these determinations it may be seen that, with the solutions as previously described, the proportion;

Furfural solution : Phloroglucinol solution : : 40 : 50

represents a minimum, but sufficient amount, of phloroglucinol to precipitate all furfural as phloroglucid. This proportion calculated in grams will be ;

Furfural in grams : Phloroglucinol in grams : : 0.00266 : 0.0033.

This proportion was followed in all subsequent determinations.

With the value of furfural solution thus established, it should be ideal to begin the regular colorimetric determinations. But a second series of determinations (two weeks after the above) revealed the unstable character of furfural solution. The difference will manifest itself when a comparison of the results given in Table I is made with those given in Table II. In the latter case six samples, of 20 cc. each, of furfural solution were taken and treated with 25 cc. of phloroglucinol solution.

TABLE II

Standard Furfural Solution

	Furfural Solution (taken) cc.	Phloroglucinol Solution (used) cc.	Phloroglucid (obtained) gms.	Furfural (calculated from phloroglucid) gms.	Furfural (per cc.) gms.
1	20	25	0.0810	0.04469	0.00223
2	20	25	0.0830	0.04573	0.00228
3	20	25	0.0840	0.04625	0.00231
4	20	25	0.0850	0.04677	0.00234
5	20	25	0.0830	0.04573	0.00228
6	20	25	0.0800	0.04418	0.00221
				Average	0.00227

For practical purposes, however, the concentration of this standard solution was too high for it was necessary to have its strength only a little higher than the average concentration of distillates obtained from pentosan determinations. It was desirable that the standard furfural solution should have a furfural value of 0.000183 gm. per cubic centimeter.

Therefore about 170 cc. of the original solution was roughly measured and diluted to 2150 cc.

Upon standardization the results showed that the furfural content of the dilute solution was 0.000179 per cubic centimeter. Restandardization was made at different periods of from 2 to 4 weeks, but the average of values obtained showed that the solution had not changed substantially, and that it had attained a fairly stable condition as will be evident from Table III. The figures there represent the average weight of furfural per cubic centimeter solution at the times denoted.

TABLE III

Comparison of Furfural Solution at Different Periods in grams per Cubic Centimeter

Jan. 14, 1926	Jan. 28, 1926	Feb. 16, 1926	March 14, 1926
0.000175	0.000179	0.0001753	0.0001748

Aliquot portions for the first two were taken from the same solution, while those for the last two were taken from a different but similarly prepared solution. Hence the slight difference between the two sets of values.

III. Technique of Method and of Calculations.

Having thus secured a standard furfural solution, it was necessary to find the amount of aniline to be added in order to bring about the desired color reaction.

Qualitative tests proved that 15 per cent aniline solution in 95 per cent alcohol gave the best results, and that when 25 cc. of this solution was treated with 10 cc. of standard furfural solution a very clear and distinct pink color was obtained. The color produced was intensified by small increments of furfural so that conditions were favorable to the quantitative use of the procedure.

The neutralization of hydrochloric acid by the aniline was insured by the use of sufficient aniline to make a distinct excess.

Since in pentosan determinations furfural was distilled over with 12 per cent hydrochloric acid and the strength of the acid in the distillate was approximately equal to that in standard furfural solution, equal volumes of each were taken for colorimetric purposes. The volumes of aniline solution were also identical so as to have the same amount of excess aniline in both cases.

Ten cubic centimeters aliquot portion of each distillate, collected by distilling different pentoses and pentosans, were treated with 25 cc. of 15 per cent aniline solution in 95 per cent alcohol. The intensity of the color produced was compared with that produced by an

equal and similarly trea ted volume of standard furfural. In both cases the solutions were diluted with distilled water to 50 cc.

In order to avoid erroneous results, it was necessary to let the solutions stand for fifteen minutes after adding aniline.

When first mixed, furfural and aniline react only partially and difference in color is almost imperceptible. At the end of the above specified time, however, the reaction seems to be completed and difference in color is very distinct.

For accurate measurements of color intensities a Duboscq colorimeter was used, which consists essentially of two vertically situated, fixed, hexagonal prisms about six centimeters in length. These prisms are supported by the main body of the apparatus, while their lower extremities stand slightly above two movable glass cups which allow passage of light reflected by a mirror underneath. The cups can be moved up and down thus giving the prisms position, so that the column of liquid observed is made shorter or longer.

There are two graduated scales by means of which the column of liquid can be accurately measured.

In actual measurements the cup containing the colored solution of standard furfural was always kept at a fixed distance (10 mm.) while the one containing the unknown was moved up and down until the colorsmatched each other. The matching could be watched through an eyepiece attached to the upper extremity of the apparatus.

The strength, per cubic centimeter solution, of unknown was calculated according to the following formula:

Let C represent concentration of standard

C_1 " " " unknown

R " reading of standard

R_1 " " " unknown,

$$\text{then } C_1 = \frac{C}{\frac{R_1}{R}} = C \times \frac{R}{R_1}$$

Having thus determined the concentration of the unknown solution, the total distillate was multiplied by the new factor. This gave the total furfural content of the solution under consideration.

By the method being studied, factors were needed to convert this furfural into pentoses and pentosans. Nothing was mentioned to this effect in Kröber's work as his factors were derived on the basis of phloroglucinol method. His system, as given below, called for different conversion factors for different quantities of phloroglucid.

Formulas Devised by Kröber

(1) For a weight of phloroglucid, under 0.03 gram, designated by "a" in the following formulas;

Furfural = (a + 0.0052) x 0.5170
Pentoses = (a + 0.0052) x 1.0170
Pentosans = (a + 0.0052) x 0.8949

(2) For a weight of phloroglucid "a" between 0.03 and 0.300 gram,

Furfural = (a + 0.0052) x 0.5185
Pentoses = (a + 0.0052) x 1.0075
Pentosans = (a + 0.0052) x 0.8866

(3) For a weight of phloroglucid "a" over 0.300 gram,

Furfural = (a + 0.0052) x 0.5180
Pentoses = (a + 0.0052) x 1.0026
Pentosans = (a + 0.0052) x 0.8824

From this table as worked out by Kröber, factors may easily be devised for a similar conversion of furfural into pentoses and pentosans, as by the following proportion from Kröber's formulas (2).

wt. furfural : wt. pentosan :: K - factor for furfural : K'-factor for pentosan

1.0 : X :: .5185 : .8866

X = 1.710

Therefore the factor for converting furfural into pentosan, in case the furfural is between certain limits corresponding to Kröber's phloroglucid limits between .03 gm. and .30 gm., is 1.710.

We can thus derive factors for pentoses and pentosans applying to certain limits of furfural corresponding to those of Kröber for like limits of phloroglucid. Such factors are as follows:

Factors for converting furfural into pentoses and pentosans.

(1) For a weight of furfural under 0.018251 gm.

Pentose = Furfural x 1.967
Pentosan = Furfural x 1.731

(2) For a weight of furfural between 0.018251 gm. and 0.158246 gm.

Pentose = Furfural x 1.943
Pentosan = Furfural x 1.710

(3) For a weight of furfural over 0.158246 gm.

Pentose = Furfural x 1.935
Pentosan = Furfural x 1.703

IV. Details of Procedure Followed

To put the method in a concise form, the detailed directions thereof can be given as follows:

Collect the furfural, produced from a sample of pentose or pentosan and distilled over with 12 per cent hydrochloric acid (sp. gr. 1.06), according to the Official Method. Shake the total volume of distillate to insure homogeneous distribution of furfural and measure out 10 cc. accurately, from a burette into a Nessler tube. Into another Nessler tube measure similarly an equal volume of standard furfural solution. Add to each 25 cc. of 15 per cent aniline solution in 95 per cent alcohol. Dilute each to the 50 cc. mark and let them stand for 15 minutes. Compare the relative intensities of color by means of a Duboscq colorimeter, keeping the reading of standard constant and adjusting the reading of the unknown until the colors match. From the concentration of the standard and the readings taken, calculate the concentration of the unknown according to the following formula:

$$C_1 = C \times \frac{R}{R_1}$$

C_1 = concentration of the unknown per cc.
C = " " " standard " "
R = reading of the standard
R_1 = " " unknown.

Multiply the volume of the distillate collected by the concentration per cubic centimeter to get the total weight of furfural. By use of the proper factor which applies to the weight of furfural found, as given on page 27, convert the weight of furfural into either pentose or pentosan as desired.

V. Experimental Results and Their Tabulation

In order to test the accuracy of the method several samples of pentoses and pentosans were distilled according to Official Method and the furfural contained in the distillates determined both gravimetrically, by the Official Method, and colorimetrically, the results being compared on percentage basis.

The first pentosan worked with was Gum Arabic. Its furfural yield was first determined gravimetrically, from the weight of phloroglucid obtained. From the amount of phloroglucid the per cent pentosan was also calculated. Table IV shows the results obtained.

The furfural obtained from Gum Arabic was also determined colorimetrically as just described, and from the amount of furfural the amount of pentosan was calculated by use of the conversion factor previously given (page 27).

TABLE IV

Gum Arabic:-Furfural and Pentosan

Gravimetric Method

Sample	Weight of Sample gms.	Volume of Distillate cc.	Phloroglucinol sol. (used) cc.	Phloroglucid (obtained) gms.	Furfural gms.	Furfural %	Pentosan gms.	Pentosan %
1	0.1100	360	50	0.0340	0.020325	18.48	0.03475	31.59
2	0.2320	360	50	0.0810	0.044694	19.26	0.07642	32.90
3	0.3700	360	50	0.1220	0.065950	17.81	0.11278	30.48
4	0.3540	360	50	0.1150	0.062332	17.60	0.10657	30.10
5	0.0900	360	50	0.0250	0.015610	17.34	0.02703	30.03
6	0.1860	360	50	0.0590	0.033290	17.90	0.05692	30.60

TABLE V

Gum Arabic:-Furfural and Pentosan

Colorimetric Method

Sample	Weight of Sample gms.	Volume of Distillate cc.	Furfural per cc. (standard) gms.	Furfural per cc. (unknown) gms.	Furfural gms.	Furfural %	Pentosan gms.	Pentosan %
1	0.1530	360	0.000179	.0000840	0.03024	19.76	0.05171	33.80
2	0.1500	360	0.000179	.0000829	0.02985	19.30	0.05105	34.03
3	0.1480	360	0.000179	.0000813	0.02929	19.78	0.05008	33.84
4	0.1600	360	0.000179	.0000865	0.03114	19.46	0.05325	33.28
5	0.2400	360	0.000179	.0001313	0.04728	19.70	0.08084	33.68

TABLE VI

Gum Arabic:-Comparison of Results by Gravimetric and Colormetric Methods

Sample	Weight of Sample gms.		Volume of Distillate cc.		Furfural gms.		Furfural %		Pentosan gms		Pentosan %	
	Grav.	Color.	Grav.	Color.	Grav.	Color.	Grav.	Color.	Grav.	Color	Grav.	Color.
1	0.1100	0.1530	360	360	.020325	.03024	18.48	19.76	.03475	.05171	31.59	33.80
2	0.2320	0.1500	360	360	.044694	.02985	19.26	19.30	.076425	.05105	32.90	34.03
3	0.3700	0.1480	360	360	.065950	.02929	17.81	19.78	.11278	.05008	30.48	33.84
4	0.3540	0.1600	360	360	.062320	.03114	17.60	19.46	.10657	.05325	30.10	33.28
5	0.0900	0.2400	360	360	.015610	.04728	17.34	19.70	.02703	.08085	30.03	33.68
6	0.1860	-	360	-	.033290	-	17.90	-	.05692	-	30.60	-

TABLE VII

Arabinose:-Furfural and Pentose

Gravimetric Method

Sample	Weight of Sample gms.	Volume of Distillate cc.	Phloroglucinol sol. (used) cc.	Phloroglucid (obtained) gms.	Furfural gms.	Furfural %	Pentose gms.	Pentose %
1	0.1125	360	50	0.0988	.053924	47.93	.104780	93.14
2	0.1310	360	50	0.1130	.061287	46.79	.119087	90.91
3	0.1125	360	50	0.0980	.053509	47.56	.103974	92.42
4	0.0883	360	50	0.0740	.041065	46.51	.079794	90.37
5	0.1000	360	50	0.0900	.049361	49.36	.095914	95.91

TABLE VIII

Arabinose:-Furfural and Pentose

Colorimetric Method

Sample	Weight of Sample gms.	Volume of Distillate cc.	Furfural per cc. (standard) gms.	Furfural per cc. (unknown) gms.	Furfural gms.	Furfural %	Pentose gms.	Pentose %
1	0.1125	360	0.000179	.0001492	.053712	47.74	.104370	92.77
2	0.1310	360	0.000179	.0001700	.061200	46.79	.118918	90.78
3	0.1125	360	0.000179	.0001479	.053244	47.33	.103460	91.96
4	0.0883	360	0.000179	.0001460	.041240	46.70	.080133	90.75
5	0.1040	360	0.000179	.0001420	.051120	49.15	.099330	95.51

TABLE IX

Arabinose:-Comparison of Results by Gravimetric and Colorimetric Methods

Sample	Weight of Sample gms.		Volume of Distillate cc.		Furfural gms.		Furfural %		Pentose gms.		Pentose %	
	Grav.	Color.	Grav.	Color.	Grav.	Color.	Grav.	Color.	Grav.	Color.	Grav.	Color.
1	0.1125	0.1125	360	360	.053924	.053712	47.93	47.74	.104780	.104370	93.14	92.77
2	0.1310	0.1310	360	360	.061287	.061200	46.79	46.79	.119087	.118918	90.91	90.78
3	0.1125	0.1125	360	360	.053509	.053244	47.56	47.33	.103974	.103460	92.42	91.96
4	0.0883	0.0883	360	360	.041065	.041250	46.51	46.70	.079794	.080133	90.37	90.75
5	0.1000	0.1040	360	360	.049361	.051120	49.36	49.15	.095914	.099330	95.91	95.51

TABLE X

Xylose:-Furfural and Pentose

Gravimetric Method

Sample	Weight of Sample gms.	Volume of Distillate cc	Phloroglucinol sol. (used) cc.	Phloroglucid (obtained) gms.	Furfural gms.	Furfural %	Pentose gms.	Pentose %
1	0.0435	360	50	0.0382	.022503	51.73	.043726	100.50
2	0.0555	360	50	0.0500	.028621	51.57	.055614	100.20
3	0.0640	360	50	0.0586	.033080	51.68	.0642785	100.40
4	0.0516	360	50	0.0454	.026236	50.85	.050979	98.76
5	0.0430	360	50	0.0374	.022088	51.37	.042919	99.80

TABLE XI

Xylose:-Furfural and Pentose

Colorimetric Method

Sample	Weight of Sample gms.	Volume of Distillate cc.	Furfural per cc. (standard) gms.	Furfural per cc. (unknown) gms.	Furfural gms.	Furfural %	Pentose gms.	Pentose %
1	0.0435	360	.0001753	.0000624	.022464	51.64	.043651	100.34
2	0.0555	360	.0001727	.0000795	.028649	51.61	.055668	100.30
3	0.0640	360	.0001753	.0000917	.033012	51.58	.064147	100.23
4	0.0516	360	.0001753	.0000730	.026298	50.97	.051099	99.03
5	0.0673	360	.0001753	.0000958	.034484	51.24	.067007	99.56
6	0.0564	360	.0001753	.0000796	.028684	50.86	.055739	98.83
7	0.0520	360	.0001753	.0000746	.026856	51.65	.052184	100.35

TABLE XII

Xylose:-Comparison of Results by Gravimetric and Colorimetric Methods

Sample	Weight of Sample gms.		Volume of Distillate cc.		Furfural gms.		Furfural %		Pentose gms.		Pentose %	
	Grav.	Color.	Grav.	Color.	Grav.	Color.	Grav.	Color	Grav.	Color.	Grav.	Color.
1	.0435	.0435	360	360	.022503	.022464	51.73	51.64	.043726	.043651	100.50	100.34
2	.0555	.0555	360	360	.028621	.028649	51.57	51.61	.055614	,055668	100.20	100.30
3	.0640	.0640	360	360	.033080	.033012	51.68	51.58	.064278	.064147	100.40	100.23
4	.0516	.0516	360	360	.026236	.026298	50.85	50.97	.050979	.051099	98.76	99.56
5	.0430	.0673	360	360	.022088	.034484	50.85	51.24	.042919	.067007	99.80	99.56
6	--	.0564	360	--	--	.028684	--	50.85	--	.055739	--	98.83
7	--	.0520	360	--	--	.026856	--	51.65	--	.052184	--	100.35

TABLE XIII

Ground Oats (#626):-Furfural and Pentosan

Gravimetric Method

Sample	Weight of Sample gms.	Volume of Distillate cc.	Phloroglucinol sol. (used) cc.	Phloroglucid (obtained) gms.	Furfural gms.	Furfural %	Pentosan gms.	Pentosan %
1	0.3070	450	150	0.0414	0.024132	7.87	0.041315	13.46
2	0.3040	450	150	0.0412	0.024058	7.90	0.041140	13.51
3	0.2341	400	75	0.0268	0.016544	7.07	0.028637	12.23
4	0.2485	480	75	0.0292	0.017785	7.15	0.030785	12.38

TABLE XIV

Ground Oats (#626):-Furfural and Pentosan

Colorimetric Method

Sample	Weight of Sample gms.	Volume of Distillate cc.	Furfural per cc. (Standard) gms.	Furfural per cc. (unknown) gms.	Furfural gms.	Furfural %	Pentosan gms.	Pentosan %
1	0.2956	450	0.0001753	.0000515	.023202	7.85	.039675	13.42
2	0.2988	450	0.0001753	.0000551	.024804	8.30	.042413	14.19

T A B L E XV

Ground Oats (#626):-Comparison of Results by Gravimetric and Colorimetric Methods

Sample	Weight of Sample gms.		Volume of Distillate cc		Furfural gms.		Furfural %		Pentosan gms.		Pentosan %	
	Grav.	Color.	Grav.	Color.	Grav.	Color.	Grav.	Color.	Grav.	Color	Grav.	Color.
1	0.3070	0.2956	450	450	.024162	.023202	7.87	7.85	.0413156	.039675	13.46	13.46
2	0.3040	0.2988	450	450	.024058	.024804	7.90	8.30	.041140	.042413	13.51	14.19
3	0.2341	--	450	--	.016544	--	7.07	--	.028637	--	12.23	--
4	0.2485	--	450	--	.017785	--	7.15	--	.030785	--	12.38	

TABLE XVI

Alfalfa Hay (#652):-Furfural and Pentosan

Gravimetric Method

Sample	Weight of Sample gms.	Volume of Distillate cc.	Phloroglucinol sol. (used) cc.	Phloroglucid (obtained) gms.	Furfural gms.	Furfural %	Pentosan gms.	Pentosan %
1	0.1956	400	75	0.0242	.0151998	7.77	.026210	13.40
2	0.1669	400	75	0.0196	.0128216	7.68	.022194	13.29

TABLE XVII

Alfalfa Hay (#652):-Furfural and Pentosan

Colorimetric Method

Sample	Weight of Sample gms.	Volume of Distillate cc.	Furfural per cc. (standard) gms.	Furfural per cc. (unknown) gms.	Furfural gms.	Furfural %	Pentosan gms.	Pentosan %
1	0.4014	450	.0001753	.00006742	.030339	7.56	.051879	12.93
2	0.2916	450	.0001753	.00005009	.0225411	7.73	.038544	13.22

TABLE XVIII

Oat Feed (#677):-Furfural and Pentosan

Gravimetric Method

Sample	Weight of Sample gms.	Volume of Distillate cc.	Phloroglucinol sol. (used) cc.	Phloroglucid (obtained) gms.	Furfural gms.	Furfural %	Pentosan gms.	Pentosan %
1	0.3294	450	150	0.1022	0.055687	16.90	.095221	28.90
2	0.2822	450	150	0.0872	0.047909	16.97	.081922	29.02

TABLE XIX

Oat Feed (#677):-Furfural and Pentosan

Colorimetric Method

Sample	Weight of Sample gms.	Volume of Distillate cc.	Furfural per cc. (standard) gms.	Furfural per cc. (unknown) gms.	Furfural gms.	Furfural %	Pentosan gms.	Pentosan %
1	0.2752	450	.0001753	.0000974	.043830	15.93	.074947	27.23
2	0.3372	450	.0001753	.0001170	.052650	15.61	.090028	26.70

TABLE XX

Alfalfa Hay (#652):-Comparison of Results by Gravimetric and Colorimetric Methods

Sample	Weight of Sample gms.		Volume of Distillate cc		Furfural gms.		Furfural %		Pentosan gms.		Pentosan %	
	Grav.	Color.	Grav.	Color.	Grav.	Color.	Grav.	Color.	Grav.	Color	Grav.	Color.
1	0.1956	0.4014	400	450	.015199	.030339	7.77	7.56	.026210	.051879	13.40	12.93
2	0.1669	0.2916	400	450	.012821	.022541	7.68	7.73	.022194	.038544	13.29	13.22

TABLE XXI

Oat Feed (#677)

1	0.3294	0.2752	450	450	.055687	.043830	16.90	15.93	.095221	.074947	28.90	27.23
2	0.2822	0.3372	450	450	.047909	.052650	16.97	15.61	.081922	.090028	29.02	26.70

TABLE XXII

Oat, Vim Feed (#676):-Furfural and Pentosan

Gravimetric Method

Sample	Weight of Sample gms.	Volume of Distillate cc.	Phloroglucinol sol. (used) cc.	Phloroglucid (obtained) gms.	Furfural gms.	Furfural %	Pentosan gms.	Pentosan %
1	0.5069	400	125	0.1552	0.083167	16.41	0.142211	28.05
2	0.2669	400	100	0.0800	0.044176	16.55	0.075538	28.30

TABLE XXIII

Oat, Vim Feed (#676):-Furfural and Pentosan

Colorimetric Method

Sample	Weight of Sample gms.	Volume of Distillate cc.	Furfural per cc. (standard) gms.	Furfural per cc. (unknown) gms.	Furfural gms.	Furfural %	Pentosan gms.	Pentosan %
1	0.5069	400	0.0001753	0.0002062	.082480	16.27	.141040	27.82
2	0.2669	400	0.0001753	0.0001109	.044360	16.62	.075852	28.42

TABLE XXIV

Wheat Bran (#622)a-Furfural and Pentosan

Gravimetric Method

Sample	Weight of Sample gms.	Volume of Distillate cc.	Phloroglucinol sol. (used) cc.	Phloroglucid (obtained) gms.	Furfural gms.	Furfural %	Pentosan gms.	Pentosan %
1	0.3915	400	100	0.1068	0.058072	14.83	.099299	25.38
2	0.2805	400	100	0.0754	0.041791	14.89	.071459	25.47

TABLE XXV

Wheat Bran (#622):-Furfural and Pentosan

Colorimetric Method

Sample	Weight of Sample gms.	Volume of Distillate cc.	Furfural per cc. (standard) gms.	Furfural per cc. (unknown) gms.	Furfural gms.	Furfural %	Pentosan gms.	Pentosan %
1	0.3915	400	0.0001753	0.000145	0.058000	14.81	.099178	25.33
2	0.2805	400	0.0001753	0.0001043	0.041720	14.87	.071338	25.40

T A B L E XXVI

Oat, Vim Feed (#676):-Comparison of Results by Gravimetric and Colorimetric Method

Sample	Weight of Sample gms.		Volume of Distillate cc.		Furfural gms.		Furfural %		Pentosan gms.		Pentosan %	
	Grav.	Color.	Grav.	Color.	Grav.	Color.	Grav.	Color.	Grav.	Color	Grav.	Color.
1	0.5069	0.5069	400	400	.083167	.082480	16.41	16.27	.142211	.141040	28.05	27.82
2	0.2669	0.2669	400	400	.044176	.044360	16.55	16.62	.075538	.075852	28.30	28.42

T A B L E XXVII

Wheat Bran (#622)

1	0.3915	0.3915	400	400	.058072	.058000	14.83	14.81	.099299	.099178	25.38	25.33
2	0.2805	0.2805	400	400	.041791	.041720	14.89	14.87	.071459	.071338	25.47	25.40

TABLE XXVIII

Barley Hulls (#485):-Furfural and Pentosan

Gravimetric Method

Sample	Weight of Sample gms.	Volume of Distillate cc.	Phloroglucinol sol. (used) cc.	Phloroglucid (obtained) gms.	Furfural gms.	Furfural %	Pentosan gms.	Pentosan %
1	0.2810	400	100	0.0640	0.035880	12.77	.061353	21.83
2	0.4498	360	100	0.1078	0.058590	13.03	.100186	22.29
3	0.2659	400	100	0.0622	0.023947	13.14	.059657	22.44

TABLE XIX

Barley Hulls (#485):-Furfural and Pentosan

Colorimetric Method

Sample	Weight of Sample gms.	Volume of Distillate cc.	Furfural per cc. (standard) gms.	Furfural per cc. (unknown) gms.	Furfural gms.	Furfural %	Pentosan gms.	Pentosan %
1	0.4498	360	.0001753	.0001498	.053928	11.99	.092213	20.50
2	0.2659	400	.0001753	.0000863	.034540	12.99	.059063	22.21
3	0.2810	400	.0001753	.0000922	.036904	13.13	.063158	22.46

TABLE XXX

Oat Hulls (#248):-Furfural and Pentosan

Gravimetric Method

Sample	Weight of Sample gms.	Volume of Distillate cc.	Phloroglucinol sol. (used) cc.	Phloroglucid (obtained) gms.	Furfural gms.	Furfural %	Pentosan gms.	Pentosan %
1	0.2505	400	100	0.0938	.051332	20.49	.087734	35.04
2	0.3098	360	100	0.1196	.064709	20.89	.011064	35.76
3	0.4231	360	75	0.1698	.090738	21.45	.0155155	36.66

TABLE XXXI

Oat Hulls (#248):-Furfural and Pentosan

Colorimetric Method

Sample	Weight of Sample gms.	Volume of Distillate cc.	Furfural per cc. (standard) gms.	Furfural per cc. (unknown) gms.	Furfural gms.	Furfural %	Pentosan gms.	Pentosan %
1	0.3098	360	0.0001753	.0001789	.064404	20.79	.110103	35.58
2	0.2505	400	0.0001753	.0001300	.052000	20.76	.088920	35.49
3	0.2975	400	0.0001753	.0001524	.060960	20.49	.104245	35.04

TABLE XXXII

Barley Hulls (#485):-Comparison of Results by Gravimetric and Colorimetric Methods

Sample	Weight of Sample gms.		Volume of Distillate cc		Furfural gms.		Furfural %		Pentosan gms.		Pentosan %	
	Grav.	Color.	Grav.	Color.	Grav.	Color.	Grav.	Color.	Grav.	Color.	Grav.	Color.
1	0.2810	0.4498	400	360	.035880	.053928	12.77	11.99	.061353	.092213	21.83	20.50
2	0.4498	0.2559	360	400	.058590	.034540	13.03	12.99	.100186	.059063	22.29	22.21
3	0.2559	0.2810	400	400	.034947	.036904	13.14	13.13	.059657	.063158	22.44	22.46

TABLE XXXIII

Oat Hulls (248)

1	0.2505	0.3098	400	360	.051332	.064404	20.49	20.79	.087773	.110103	35.04	35.58
2	0.3098	0.2505	360	400	.064709	.052000	20.89	20.76	.110648	.088920	35.76	35.49
3	0.4231	0.2975	360	400	.090738	.060960	21.45	20.49	.155155	.104245	36.66	35.04

TABLE XXXIV

Sheep Manure (#249):-Furfural and Pentosan

Gravimetric Method

Sample	Weight of Sample gms.	Volume of Distillate cc.	Phloroglucinol sol. (used) cc.	Phloroglucid (obtained) gms.	Furfural gms.	Furfural %	Pentosan gms.	Pentosan %
1	0.1561	400	100	.0364	.021569	13.81	.036883	23.63
2	0.1804	400	100	.0426	.024784	13.74	.042379	23.49

TABLE XXXV

Sheep Manure (#249):-Furfural and Pentosan

Colorimetric Method

Sample	Weight of Sample gms.	Volume of Distillate cc.	Furfural per cc. (standard) gms.	Furfural per cc. (unknown) gms.	Furfural gms.	Furfural %	Pentosan gms.	Pentosan %
1	0.1804	400	.0001753	.0000701	.028048	15.53	.047962	26.59
2	0.1561	400	.0001753	.0000637	.025496	16.33	.043598	27.93

TABLE XXXVI

Rice Hulls (#337):-Furfural and Pentosan

Gravimetric Method

Sample	Weight of Sample gms.	Volume of Distillate cc.	Phloroglucinol sol. (used) cc.	Phloroglucid (obtained) gms.	Furfural gms.	Furfural %	Pentosan gms.	Pentosan %
1	0.3963	400	75	0.0776	.042931	10.83	.073410	18.53
2	0.2875	400	75	0.0548	.031110	10.82	.053196	18.50
3	0.3292	400	75	0.0632	.035465	10.71	.060643	18.42

TABLE XXXVII

Rice Hulls (#337):-Furfural and Pentosan

Colorimetric Method

Sample	Weight of Sample gms.	Volume of Distillate cc.	Furfural per cc. (standard) gms.	Furfural per cc. (unknown) gms.	Furfural gms.	Furfural %	Pentosan gms.	Pentosan %
1	0.3963	400	.0001753	.0001106	.044240	11.17	.0755136	19.05
2	0.2875	400	.0001753	.0000815	.032632	10.35	.055801	19.41

T A B L E XXXVIII

Sheep Manure (#249):-Comparison of Results by Gravimetric and Colorimetric Methods

Sample	Weight of Sample gms.		Volume of Distillate cc.		Furfural gms.		Furfural %		Pentosan gms.		Pentosan %	
	Grav.	Color.	Grav.	Color.	Grav.	Color.	Grav.	Color.	Grav.	Color.	Grav.	Color.
1	0.1561	0.1804	400	400	.021569	.028048	13.81	15.53	.036883	.047962	23.63	26.59
2	0.1804	0.1561	400	400	.024784	.025496	13.74	16.33	.042379	.043598	23.49	27.93

T A B L E XXXIX

Rice Hulls (#337)

1	0.3963	0.3963	400	400	.042931	.044240	10.83	11.17	.073410	.0755136	18.53	19.05
2	0.2875	0.2875	400	400	.031110	.032632	10.82	10.35	.053196	.0558010	18.50	19.41
3	0.3292	--	400	--	.035465	--	10.71	--	.060643	--	18.42	

CONCLUSION

The sources of error involved in the use of the phloroglucinol method for pentosan determinations, are many. Starting with the basic principle of distilling furfural from pentoses and pentosans by means of 12 per cent hydrochloric acid, we find that the actual furfural yield is governed by the concentration of the acid during the distillation and the rate at which the distillation is effected. Theoretically the strength of the acid is kept constant by replacing 30 cc. distilled with a like quantity of 12 per cent hydrochloric acid.

Pentosans in plant materials are, however, very often accompanied by methyl pentosans, which on hydrolysis with hydrochloric acid, yield fucose or rhamnose and these on distillation with acids are converted into methyl furfural. Now methyl furfural resembles furfural in most of its properties, and phloroglucinol precipitates it as a phloroglucid.

It is claimed also that various other pure substances, including natural products which contain no pentosan grouping at all, such as dextrose and starch, yield on distillation with hydrochloric acid, volatile substances which are capable of being precipitated by phloroglucinol. The percentage of error from these sources does not exceed two per cent in extreme cases, yet some pentosan determinations are thereby rendered doubtful in value.

A colorimetric method has distinct advantages for it does away with some of the errors involved in the phloroglucinol method, viz., those which are due to the precipitation of the phloroglucid. While

the errors, if such, that are due to the distillation with 12 per cent hydrochloric acid, are not avoided by a colorimetric method for determining the furfural, still the advantages first mentioned seem in themselves desirable.

From a consideration of the results of this investigation it may be safely concluded that the colorimetric method herein described and carried out yields results with pure furfural and with pure pentoses that are comparable with those obtained by the Official Method. On ordinary pentosan materials, such as the feed stuffs studied, the new method also seems as accurate as the phloroglucinol method.

Further investigation should be made to determine the accuracy of this colorimetric method for the determination of furfural in the presence of methyl furfural or other furfural derivatives obtained from hexoses or hexosans.

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