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SIMPLIFIED VOLUMETRIC DETERMINATION OF ALPHA, BETA, AND GAMMA CELLULOSE IN PULPS AND PAPERS

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ABSTRACT

A relatively rapid and simple method for the determination of alpha, beta, and gamma cellulose is described. The method ordinarily employs a 0.3-g sample, which need not be weighed accurately, but a 0.03-g sample also gives fair results. Neither ash nor moisture determinations are involved, in fact, no precision weighings are made. The cellulose is oxidized by potassium dichromate solution, the strength of which need not be known accurately, as the concentrations of the oxidimetric solutions do not enter into the calculations. The volumetric results are in good agreement with those of a gravimetric method, and are as reproducible, for widely different materials. The actual working time for four complete determinations is 1½ to 2½ hours. Fundamental facts recently found concerning the separation of the cellulose fractions have been incorporated in the method. A calculation based upon the volumetric and gravimetric data for alpha cellulose indicates that the pentosans in the pulps studied are distributed among the alkali-soluble and alkali-insoluble fractions in approximately the same ratio as cellulose. It was also found that the amount of beta cellulose which precipitates is dependent upon the temperature, and that the separation should be made without heating the acidified filtrate.

CONTENTS

I. INTRODUCTION

Cellulose consists analytically of three fractions, alpha, beta, and gamma, which terms have been defined frequently in the literature.[1][2][3][4][5][6][7]

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[1] Jentgen, also Bubeck. See Schwalbe, Papier-Fabr. **26**, 196 (1928), for these and further references.

[2] Burton and Rasch, BS J. Research **6**, 603 (April 1931) RP295. See also TAPPI tentative standard T429m, Alpha Cellulose in Paper, also T203m, Alpha Cellulose in Pulp.

[3] Ritter, Ind. Eng. Chem., Anal. Ed. **1**, 52-4 (1929).

[4] Bray and Andrews, Ind. Eng. Chem., **15**, 377 (1923). See discussion also in Hawley and Wise, The Chemistry of Wood, p. 144-148 (Chemical Catalog Co., Inc., New York, N. Y.)

[5] Lewis and Browning, Paper Trade J. **97**, 39 (Dec. 1933).

[6] Methods used at the U. S. Forest Prod. Lab., Compiled by Bray, Paper Trade J. **87**, no. 25, 63-4 (Dec. 20, 1928).

[7] Porrvik, Papier-Fabr. **26**, 81 (1928).

The alpha fraction is the cellulose which can be filtered from a mixture consisting of sodium hydroxide solution and the material being analyzed. Further differentiation is obtained by acidification of the filtrate, whereupon the beta fraction precipitates, and the gamma fraction remains in solution. Such a definition is dependent upon the factors involved in the separation, such as amount and concentration of the sodium hydroxide solution, the physical state of the fibers, such as freeness and extent of fibrillation, the time of contact between solution and fibers, and the method of filtering and washing. Thus, the values obtained for the cellulose fractions depend upon the particular method used, although the values found in the literature for certain well-known materials differ by only 1 to 2 percent.

A high content of alpha cellulose usually indicates good quality, as for example, stability of the finished material, other things being equal. The interest in beta and gamma cellulose seems to be solely academic. The correlation between the quality of the cellulose product and the alpha-cellulose content is, however, not close enough to indicate which of the existing methods yields the most useful values. Furthermore, the experiments of Porrvik [8] and of Lewis and Browning indicate that alpha cellulose will dissolve indefinitely if treated with fresh portions of sodium hydroxide solutions. Apparently no practicable method for routine and control work can yield a value which is a fundamental constant for a given material.

It seems, therefore, that the only criteria for the suitability of a given method are its simplicity and rapidity of execution, and its reproducibility, not only as regards agreement between duplicate determinations, but also as regards comparison between various papers among themselves, or with the original pulp. It frequently happens that a pulp may be filtered in 5 to 30 minutes, whereas a paper made from the pulp may require 3 to 5 times as long, sometimes 3 to 4 hours in extreme cases. The corresponding alpha-cellulose values obtained by commonly used methods would not be comparable for such a case, for, as Porrvik and Lewis and Browning have shown, large differences (2 percent, within a given method) in alpha-cellulose content may arise from variations in the rates of filtration, unless the cellulose-alkali mixture is allowed to stand a certain length of time after dilution. The rate of filtration appears to have very little effect if the mixture is filtered 1 hour or more after dilution. It appears that all the reactions between cellulose and alkali should be given a sufficient length of time to reach equilibrium. This applies to the washing as well as to the mercerization.

The alternative of allowing a reaction to reach equilibrium in order to achieve reproducibility is to allow the reaction to proceed for a definite length of time. The Faserstoff-Analysenkommission [9] specify exactly 5 minutes for washing the alpha cellulose with a definite quantity of 8-percent alkali. This is impossible to regulate in the case of paper, which fact is tacitly recognized by them, since they consider their method to be applicable only to pulps.

At the National Bureau of Standards it was necessary to develop a method which would be valid for the analysis not only of pulps but also of the papers usually causing difficulties in filtering. Special

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[8] See footnotes 5 and 7.

[9] Faserstoff-Analysenkommission des Vereins der Zellstoff und Papier-Chemiker und -Ingenieure, Papier-Fabr. **32**, 521 (1934).

attention was paid to the aspects of simplicity, rapidity of operation, and reproducibility, especially of the type mentioned. The mercerizing procedure of Lewis and Browning was adopted, including observance of the time necessary to reach equilibrium in the swelling in 17.5-percent, and subsequent standing in the diluted (7.3-percent) alkali. The alpha cellulose was washed with water only.[10] In this way, any uncertainties arising from variations in the rate of washing with sodium hydroxide solutions are avoided. Furthermore, the ratio of the volume of alkali to the weight of sample has been made unusually large to minimize errors due to "drop losses."

The method described in the present article is based entirely upon volumetric procedures. It is simple and rapid, since no precision weighings are involved, and since the sample taken for analysis is small, 0.3-g. Moisture and ash determinations on the ground material, indispensable in other methods, are not made. The entire alpha-cellulose portion, and large aliquot parts of the filtrate, one-half and one-quarter, for the beta plus gamma, and gamma portions, respectively, are oxidized with dichromate solution, the strength of which need not be known accurately. The method, using a 0.3-g sample, is shown to be equal in precision to gravimetric methods employing much larger samples. Even a 0.03-g sample was found to yield fair results. Aside from the obvious advantages of a precision method which is applicable when only small samples are available, the use of a small sample has the advantage that the entire separation even in the worst cases requires less than one-half hour. The 3- to 5-g samples ordinarily employed require up to 3 or 4 hours in such cases. For most pulps, eight complete separations of the alpha from the soluble cellulose can usually be made per hour with the method described in this article. For most papers, the corresponding number per hour is six to seven. Thus, four complete determinations of alpha, beta, and gamma cellulose require an actual working time of 1½ to 2½ hours, which is about one-eighth to one-fourth of the time necessary for the same number of determinations by any other method.

Bray and Andrews,[11] who adapted Bronnert's[12] method for determining alkali-soluble cellulose with dichromate to the alpha, beta, and gamma cellulose determination, discuss further advantages inherent in volumetric methods. Their procedure involves, however, the usual moisture and ash determinations, and recommends the standardization of the potassium dichromate solution against "Cross and Bevan cellulose" from sulfite pulp. They limit their comparison of the volumetric and gravimetric results to a study of spruce sulfite pulp. However, their method of filtration is not suitable for paper analyses and they take one-tenth and one twenty-fifth aliquot parts for the alpha, beta plus gamma, and also gamma fractions, respectively, whereby errors in the dichromate determinations are multiplied by 10 and 25.

Porrvik[13] uses a volumetric method which is peculiarly adapted to the needs of the rayon industry. In this method only a partial (5/8) separation of alpha from beta and gamma cellulose is attempted, and

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[10] Thirty-five mililiters of water is sufficient. It was found that further washing extracts no more cellulose.

[11] Bray and Andrews, Ind. Eng. Chem. **15,** 377 (1923). See discussion also in Hawley and Wise, The Chemistry of Wood, p. 144-148. Chemical Catalog Co., New York, N. Y.). The method is quite similar to that of the Faserstoff-Analysenkommission (footnote 9).

[12] In Schriften des Vereins der Zellstoff und Papier-Chemiker **13.** Die chemische Untersuchung pflanzlicher Rohstoffe und der daraus abgeschiedenen Zellstoff, compiled by C. G. Schwalbe. Published by Verlag der Papier-Zeitung. C. Hofmann, Berlin (1920). It is a report on the secret process of the Bayerische Glanzstoffwerke, and is very incomplete.

[13] Porrvik, Papier-Fabr. **26,** 81 (1928).

very small aliquot parts, 1/120 and 1/150, for the alpha and gamma portions, respectively, are taken. Furthermore, Porrvik works only with bleached sulfite pulp and makes no comparison with the results of a gravimetric method for alpha cellulose.

The gravimetric methods [14] include for duplicate determinations, 22 precision weighings, including 12 for moisture and ash; 6 more are necessary if beta cellulose is to be determined.

The materials studied in this work were soda pulp, refined sulfite and sulfate pulps, known on the market as "alpha" pulp and bleached sulfate, respectively, also no. 1 old white rags, no. 1 new white rags, and no. 1 new white rag paper. The resins in these materials did not in any case exceed 0.2 percent, and were neglected. It will be shown in a later paper that this has no effect upon the results and also that a correction may be applied for larger amounts of resin.

II. METHOD IN DETAIL

1. MERCERIZATION AND FILTRATION

Approximately 0.3-g of the material reduced to fibrous condition in a "Dr. Koerner-type" grinder and well-mixed [15] is weighed in a 100-ml beaker to the nearest 10 mg. 20.0 ml of 17.5-percent [16] sodium hydroxide solution is added to the sample, which is then macerated until uniformly wet and dispersed, and allowed to stand for 10 minutes. 33.0 ml of water is then added, the mixture thoroughly stirred, and allowed to stand for 1 hour, stirring once during the interval. After stirring once more, about 5 ml of the unsettled mixture is poured into a Gooch crucible and allowed to drain without suction. The filtrate and wash water run directly into a 100-ml volumetric flask. With very gentle suction (pressure differential 10 to 20 mm of Hg) the mat is formed through which the rest of the mixture is filtered. By avoiding excessive packing of the fibers owing to strong suction, very rapid filtering is usually secured. If the mat was successfully formed at the outset the filtrate is poured back through it only once. The mat without being broken up is then washed with 35 ml of water. The filtrate is diluted to the mark and treated as described later in section 3. The alkali-cellulose mixture, as well as the water and sodium hydroxide solution, are kept at 20.0 ± 0.1° C.

2. TREATMENT OF THE ALPHA CELLULOSE

The alpha cellulose is moistened and removed from the crucible. The crucible is placed upright in a 400-ml beaker and filled with 25 ml of $12M$ (approximately 75-percent, by weight) sulfuric acid, at room temperature, and then rinsed after a few minutes with 50 ml more of the acid. The alpha-cellulose pad is then disintegrated in the acid using a thermometer as stirring rod. After the alpha cellulose has dissolved, 25.00 ml of potassium dichromate solution [17] is added. The

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[14] See footnotes 1, 2, 3, 5, and 6.

[15] The use of a small sample requires that the material be well mixed after grinding. This can readily be accomplished by such an apparatus as is described by Lewis and Browning. The present writer used an upturned bell jar, 30 cm diameter by 22 cm depth, upon which fits a heavy wooden lid, carrying a small motor and fan. By the proper placing of a vane to produce cross currents, the mixing of 40 g of material in 20 min was found to produce a sufficiently homogeneous sample, as the chemical tests showed.

[16] Made by diluting the 50-percent solution, from which the sodium carbonate has been allowed to settle, to $5.22N$, when titrated with standard acid using phenolphthalein. An excess of barium chloride is added at the beginning of the titration to remove carbonate from solution.

[17] The solution is made up directly from oven-dry (100 to 110° C) $K_2Cr_2O_7$ by dissolving 90.00 g in water at 70 to 90° C, allowing to cool to 20° C, and diluting to 1 liter. Its calculated normality is 1.835, but one of the advantages of the present method is that an exact knowledge of the strength of any of the oxidimetric solutions is not necessary.

solution is heated to 140 to 150° C, at which temperature it is maintained for approximately 10 minutes. Air is constantly bubbled in a fine stream through the solution to prevent troublesome bumping. The breaker should be covered with a watch-glass cut or notched to permit entrance of the thermometer and bubbling tube.

After the solution has cooled to 130 to 140° C, 50 ml of water is added, the thermometer, etc., are rinsed down, and the solution cooled to 60° C or lower. The remaining dichromate is then most simply titrated electrometrically [18] with 0.5*M* ferrous ammonium sulfate solution.[19]

3. TREATMENT OF THE FILTRATE

(a) BETA PLUS GAMMA PORTION

50.00 ml of the filtrate is pipetted into a 400-ml beaker containing 5.00 ml of the potassium dichromate solution. Cautiously, and with constant stirring, 50 ml of concentrated sulfuric acid is slowly poured down the side of the beaker. The solution is then heated and later titrated as in part 2.

(b) GAMMA PORTION

The pipette used to deliver the beta plus gamma portion is rinsed out into the remaining filtrate, which is then acidified with 15 to 16 ml of 6.0*N* sulfuric acid, using no indicator. After cooling, the cloudy mixture is diluted to 100 ml, poured into a Nessler tube or graduate cylinder and allowed to stand overnight. After the beta cellulose has settled, a 50.00-ml portion of the supernatant liquid is cautiously removed and treated exactly as noted in part (a). The beta plus gamma mixture should be at room temperature while the gamma portion is removed.

III. TREATMENT OF THE VALUES OBTAINED

1. CALCULATION OF THE PERCENTAGES OF ALPHA, BETA, AND GAMMA CELLULOSE

The percentage of each fraction of cellulose is calculated by dividing the volume of dichromate corresponding to it by the total volume of dichromate for all three fractions. For example, if the alpha cellulose used 18.48 ml, and the beta plus gamma cellulose used 3.48 ml of dichromate, then the total cellulose dichromate value is 21.96 ml, and the alpha-cellulose content [20] is

$$\frac{18.48}{18.48+3.48}\times 100=83.8\%.$$

The gamma-cellulose content is calculated in a like manner. The beta-cellulose content is found by difference.

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[18] A relatively inexpensive galvanometer with a sensitivity of 0.5 to 1 microampere per millimeter scale division, used in circuit with an ordinary sliding-contact rheostat, platinum electrode and calomel half-cell will suffice. The same titration may also be carried out, however, less rapidly, using potassium ferricyanide as outside indicator, in which case, 400, rather than 50, ml of water is added before titrating the dichromate in the alpha-cellulose determinations.

[19] Contains 195 g of $Fe(NH_4)_2(SO_4)_2.6H_2O$ and 10 ml of concentrated H_2SO_4 per liter. If the solution is kept out of contact with oxygen its strength remains fairly constant.

[20] These as well as all corresponding figures have been corrected for the sulfuric acid blank, which is usually 0.01 to 0.02 ml of dichromate per 50 ml of sulfuric acid. This is determined under typical test conditions.

2. CALCULATION OF THE TOTAL CELLULOSE CONTENT OF THE SAMPLE

A knowledge of the total cellulose content of the ground material, although not involved in this method for determining alpha, beta, and gamma cellulose, is necessary for use in other chemical tests, such as copper number, pentosans, etc. If these tests are to be made, the sample for the determination of alpha, beta, and gamma cellulose is weighed to the nearest 1 to 2 mg instead of 10 mg. From this weight and from the volume of dichromate for total cellulose, the total cellulose content may be calculated.

For this calculation the equivalent weight of cellulose, $C_6H_{10}O_5$, is taken to be 162.1/24=6.75 g. From this and from the strength of the dichromate solution, 1.835*N*, it is calculated that 1 ml of dichromate solution will oxidize 0.0124 g of cellulose. From the weight of the sample taken for the determination of alpha cellulose 0.300 g, and the volume of dichromate for total cellulose,[21] 21.96 ml, for example, the total cellulose content of the sample is

$$\frac{21.96\times 0.0124}{0.300}\times 100=90.8 \text{ percent.}$$

The values so calculated are listed in table 1 as total cellulose content (volumetric), and may be compared with the values of total cellulose content (gravimetric). The latter were obtained by determining gravimetrically the moisture and ash content, using standard procedures, and assuming the remainder of the material to be cellulose.[22]

The values for the total cellulose content (volumetric) are sufficiently accurate [23] for the purpose stated.

The elimination of the moisture and ash determinations on the ground sample constitutes a substantial saving of time in routine control and even research work.

TABLE 1.—*Comparison of the two methods for obtaining the total cellulose content of pulps and papers*

Method	Materials					
	[a] 1035 (no. 1 new white rag paper)	1009 (no. 1 old white rags)	1039 (refined sulfate pulp)	1018 (soda pulp)	988 (refined sulfite pulp)	1008 (no. 1 new white rags)
Total cellulose content, gravimetric (%)	84.96	93.38	91.25	91.86	92.27	93.12
Total cellulose content, volumetric (%)	84.3	93.4	90.8	91.4	91.6	92.8

[a] The numbers are those used in connection with other experiments. See Shaw and O'Leary, *Study of the effect of fiber components on the stability of book papers.* J. Research NBS **17**, 859 (1936) RP949.

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[21] Total cellulose dichromate values are given in table 2, column 5.

[22] The values so obtained are used directly in the copper-number determination, wherein no attempt is made to distinguish pentosans from cellulose. The corrections for resin, etc., are negligible for the materials listed but may be made when significant, as will be shown in a later paper.

[23] The greatest disagreement between volumetric and gravimetric values in table 1 is 0.7 percent and the average is 0.4 percent. The standard method for the determination of copper number in paper, TAPPI tentative standard, T430m, specifies an agreement between duplicates of 0.1 copper-number unit. This corresponds to 2.5 percent for even relatively high copper numbers of 4.0.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

1. VOLUMETRIC VALUES FOR ALPHA CELLULOSE COMPARED WITH THE GRAVIMETRIC RESULTS

The validity of a volumetric method is usually determined by a comparison with the results of a gravimetric method. Accordingly, a 1-g sample of each material studied was subjected to the same treatment as the 0.3-g sample for the separation of the cellulose fractions. The same ratio of alkali volume to weight of sample, was, of course, maintained. The alpha cellulose was filtered in a Gooch crucible provided in this case with a small piece of cotton cloth as filtering medium. The residue was first washed with 100 ml of water, allowed to soak for 10 minutes in 20-percent acetic acid, and finally washed with 500 cc of water, the pad being constantly broken up with a pointed stirring rod. It was then dried, weighed, and ignited as usual. The alpha-cellulose values were calculated on the basis of the oven-dry ground sample, corrected likewise for ash.

TABLE 2.—*Alpha-cellulose values by the volumetric and the gravimetric methods compared*

1	2	3	4	5	6
Materials	Gravimetric method for alpha cellulose	Volumetric method for alpha cellulose	Alpha-cellulose dichromate values	Total cellulose dichromate values	Bray and Andrews method for alpha cellulose
	Percent	*Percent*	*Milliliters*	*Milliliters*	*Percent*
1035 (no. 1 new white rag paper)	95.1	95.0	19.39	20.41	
	94.8	94.8	19.32	20.37	
	94.9	95.0	19.38	20.40	
		94.9	19.35	20.38	
Average	94.9	94.9	19.36	20.39	93.2
1009 (no. 1 old white rags) (washed)	90.6	90.6	20.46	22.58	
	90.4	90.4	20.40	22.58	
	90.6	90.1	20.38	22.61	
		90.5	20.45	22.60	
Average	90.5	90.4	20.42	22.59	90.4
1039 (refined sulfate pulp) (bleached sulfate)	84.0	83.9	18.42	21.94	
	84.0	84.2	18.51	21.97	
	83.6	84.2	18.48	21.95	
		84.2	18.49	21.97	
Average	83.9	84.1	18.48	21.96	83.8
1018 (soda pulp)	77.5	78.6	17.37	22.10	
	77.7	78.3	17.35	22.13	
	77.9	77.5	17.15	22.12	
		78.6	17.38	22.10	
Average	77.7	78.2	17.31	22.11	77.8
988 (refined sulfite pulp) ("Alpha" pulp)	90.8	90.5	20.09	22.19	
	90.6	90.6	20.08	22.16	
	90.7	90.5	20.05	22.15	
		90.6	20.04	22.13	
Average	90.7	90.6	20.06	22.16	89.8
1008 no. 1 new white rags (washed)	96.6	96.0	21.56	22.46	
	96.5	96.3	21.65	22.48	
	96.4	96.3	21.56	22.39	
		96.2	21.57	22.41	
Average	96.5	96.2	21.59	22.42	95.8

The gravimetric results are shown in column 2, table 2, and are to be compared with the volumetric results in column 3. The values agree well with those in the literature for the corresponding materials.[24] The values for alpha cellulose in column 6 are calculated according to the method of Bray and Andrews,[25] using, however, the theoretical factor 0.0124 g of cellulose per milliliter of $1.835N$ dichromate solution.

Aside from demonstrating the validity of the volumetric results, table 2 allows some interesting deductions concerning the behavior of the pentosans in these materials. Pulps 1039, 1018, and 988 had pentosan contents of 10.7, 21.3, and 3.8 percent, respectively.[26] It is evident that the distribution of pentosans between the alpha and the beta plus gamma fractions was such that the presence of pentosans did not cause serious differences between the volumetric and gravimetric results. This requires that the pentosans be distributed between the alkali-soluble and alkali-insoluble portions in approximately the same ratio as cellulose, which may be calculated from the following considerations. On the basis of the formula for pentosans, $C_5H_8O_4$, it is calculated that 1 ml of dichromate will oxidize 0.0220 g of pentosans, as against 0.0124 g of cellulose.

From the simple relation:

$$\frac{\dfrac{\text{wt of cellulose in alpha portion}}{0.0124}+\dfrac{\text{wt of pentosans in alpha portion}}{0.0220}}{\dfrac{\text{total wt of cellulose in sample}}{0.0124}+\dfrac{\text{total wt of pentosans in sample}}{0.0220}}=\frac{\text{volumetric alpha percent}}{100},$$

the following expression for the percentage of the total pentosans remaining with the alpha portion can be derived:

$x=(229/p)\ [(g-v)+v]$

x=percentage of total pentosans remaining with the alpha portion

p=total pentosans in sample, percent

g=gravimetric alpha-cellulose value (table 2, column 2)

v=volumetric alpha-cellulose value (table 2, column 3).

Substituting the corresponding data in this expression it is calculated that 79.8, 72.8, and 96.6 percent of the pentosans in the pulps 1039, 1018, and 988, respectively, remain in the alpha-cellulose portion. It is seen that these values for "alpha pentosans" are of the same order of magnitude as the values for alpha cellulose in the pulps. It may, of course, be argued that the difference between g and v is not significant, that perfect agreement between the gravimetric and volumetric results would be obtained if certain mechanical differences of treatment could be eliminated. In that case, $g-v=0$ and $x=v$, that is, the pentosans are distributed between the alpha and the beta plus gamma portions exactly as is the cellulose.

It was of interest to ascertain the precision of the method when unusually small samples are taken for analysis. Therefore, 0.03-g samples, corresponding to a piece of paper the size of an ordinary postage

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[24] Lewis and Browning, Paper Trade J. **97**, 39 (Dec. 1933). The method of Lewis and Browning gave the values 90.4% and 77.4% for pulps 988 and 1018, respectively.

[25] Bray and Andrews, Ind. Eng. Chem. **15**, 377 (1923). See discussion also in Hawley and Wise, The Chemistry of Wood, p. 144–148 (Chemical Catalog Co., Inc., New York, N. Y.).

[26] See footnote (a) in table 1.

stamp, were taken of the materials 1035, 1039, and 1018. The process for separating the cellulose fractions was the same as above, except that a Schott fritted glass filtering crucible, no. 3, was used. The oxidimetric solutions used above were diluted tenfold for these experiments. The results obtained for the alpha-cellulose values for these 0.03-g samples were 94.2, 85.6, and 77.0 percent, respectively. It is seen that these values are in fair agreement with the corresponding ones listed in table 2. The writer believes that the precision when a 0.03-g sample is used could be increased by the use of a larger ratio of the volume of alkali to the weight of sample.

2. VOLUMETRIC RESULTS FOR BETA AND GAMMA CELLULOSE

The gravimetric determination of beta cellulose is usually extremely difficult and time consuming. Beta cellulose precipitates upon acidification of the filtrate from the alpha cellulose, as a very gelatinous substance. It clogs the pores of all filters, and usually requires from 2 to 4 hours for its separation. For that reason the directions [27] [28] advise coagulating the precipitate by boiling and filtering hot, followed by washing with hot water.

The boiling procedure, however, yields results which differ from those obtained when the separation is made at "room temperature", since the solubility of beta cellulose is rather strongly influenced by temperature. This is shown by experiments in which the gamma portions of acidified equal parts (1/10) of a beta+gamma filtrate from a 1-g sample of 1018 soda pulp were removed at various temperatures. After a mixture had been kept at a given temperature for several hours, with frequent stirring, the beta cellulose was allowed to settle at that temperature, and a definite part of the supernatant liquid was removed and analyzed volumetrically for dissolved cellulose. The results are listed in table 3. If a system in which the beta cellulose has been "coagulated" by heating to 100° C is allowed to cool, additional beta cellulose will precipitate.

Obviously, the beta cellulose should not be removed from the hot solution or washed with hot water if it is desired to obtain a measure of the cellulose, which simply precipitates upon acidification of the filtrate from the alpha cellulose. If the separation is made at room temperature, however, very little beta cellulose will be in the acidified solution. This can be seen simply by plotting temperature against beta cellulose content, using the data of table 3.

TABLE 3.—*Effect of temperature on the solubility of beta cellulose*

Temperature	Volume of dichromate for gamma portion	Apparent gamma cellulose	Beta cellulose
° C	*Milliliters*	*Percent*	*Percent*
20	0.31	3.4	18.4
60	.36	3.9	17.9
80	.43	4.7	17.1
100	.55	6.0	15.8

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[27] Hawley and Wise, Chemistry of Wood, p. 145. Chemical Catalog Co., Inc., New York, N. Y. (1924.).

[28] Schwalbe-Sieber. Die Chemische Betriebskontrolle in d. Zellstoff-und Papier-Industrie, 3d ed., p. 411 Berlin (1931).

The extent to which the filtrate is acidified, implied in some methods as being of consequence, was found to have no appreciable effect upon the amount of beta cellulose precipitating, and, therefore, no appreciable effect upon the gamma-cellulose content over a very wide range (acidity$=10^{-6}$ N to $3N$). An amount of acid is, therefore, added which is known to be in excess of the base present, thereby avoiding the use of an indicator or of acetic acid, both of which were found to introduce large errors by reduction of dichromate. The values for the beta and gamma cellulose in the materials listed in table 2 are shown in table 4. The calculations were carried out as previously described.

TABLE 4.—*Volumetric results of the beta- and gamma-cellulose determinations*

Materials	Gamma cellulose dichromate values	Gamma cellulose	Beta cellulose
	Milliliters	*Percent*	*Percent*
1035 (rag paper)	0.26	1.3	3.8
	.27	1.3	3.9
	.25	1.2	3.8
	.26	1.3	3.8
Average		1.3	3.8
1009 (no. 1 old white rags)	0.30	1.3	8.1
	.33	1.5	8.1
	.32	1.4	8.5
	.39	1.7	7.8
Average		1.5	8.1
1039 (refined sulfate pulp)	2.50	11.4	4.7
	2.37	10.8	5.0
	2.42	11.0	4.8
	2.54	11.6	4.2
Average		11.2	4.7
1018 (soda pulp)	0.67	3.0	18.4
	.72	3.3	18.4
	.68	3.1	19.4
	.72	3.3	18.1
Average		3.2	18.6
988 (refined sulfite pulp)	0.98	4.4	5.1
	1.03	4.6	4.8
	1.03	4.6	4.9
	1.01	4.6	4.8
Average		4.6	4.9
1008 (no. 1 new white rags)	0.16	0.7	3.3
	.20	.9	2.8
	.22	1.0	2.7
	.22	1.0	2.8
Average		0.9	2.9

WASHINGTON, January 19, 1937.