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DETERMINATION OF ALPHA-CELLULOSE

Report of Work of Subcommittee 2 of the Division of Cellulose Chemistry of the American Chemical Society

By GEORGE J. RITTER
Chairman

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By GEO. J. RITTER, Chairman

To make comparable the results of the determination of alpha-cellulose by various investigators, producers, and consumers of cellulosic materials such as cotton linters and wood pulps, the Alpha-Cellulose Committee was appointed by the chairman of the Division of Cellulose Chemistry of the American Chemical Society. The Committee was instructed to conduct the necessary investigative work in order that a tentative standard method might be recommended to the Cellulose Division.

H. LeB. Gray, chairman of the Cellulose Division, appointed the following members of the Alpha-Cellulose Committee February 16, 1925: George J. Ritter, C. A. Brautlecht, W. W. Farnum, H. LeB. Gray, L. O. Littleton, F. Olsen, J. L. Parsons, C. J. Staud, C. S. Venable, and S. Wang.

Attributes of a Standard Method

A method which is to be used by scientific investigators, cellulose-producing, and cellulose-using industries should be simple and accurate, and it should give check results by different analysts who are analyzing the same materials.

Method of Attack

Scope of work.--Believing that a review of the literature on the various methods, supplemented by any necessary experimental work on variables, would make it possible to draw up a simple, specific, tentative standard method, the Committee followed such a program and prepared directions for two methods. These two methods were tested for accuracy in cooperating laboratories. The test was made on five different cellulose materials consisting of two grades of cotton linters and three grades of sulfite pulp. From a study of the results and comments obtained from the tests of Methods I and II, the Committee prepared directions for Method III, which was tested in a manner similar to that of the first two methods, and, finally from the experience, results, and comments accumulated from tests of the three methods

some further modifications to the procedure for determining alpha-cellulose were made. These modifications were incorporated in the directions for Method IV, which was also tested by cooperating laboratories on materials similar to those used for the three preceding methods.

Review of Literature

A large number of methods for determining alpha-cellulose were reviewed. The procedures were compared for the purpose of classifying the common, specific, desirable, and undesirable features of each. Such a classification served as a guide in deciding which variables in the procedure needed further study and which should be incorporated in the tentative standard method.

Fortunately, the Committee had the benefit of the findings obtained by several other investigations in the same and closely allied fields. D'Ans and Jaeger[1] reported the effect of varying the concentrations of alkali on the swelling of cellulose. Schwalbe[2] has discussed in several reports the results obtained by comparing the yields of alpha-cellulose obtained when the determination was made by different methods. Ross[3] studied the effect on the yields of alpha-cellulose when some of the more important steps in the procedure were varied. Parsons[4] summarized the status of the alpha-cellulose determination in 1926. Porrvik[5] in a series of papers added a valuable contribution to the status of the alpha-cellulose determination. Jahn and Wise[6] studied the effect of various concentrations of the mercerization solution on the yields of alpha-cellulose.

Experiments on variables.--Inasmuch as certain variables in the test procedure cause conflicting results and opinions both directly and indirectly when the various methods for determining alpha-cellulose and their accompanying literature are compared, the Committee decided to study the effect of the following variables on the alpha-cellulose yield:

1. Dilution of the alkali-cellulose mixture with water before filtering
2. Temperature of wash water

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[1] D'Ans and Jaeger, Cellulosechemie 6, 137 (1925).

[2] Schwalbe, Papier-Fabr., 23, 477, 697 (1925); 26, 189 (1928).

[3] Ross, Research Notes, Can. Pulp Paper Assocn., 1, 37, 57 (1926).

[4] Parsons, Paper Trade J., 82, No. 8, 211 (1926).

[5] Porrvik, Papier-Fabr., 26, 81, 120, 133, 151, 179 (1928).

[6] Jahn and Wise, Paper Ind., 10, 250 (1928).

3. Solubility of cellulose in the mercerization solution:
   (a) In 17.5 per cent sodium hydroxide solution
   (b) In 17.5 per cent "sodium hydroxide-cellulose" solution
4. Concentration of the mercerizing solution
5. Mercerization in air compared to nitrogen

The results obtained from the study of the variables are given.

(1) Dilution of the sodium hydroxide-cellulose solution with an equal volume of water and stirring immediately preceding filtering does not precipitate any beta-cellulose. It does reduce the viscosity of the solution, facilitates filtering, and is therefore a desirable feature to include in a method.

(2) Wash water at 20° C. was compared with water at higher temperatures to determine the effect on the yields of alpha-cellulose. The results were in close agreement. A tentative standard temperature of 20° C. was chosen for the wash water.

(3) The solubility of cellulose in sodium hydroxide solution and sodium hydroxide solution containing dissolved cellulose was compared. The cellulose was more soluble in the sodium hydroxide solution.

(4) Of the methods studied, some used 17.5 per cent and others 15.6 per cent sodium hydroxide as the mercerizing solution. A comparison was made of the yields of alpha-cellulose obtained by using those two concentrations of alkali. The yields checked within the experimental error. The weaker solution was considered an economic saving and also more desirable to filter. Therefore, 15.6 per cent was chosen as the concentration to be used in Methods I and II.

(5) A comparison of the mercerization in air and in nitrogen showed the alpha-cellulose yields to check within the experimental error.

Method I

Conditioning of sample.--The cotton is given no preliminary treatment. Pulps are cut into 0.75-inch (1.9-cm.) squares. The material to be used for moisture and alpha-cellulose determinations is placed in a glass-stoppered bottle or equivalent fruit jar for 48 hours to attain a uniform moisture content throughout the sample.

Method.--Approximately a 3-gram sample, weighed accurately, is placed in a 250-cc. Pyrex beaker. Sixty cubic centimeters of 15.6 per cent, carbonate-free sodium hydroxide solution (17.5 grams of

sodium hydroxide in 100 cc. of solution) at 20° C. are added. With a short glass rod, the end of which has been flattened out to form a disk 1 cm. in diameter, the pulp is macerated until thoroughly disintegrated and penetrated with the alkali solution. The beaker is covered with a watch glass. After 30 minutes' mercerizing treatment in a water bath at 20° C., 60 cc. of distilled water (20° C.) are added to the alkali-cellulose mixture followed by thorough stirring. The contents of the beaker are transferred immediately to a tared Gooch crucible having a finely perforated bottom, and the cellulose is allowed to form its own mat. The filtrate is poured through the mat a second and third time, if necessary, to catch any fine material. The residue in the Gooch is washed, by means of suction, with 750 cc. of distilled water (20° C.). The suction tube is disconnected, 50 cc. of 10 per cent acetic acid (20° C.) are added and allowed to soak 5 minutes. Then suction is applied to remove the acid. The alpha-cellulose is washed with distilled water (20° C.) until free from acid. Without removing from the Gooch, the alpha-cellulose is dried at 105° C. to a constant weight. The Gooch and contents are placed in a glass weighing bottle, cooled in a desiccator for 30 minutes, and weighed.

The alpha-cellulose yield is calculated on the oven-dry weight of the material. Duplicate 3-gram samples for moisture determination are weighed out at the same time that the samples for alpha-cellulose determination are taken.

Results of test.--The results obtained from the analyses of the five samples of cellulosic materials by eight cooperating laboratories are recorded in the accompanying table.

Method II

The procedure for Method II is the same as for Method I, except that the time of mercerization for Method II is 120 minutes.

Results of test.--The results obtained from the analyses of five samples of cellulosic materials by seven cooperating laboratories are recorded in the accompanying table.

Discussion of results of Methods I and II.--There is no uniform difference in the alpha-cellulose yields on the five substances among the cooperating laboratories. That is, neither Method I nor II give slightly higher yields consistently. From the results it is apparent that, under the conditions of maceration used in Methods I and II, a 30-minute treatment of the cellulose with the alkali is as efficient in removing the so-called beta- and gamma-cellulose as is a 120-minute treatment.

Development of Method III.--From a consideration of the comments received with the analytical results from the cooperating laboratories, it was decided that 17.5 per cent sodium hydroxide would be more acceptable than a 15.6 per cent sodium hydroxide as a mercerizing solution. In order to remedy some other objections to the method, the ratio of alkali to the cellulose was increased from 60 to 75 cc. for 3 grams of cellulose. The period of mercerization was increased to 45 minutes to allow more specific directions for macerating troublesome cellulosic materials. The size of the pulp particles in the sample was decreased from 0.75- (1.9-cm.) to 0.50-inch (1.25-cm.) squares.

Method III

Preparation and conditioning of sample.--The cotton is given no preliminary treatment. Pulps are cut into 0.5-inch (1.25-cm.) squares. The material to be used for moisture and alpha-cellulose determinations is placed in a glass-stoppered bottle or fruit jar for 48 hours to attain a uniform moisture content throughout the sample.

Method.--Approximately a 3-gram sample weighed accurately in a weighing bottle is placed in a 250-cc. Pyrex beaker. Seventy-five cubic centimeters of 17.5 per cent, carbonate-free sodium hydroxide solution (17.5 grams of sodium hydroxide in 100 grams of solution) at 20° C. are added. (See Notes for the preparation of same.) With a short glass rod, the end of which has been flattened out to form a disk 1 cm. in diameter, the pulp or cotton is macerated until thoroughly disintegrated and penetrated with the alkali solution. The beaker is covered with a watch glass. After 45 minutes' mercerization treatment in a water bath at 20° C., 75 cc. of distilled water (20° C.) are added to the alkali-cellulose mixture followed by thorough stirring. The contents of the beaker are immediately transferred to a 40-cc. Gooch crucible (see Notes) having a finely perforated bottom, and the cellulose is allowed to form its own mat. The filtrate is poured through a second and third time, if necessary, to catch any fine material. The residue in the Gooch crucible is washed by means of suction with 750 cc. of distilled water (20° C.). The suction is disconnected, 40 cc. of 10 per cent acetic acid (20° C.) are added and allowed to soak 5 minutes. Then the suction is applied to remove the acid. The alpha-cellulose is washed with distilled water (20° C.) until free from acid. Litmus paper is used to test the filtrate (see Notes). The alpha-cellulose is carefully removed from the Gooch to a tared, flat, glass-stoppered weighing bottle. The alpha-cellulose sample is opened and dried at 105° C. to a constant weight (see Notes). The weighing bottle and its contents are allowed to cool in a desiccator for 30 minutes and then weighed.

The alpha-cellulose yield is calculated on the oven-dry weight of the material. Duplicate 3-gram samples for moisture determination are weighed out at the same time that the samples for alpha-cellulose determination are taken.

Notes on Method III.--(1) Preparation of sodium hydroxide solution. The sodium hydroxide solution is prepared by dissolving sticks of alkali in an equal weight of water and allowing to stand 10 days for the sodium carbonate and impurities to settle. The clear supernatant liquid is decanted, diluted with an equal volume of carbon dioxide-free water, cooled at room temperature, and its strength determined by titration with a standard acid. It is then diluted to give a solution containing 17.5 per cent by weight of sodium hydroxide (17.5 grams of sodium hydroxide in 100 grams of the solution).

(2) Time interval for steps in procedure. An interval of 10 minutes should elapse between the times of starting the alkali treatment of the individual triplicate samples. Such a procedure allows time before proceeding to the next sample in the triplicate determination for the various steps such as impregnating, macerating, filtering, and partial washing.

If 2 minutes are allowed between the addition of the alkali and the beginning of maceration, it will be found that sulfite pulp swells to five or six times its original volume, and the fibers can be much more easily macerated. The remaining 8-minute interval has been found ample time for the maceration of most pulps. With such a scheme, for example, the alkali would be added to the samples at 9:00 o'clock, 9:10, and 9:20, respectively. Filtering would begin at 9:45 o'clock, 9:55, and 10:05, respectively.

(3) Filtering medium. A coarse Jena glass filter crucible may be used in place of the Gooch crucible specified in the directions.

(4) Testing for acidity. To test the acidity of the wash water on litmus paper the last few drops removed after the addition of water should be used.

(5) Drying to constant weight. The constant weight obtained in a minimum time should be used; that is, the first constant consecutive weights at hour intervals after approximately 4 hours of drying. It is reported that cellulose dried 12 to 16 hours increases in weight.

Results of test of Method III.--The results obtained from the analyses of five samples of cellulosic materials by eight cooperating laboratories are recorded in the accompanying table.

Development of Method IV.--A careful study of the results from the test of Method III and of the comments from the cooperating laboratories led the Committee to believe that the time allowed for macerating hard pulps should be increased and that only part of the alkali should be added to the sample before maceration is begun; the remainder added during maceration as noted in the directions. The method for standardizing the sodium hydroxide solution was also simplified.

Pulp T-600 consisted of a mixture of a medium soft and a hard pulp. This sample caused the analysts considerable difficulty in macerating it. Cotton C-200 was known to furnish difficulties in alpha-cellulose determination and was also included to give the method a severe test.

Method IV

Preparation and conditioning of sample.--The cotton is given no preliminary treatment. Pulps are cut into 0.5-inch (1.25-cm.) squares. The material to be used for moisture and alpha-cellulose determinations is placed in a glass-stoppered bottle or equivalent fruit jar for 48 hours to attain a uniform moisture content throughout the sample.

Method.--Approximately a 3-gram sample, weighed accurately in a weighing bottle, is placed in a 250-cc. Pyrex beaker. Thirty-five cubic centimeters of 17.5 per cent, carbonate-free sodium hydroxide solution (17.5 grams of sodium hydroxide in 100 grams of solution) (20° C.) are added (see Notes for the preparation of the same) and the solution is allowed to stand for 5 minutes. With a short glass rod, the end of which has been flattened out to form a disk 1 cm. in diameter, the pulp or cotton is macerated for 10 minutes, adding intermittently in 10-cc. portions a total of 40 cc. of sodium hydroxide solution (20° C.) during this interval (see Notes). The beaker is covered with a watch glass. After 30 minutes' additional mercerizing treatment in a water bath at 20° C. (total mercerization time, 45 minutes), 75 cc. of distilled water (20° C.) are added to the alkali-cellulose mixture followed by thorough stirring. The contents of the beaker are filtered immediately by means of suction on a 40-cc. Gooch crucible (see Notes) having a finely perforated bottom, allowing the cellulose to form its own mat. The filtrate is poured through the mat a second and a third time, if necessary, to catch any fine material. The residue in the Gooch crucible is washed with 750 cc. of distilled water (20° C.) by means of suction. The suction tube is disconnected, 40 cc. of 10 per cent acetic acid (20° C.) are added and allowed to soak 5 minutes. Then the suction is applied to remove the acid. The alpha-cellulose is washed with distilled water (20° C.) until free from acid. Litmus paper is used to test the filtrate (see Notes). The alpha-cellulose is carefully removed from the Gooch to a tared, flat, glass-stoppered weighing bottle. The alpha-cellulose is opened and dried at 105° C. to a constant weight; that is, the first constant consecutive weights obtained after 1-hour heating intervals following an initial drying of at least 6 hours. The weighing bottle and its contents are allowed to cool in a desiccator for 30 minutes and then weighed.

The alpha-cellulose yield is calculated on the oven-dry weight of the material. Duplicate 3-gram samples for moisture determination should be weighed out at the same time that the samples for the alpha-cellulose determination are taken.

Notes on Method IV.--(1) Preparation of sodium hydroxide solution. The sodium hydroxide solution is prepared by dissolving sticks of alkali in an equal weight of water, and allowing it to stand 10 days for the sodium carbonate and impurities to settle. The clear, supernatant liquid is decanted and diluted with carbon dioxide-free water until its density at 15° C. is 1.197. Such a solution contains 17.5 ± 0.1 grams of sodium hydroxide per 100 grams of solution.

(2) Time interval for steps in the procedure. An interval of 15 minutes should elapse between the times of starting the alkali treatment of the individual triplicate samples. Such a procedure allows time before proceeding to the next sample in the triplicate determination for the various steps in the procedure, such as impregnation, maceration, filtration, and partial washing.

If 5 minutes are allowed between the addition of a part of the alkali and the beginning of maceration, it will be found that sulfite pulp swells to five or six times its original volume, and the fibers can be much more easily macerated. The remaining 10-minute interval, during which the remaining 40-cc. portion of the alkali is added, making a total of 75 cc., has been found ample time for the maceration of pulps. With such a scheme, for example, one would add the alkali to the samples at 9:00 o'clock, 9:15, and 9:30, respectively. Filtering would begin at 9:45 o'clock, 10:00, and 10:15, respectively.

(3) Filtering medium. Jena glass filter crucibles (coarse) may be used in place of the gooch crucibles specified in the directions.

(4) Testing for acidity. To test the acidity of the wash water on litmus paper, the last few drops removed after the addition of water should be used.

Results of test of Method IV.--The results obtained from the analysis of four samples of cellulosic material by nine cooperating laboratories are recorded in the accompanying table.

Some standard cotton cellulose[7] was also analyzed according to Method IV for its alpha-cellulose content. Two sets of triplicate analyses gave the following results:

	(1)	(2)
	99.45	99.60
	99.52	99.70
	99.59	99.72
Av.	99.52	99.67

[7] Corey and Gray, Ind. Eng. Chem., 16, 853, 1130 (1924).

Discussion of results of Method IV.--With materials in which it is possible to obtain a uniform sample and with which the maceration offers no extreme difficulties such as Cotton C-100 and Pulp T-500, the cooperating laboratories checked one another closely; with materials Cotton C-200 and Pulp T-600, the results were less uniform.

Recommendations

The Committee feels that further modifications of any of the steps in the procedure will not overcome irregularities in the uniformity of the alpha-cellulose determination of certain cellulosic materials occasionally found in the industry. The Committee suggests that in event a dispute arises between the producer and consumer as to the alpha-cellulose content in cellulosic materials, the dispute be settled by a referee through a procedure similar to that followed in the Association of Official Agricultural Chemists. On the other hand, the Committee has found that where good grades of cotton or pulp are used, such as are required for manufacturing cellulose derivatives and artificial silk, there should be no occasion for a dispute as to the alpha-cellulose content if Method IV is used. Therefore, Method IV is recommended to the Cellulose Division of the American Chemical Society as a tentative standard method for the determination of alpha-cellulose.

The Committee urges workers to use Method IV and to send the Committee suggestions, so that proper action may be taken to have a standard method available which may meet the demands of future developments in cellulose chemistry.

The Committee wishes to thank the cooperating laboratories and companies for their splendid spirit shown in supplying the cotton linters and pulps, and doing the necessary analyses which were required to investigate the determination of alpha-cellulose.

The Committee further recommends that this report be published by the American Chemical Society.

Average of Triplicate Determinations of Alpha-Cellulose Content and Variation from Average of Materials Tested

(Results based on oven-dry weight of materials)

Laboratory	Cotton 1-A		Cotton 1-B	
	Average	Variation from average	Average	Variation from average
	Per cent	Per cent	Per cent	Per cent
Method I				
A	99.50	+ 0.07	91.64	- 0.86
B	99.62	+ .19	95.21	+ 2.70
C	99.52	+ .09	91.36	- 1.14
D	99.17	- .26	91.70	- .80
E	99.36	- .07	92.36	- .14
F	99.09	- .34	91.59	- .91
G	99.60	+ .17	93.56	+ 1.06
H	99.60	+ .17	92.60	+ .10
Average	99.43	.17	92.50	.96
Method II				
A	99.26	- .08	92.38	- .13
B	99.63	+ .29	95.09	+ 2.58
C	99.42	+ .08	91.95	- .56
D	99.30	- .04	93.00	+ .49
E	99.29	- .05	91.35	- 1.16
F	99.20	- .14	91.67	- .84
G	99.26	- .08	92.14	- .37
Average	99.34	.11	92.51	.88
	Cotton 40		Cotton 50	
Method III				
A	99.84	+ 0.52	93.46	+ 0.52
B	99.35	+ .03	92.56	- .38
C	99.41	+ .09	94.02	+ 1.08
D	99.78	+ .46	91.86	- 1.08
E	99.31	- .01	92.80	- .14
F	99.50	+ .18	92.22	- .72
G	99.60	+ .28	93.60	+ .66
H	97.87	- 1.45	93.04	+ .10
Average	99.32	.37	92.94	.58
	Cotton C-100		Cotton C-200	
Method IV				
A	99.30	+ 0.06	93.06	+ 1.59
B	99.00	- .24	91.33	- .14
C	99.47	+ .23	91.11	- .36
D	99.37	+ .13	91.07	- .40
E	99.44	+ .20	93.50	+ 2.03
F	99.27	+ .03	90.06	- 1.41
G	99.32	+ .08	91.30	- .17
H	98.84	- .40	90.78	- .69
I	99.19	- .05	91.04	- .43
Average	99.24	.15	91.47	.80

(Continued)

Laboratory	Pulp 1		Pulp 2		Pulp 3	
	Average	Variation from average	Average	Variation from average	Average	Variation from average
	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
Method I						
A	88.66	- 0.17	83.21	- 0.30	82.97	+ 0.61
B	87.71	+ .88	85.90	+ 2.39	84.68	+ 2.32
C	86.37	- .46	83.02	- .49	86.63	+ .27
D	86.79	- .04	83.57	+ .06	82.42	+ .06
E	86.33	- .50	82.24	- 1.27	80.14	- 2.22
F	86.44	- .39	83.21	- .30	81.96	- .40
G	87.05	+ .22	82.92	- .59	82.79	+ .43
H	87.34	+ .51	84.05	+ .54	81.30	- 1.06
Average	86.83	.39	83.51	.75	82.36	.92
Method II						
A	86.63	- .22	83.85	+ .47	82.74	+ .51
B	88.34	+ 1.49	85.63	+ 2.25	83.95	+ 1.72
C	86.82	- .03	82.15	- 1.23	81.68	- .55
D	86.57	- .18	83.07	- .31	81.85	- .38
E	86.41	- .44	82.54	- .84	80.25	- 1.98
F	86.28	- .57	83.12	- .26	81.85	- .38
G	86.92	+ .07	83.34	- .04	83.32	+ 1.09
Average	86.85	.43	83.38	.77	82.23	.94
	Pulp 10		Pulp 20		Pulp 30	
Method III						
A	87.35	+ 0.34	84.68	+ 0.49	84.59	+ 0.96
B	86.71	- .30	84.31	+ .12	83.36	- .27
C	87.13	+ .12	85.55	+ 1.36	83.65	+ .02
D	86.50	- .51	84.01	- .18	83.34	- .29
E	86.95	- .06	83.53	- .66	83.28	- .35
F	86.32	- .69	82.63	- 1.56	82.19	- 1.44
G	87.47	+ .46	84.40	+ .21	84.70	+ 1.07
H	87.70	- .69	84.46	+ .27	83.98	+ .35
Average	87.01	.39	84.19	.60	83.63	.59
	Pulp T-500		Pulp T-600			
Method IV						
A	86.35	- 0.01	82.56	- 0.26		
B	86.26	- .10	83.10	+ .28		
C	86.33	- .03	82.56	- .26		
D	85.78	- .58	81.58	- 1.24		
E	87.03	+ .67	84.22	+ 1.40		
F	86.53	+ .17	83.82	+ 1.00		
G	86.58	+ .22	82.37	+ .05		
H	86.00	- .36	81.67	- 1.15		
I	86.36	.00	83.02	+ .20		
Average	86.36	.23	82.82	.64		