Determination of Small Quantity of Pentosan in Cellulosic Materials

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I. Introduction

It is well known, that the phloroglucin method gives high values of pentosan content, on account of oxymethyl furfural produced from hexosan by acid distillation. In the case of chemical pulps especially high α pulps for cellulose ester or rayon tire cords, the apparent pentosan from hexosan becomes several times the true value and results in inaccuracy. Therefore, many methods have been advised to reduce or remove the influence of hexosan.

1) Barbituric acid method[1][2]

2) Decomposition of oxymethyl furfural by redistillation[3][4]

3) Dissolving oxymethyl furfural-phloroglucide by treatment with alcohol[3][5]

4) Colorimetry[6]~[9]

5) Determination utilizing the difference of the rates of thermal decomposition between furfural and oxymethyl furfural[10][11]

The method 1) gives lower values because of the solubility of the condensate in hydrochloric acid solution. As to the method 2), oxymethyl furfural is not only incompletely removed but also furfural is decomposed considerably. As for the method 3), the difference between the decomposition rates of oxymethyl furfural and furfural was smaller than expected and a good result was not obtained.

The method 3) is not a perfect one, but in Japan, phloroglucin method is predominantly adopted. So it is not useless to investigate the method more thoroughly. Colorimetric method 4) is promising as it is claimed that the influence of hexosan is under 0.1%. Then in this research, both the treatment of the phloroglucide with ethanol and the colorimetric method were investigated and the results were compared with barbituric acid, bromate and the usual phloroglucin methods, with special attention to the influence of hexosan on pentosan determination.

II. Improvement of Phloroglucin Method

1) **Experimental Procedures.**—The amounts of furfural and oxymethyl furfural produced by acid distillation, depend on the weight of the sample, distillation apparatus, variety and concentration of the acid, and rate and time of distillation. So, at first, these conditions were determined as follows:

The sample was weighed into a distillation flask (300 cc.) and 100 cc. of 12% hydrochloric acid solution was added and the mixture was heated in an oil bath. The temperature of the bath was regulated to obtain 30 cc. of the distillate in ten minutes and this was about 170°C. During the course of distillation, when every 30 cc. of the distillate was obtained, 30 cc. of 12% hydrochloric acid solution was tapped into the flask. To the total distillate (360 cc.), 40 cc. of phloroglucin-12% hydrochloric acid solution (7.33 g./l.) was added and the solution was kept standing for sixteen hours at 20°C. The phloroglucide was filtered on a glass filter 1G4, then 60 cc. of 95% ethanol was added to the precipitate in the glass filter and the mixture was kept standing for ten minutes at 60°C. The alcohol-insoluble residue was filtered on the glass filter and this procedure was repeated three times. In some cases, the initial phloroglucide was once dried at 105°C. and then treated with alcohol. Solubility in alcohol was calculated from the amount of phloroglucide before and after the alcohol-treatment and the portion dissolved in the mother liquor (hydrochloric acid solution) was

(1) E. Unger and R. Jäger, *Ber.*, **36**, 1222 (1903).
(2) S. Takehara, *J. Soc. Chem. Ind., Japan*, **47**, 74 (1944).
(3) K. Oshima and K. Kondo, *J. Coll. Agr. Hokkaido Imp. Univ.*, **16**, 52 (1926).
(4) C. Kullgren and H. Tydén *Cellulosechemie*, **11**, 15 (1930).
(5) T. Fukai and W. Nakajima, *J. Soc. Brewing, Japan*, **23**, No. 9, 18, No. 10, 18 (1928).
(6) G. E. Youngburg and G. W. Pucher, *J. Biol. Chem.*, **61**, 741 (1924).
(7) R. E. Peeves and J. Munro, *Ind. Eng. Chem., Anal. Ed.*, **12**, 551 (1940).
(8) R. A. Stillings and B. L. Browning, *Ind. Eng. Chem., Anal. Ed.*, **12**, 499 (1940).
(9) K. Kawamura and T. Higuchi, *J. Soc. Textile Cellulose Ind. (Japan)*, **7**, 95 (1951).
(10) T. Fujimura, *J. Soc. Textile Cellulose Ind. (Japan)*, **7**, 29 (1951).
(11) T. Fujimura, *J. Chem. Soc. Japan, Ind. Chem. Soc.*, **54**, 271 (1951).
(12) H. F. Launer and W. K. Wilson, *J. Res. Natl. Bur. Stand.*, **22**, 471 (1939).
(13) S. Takehara, *J. Soc. Chem. Ind., Japan*, **46**, 449 (1943).
(14) M. Hamada and I. Takano, *J. Agr. Dep. Kyushu Imp. Univ.*, **9**, No. 1 (1940).
(15) W. Gierisch, *Cellulosechemie*, **6**, 61, 81 (1925).

not considered. For calculation of xylose or pentosan content, the dissolved portion of the phloroglucide was assumed 5.2 mg. in 400 cc. of the mother liquor, even when the alcohol treatments were made.

2) **Experimental Results.**—(a) **Influence of times of the alcohol treatment.**—By means of one treatment, alcohol-soluble part was largely removed and completely eliminated by the operations of three times as shown in Table 1.

Table 1

Effect of Times of Alcohol-Treatment on Solubility in Alcohol

Glucose (g.)	3.0108	3.0091
Total phloroglucide (g.)	0.0320	0.0329
Alcohol-insoluble phloroglucide (g.)		
Time of treatment		
1	0.0142	0.0154
2	0.0137	0.0148
3	0.0137	0.0149
4	0.0138	0.0147
5	0.0139	0.0147

(b) **Apparent pentosan content from glucose, xylose and arabinose.**—According to Krōber, conversion ratios of xylose and arabinose to furfural were 88% and 73% respectively. He constructed his table in supposition that the pentosan in wood is a mixture of an equal amount of xylose and arabinose. Our experiment showed that these values were 86% and 72% respectively, and glucose also yielded phloroglucide which corresponded to 1.9% pentosan when calculated from Krōber's table. When the fresh, wet phloroglucides were treated with ethanol, 82% of the one from glucose was dissolved in ethanol but also 10~11% of those from xylose and arabinose were dissolved. After the precipitate was once dried, the alcohol-soluble portion was considerably lowered as shown in Tables 2 and 3. In the tables each experiment was duplicated and averaged.

(c) **Influence of the amount of phloroglucin added, on the alcohol-soluble portion.**—The

Table 2

Apparent Pentosan from Glucose (3.000 g.)

Condition of phloroglucide treated with alc.		Phloroglucide, mg.	Apparent pentosan, %*	Solubility, %
dry	before alc.	59.2	1.90	60.3
	after alc.	23.5	0.86	
wet	before alc.	—	—	82.1
	after alc.	10.6	0.47	

* Based on the weight of glucose and calculated from Krōber's table.

Table 3

Conversion ratios of Xylose and Arabinose to Furfural (sample, each 0.100 g., and the ratios were calculated from the amount of phloroglucide)

	Condition of phloroglucide treated with alc.		Phloroglucide, mg.	Conversion ratio, %	Solubility, %
Xylose	dry	before alc.	101.6	86.1	4.0
		after alc.	97.5	82.8	
	wet	before alc.	—	—	10.8
		after alc.	90.6	77.3	
Arabinose	dry	before alc.	84.0	71.9	1.5
		after alc.	82.7	70.9	
	wet	before alc.	—	—	10.0
		after alc.	75.6	65.2	

previous experiment showed that both the furfural- and oxymethyl furfural phloroglucide were divided into two parts, alcohol-soluble and -insoluble. It is clear that the cause is not the solubility of the precipitate in alcohol, such as in low-molecular weight compounds. Because the weight of the dissolved portion reached a constant value as the treatments were repeated.

Goodwin and Tollens[16] observed that, at room temperature, one mole of furfural condensed with one mole of phloroglucin under separation of one mole of water, but at 80°C. the precipitate was formed under dehydration of three moles of water. This indicates the oomposition of the phloroglucide is not constant and it is probable that this variation in composition would have effects on the solubility in alcohol. Then various amounts of phloroglucin were added to furfural and oxymethyl furfural solution, and the solubilities in alcohol of the phloroglucides produced were determined. 1 g. of furfural, purified twice by vacuum distillation, was dissolved in 1 l. of 12% hydrochloric acid solution, of which 10 cc., 30 cc., 50 cc. and 100 cc. were taken out and each was diluted to 360 cc. with 12% hydrochloric acid solution. To these solutions, the phloroglucin solution was added so as to make molar ratio of furfural to phloroglucin 1 : 2, 1 : 3, 1 : 5 and 1 : 10 and each was diluted with 12% hydrochloric acid solution to make the total volume 400 cc., The weights of the phloroglucides and their solubilities in alcohol were tabulated in Table 4. The solubilities were determined on the undried, wet samples, that were the same in the following experiments.

The table shows that the greater the ratio of phloroglucin to furfural, the larger is the solubility in alcohol of the precipitate. The amount of the phloroglucide (including alcohol-soluble part) always agreed well with the calculated value from the assumption that one mole of furfural condensed with one mole of phloroglucin under dehydration of two moles of water.

(16) W. C. Goodwin and B. Tollens, *Ber.*, **37**, 315 (1904).

Table 4

Effect of Phloroglucin added on the Solubility of Furfural-Phloroglucide in Alcohol

Furfural : Phloroglucin	Furfural Phloroglucide, theoretical	10 mg. 19.4 mg.	30 mg. 58.1 mg.	50 mg. 96.9 mg.	100 mg. 193.8 mg.
	Phloroglucide, observed, %*				
1 : 2	without alc.	93.8	100.3	99.1	—
	with alc.	69.5	88.6	91.1	95.5
1 : 3	without alc.	95.4	99.9	99.5	—
	with alc.	66.9	83.0	88.2	94.1
1 : 5	without alc.	93.8	100.6	99.9	—
	with alc.	54.1	78.3	84.9	91.7
1 : 10	without alc.	97.9	100.0	99.5	—
	with alc.	68.5	76.2	82.6	—

* Based on the theoretical amount.

Table 5

Effect of Phloroglucin added on the Solubility of Oxymethyl Furfural-Phloroglucied in Alcohol

Phloroglucin added*	Phloroglucide, observed, mg.		Apparent pentosan, %
1 : 2	without alc.	63.0	2.0
	with alc.	11.5	0.5
1 : 3	without alc.	63.3	2.0
	with alc.	10.8	0.5
1 : 5	without alc.	60.3	1.9
	with alc.	10.3	0.5
1 : 10	without alc.	60.9	2.0
	with alc.	11.0	0.5

* Based on apparent pentosan, 2% of the sample (glucose, 3.000 g.)

Next, similar procedures were applied to the oxymethyl furfural obtained from glucose by distillation with hydrochloric acid solution. From Table 5, it seems that neither the amount of phloroglucide nor its solubility in alcohol are influenced by the amount of phloroglucin added. But the color of the precipitate varied from brown to yellowish brown as the added amount was increased. This would indicate the composition of the phloroglucide varied according to the ratio of phloroglucin to oxymethyl furfural but its influence is not remarkable as the amount of the precipitate is small.

From the fact that the solubility of furfural-phloroglucide in alcohol increased with the amount of phloroglucin added, it is desirable to adjust the amount of phloroglucin added twice the theoretical. Therefore, expe iments were made on the mixtures of glucose and xylose (3 g. of glucose 10, 30, 50 and 100 mg. of xylose) adding twice plus the theoretical amount of phloroglucin to the distillate.

Results in Table 6 indicate the alcohol-extraction is useful especially for pentosan-poor samples,

Table 6

Solubility of Phloroglucide from Glucose-Xylose Mixtures

Sample, glucose 3 g. plus xylose, mg.	Xyolse, observed, mg.	
	without alc.	with alc.
10	72.6	17.0
30	90.5	36.1
50	105.5	58.7
100	151.8	112.0

but even in those cases, the amount of xylose observed is always greater than the true value. This is due to the presence of a greater amount of alcohol-insoluble phloroglucide from oxymethyl furfural than an alchool-soluble part of furfural-phloroglucide.

(d) **Discussion.**—The amount of alcohol-soluble phloroglucide of furfural increased with the amount of phloroglucin added. This indicates that the structure of furfural-phloroglucide is not constant. But, as above mentioned, the total amount of phloroglucide is independent of the phloroglucin added and consistent with the assumption that one mole of furfural condenses with one mole of phloroglucin under dehydration of two moles of water. From these results, the condensate is thought to be a relatively high-molecular compound as in furfural resin, with structures of chain type or more probably net-work type, and not to be a low-molecular compound. The size and shape of the condensate would vary with phloroglucin added and influence the solubility in alcohol. A distinct conclusion, however, can not be made without elementary analysis and molecular weight determination of the condensate.

In the case of oxymethyl furfural, the added amount of phloroglucin dose not influence the solubility in alcohol but the color change above mentioned may show structural variation of the condensate similar to the case of furfural-phloroglucide. In both cases, if the precipitate was

once dried, the solubility in alcohol was lowered perhaps by increased condensation. Even when wet, undried precipitate was treated with alcohol, and the solubility was considerably influenced by the method of filtration and the duration of time from filtration to the alcohol-treatment.

In conclusion, the alcohol-treatment of phloroglucide is useful to reduce remarkably the influence of hexosan on pentosan determination, but has the defects that the influence is not completely removed and the experimental reproducibility is not good because of complicated factors.

III. Colorimetry with Aniline and Comparison with Other Methods

1) **Experimental Procedures.**—Pentosan determination by colorimetry was in most cases applied to furfural produced by acid-distillation, but sometimes also applied to pentose itself obtained by acid hydrolysis.[17] Many color reagents such as benzidine,[18] xylidine,[19] orcin,[20] aniline[6]~[9] and p-bromoaniline[21] were used. It soon became evident from the preliminary work that the method of Stillings & Browning[8] gave good results. Then, this method was adopted with the following modifications.

Acetic acid-aniline reagent was prepared by dissolving 50 cc. of aniline in 500 cc. of glacial acetic acid. To 10 cc. of the neutralized distillate 50 cc. of the aniline solution was added and kept standing for half an hour at 25°C. Transmittancy of the solution was determined by the Hitachi EPO type photometer with a filter of 520 mμ, and compared with standard solution of furfural. In this and following experiments distillation was continued to 270 cc. to save the time of distillation. Furthermore, too long distillation gave rise to much quantity of oxymethyl furfural produced by side reaction (cf. Fig. 1).

2) **Experimental Results.** — Stability of the color reaction with aniline depends on temperature. As temperature lowers, rate of decolorization decreases and the stability increases as shown in Fig. 2. Colorimetry with aniline was applied to glucose-xylose mixtures and the results were compared with other methods as shown in Table 7. In Table 8, pentosan content in some cellulosi

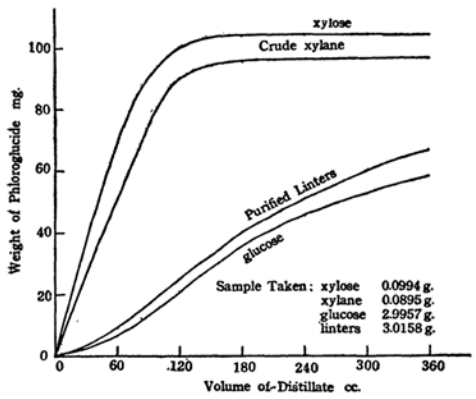

Fig. 1.—Effect of volume of distillate on the amount of phloroglucide produced.

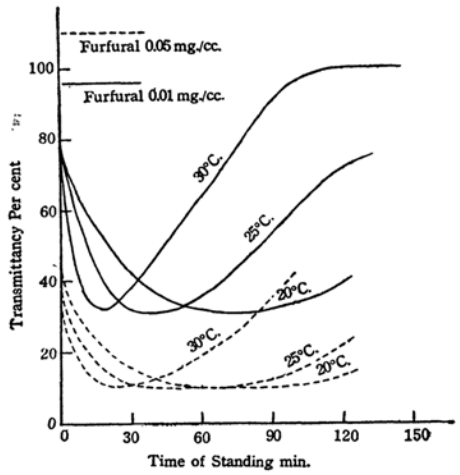

Fig. 2.—Effect of temperature on transmittancy.

Table 7

Comparison of Various Methods for Pentosan Determination

Sample, g.		Xylose, % theoretical	Xylose, % observed				Colorimetry
			Barbituric acid	Bromate	Phloroglucin		
Glucose	Xylose				without alc.	with alc.	
3.00	0	0	0	2.1	2.0	0.5	0.1
3.00	0.01	0.33	0	2.2	2.4	0.6	0.3
3.00	0.03	0.99	0	3.1	3.0	1.2	1.0
3.00	0.05	1.63	0	3.6	3.5	1.9	1.5
3.00	0.10	3.23	2.5	4.9	4.9	3.6	3.3

(17) G. L. Miller, R. H. Golder and E. E. Miller, *Anal. Chem.*, **23**, 903 (1951).
(18) R. A. McCance, *Biochem. J.*, **20**, 1111 (1926).
(19) K. Sumikura and Z. Nakamura, *Labr. Biol. Tottori Coll.*, 158 (1928).
(20) Analysis Comittee of the Central Laboratory of the Cellulose Industry, *Svensk Papperstid.*, **54**, 179 (1951).
(21) E. W. Rice, *Anal. Chem.*, **23**, 1501 (1951).

materials was determined by colorimetry. It was assumed that, in Table 8, pentosan in the samples was only xylan[22] and in Tables 6~8, conversion ratio of xylose to furfural was 86%.

Table 8

Pentosan Content in Some Cellulosic Materials (Colorimetrically Determined)

Sample	Pentosan, %
Unbleached pulp for viscose rayon	2.46
Purified pulp for cellulose ester	0.61
Rayaceta	0.74
Secondary cellulose acetate from Rayaceta	0.25
Secondary cellulose acetate (Hercules)	0.37
Secondary cellulose acetate (Eastman)	0.36
Viscose staple	0.92
Viscose rayon	0.53
Bleached linters	0.25
Raw Egypt cotton (alcohol-benzene extracted)	0.50

3) **Discussion.**—Table 7 shows that, for the estimation of a small quantity of pentosan, the colorimetry is superior to other methods. The next one is phloroglucin method with the alcohol-treatment. But, as already mentioned before, experimental reproducibility of the latter is inferior to that of the colorimetry and the method gives high values to pentosan-poor materials and presumably low values for pentosan-rich ones, because of partial solubility of furfural and oxymethyl furfural-phloroglucide in alcohol. Barbituric acid method[1] gives always low values and especially for the samples, in which pentosan content is under 1.5%, no precipitate being formed. Bromate method[23] (not corrected for oxymethyl furfural) agrees very well with phloroglucin method[24] without the alcohol-treatment but they give a higher result (about 2%) than the true value. This higher value (2%) might seem too large as compared with the values reported by other investigators but it may be accounted for by the differences in distillation apparatus and conditions which affect the amount of oxymethyl furfural as mentioned before, or for the characteristics of cellulose materials as pointed out by Meller.[25]

In conclusion, colorimetry is superior to other methods for the determination of a small quantity of pentosan. Phloroglucin method with alcohol-treatment considerably removes the influence of hexosan and has a limited usefulness.

Summary

1. For the estimation of a small quantity of pentosan in cellulosic materials, an improvement of phloroglucin method and colorimetry with aniline were investigated on mixtures of glucose and xylose, and the results were compared with bromate, the usual phloroglucin and barbituric acid methods.

2. Treatment of the undried phloroglucide with alcohol remarkably removes the influence of hexosan on pentosan determination but it is not complete. As the solubility of the furfural-phloroglucide increases with phloroglucin added, it is desirable to increase the amount of the latter to twice the theoretical.

3. Colorimetry with aniline is superior to other methods. The color reaction is stable at low temperatures.

4. Pentosan contents of some cellulosic materials, such as rayons, pulps and cellulose acetates, are tabulated.

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(22) H. Sobue and A. Hateno, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, **55**, 131 (1952).
(23) *Tappi Standard* T 19 m-50 (1950).
(24) *Toppi Standard* T 223 m-48 (1943).
(25) A. Meller, *Paper Trade J.*, **124**, No. 9, 104 (1947); **125**, No. 11, 57 (1947).