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VOLUMETRIC DETERMINATION OF ALPHA-, BETA-, AND GAMMA-CELLULOSE IN PULPS AND IN PAPERS CONTAINING SIZING, FILLER, AND OTHER MATERIALS

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ABSTRACT

The volumetric method for the determination of alpha-, beta-, and gamma-cellulose, previously described in Bureau Research Paper RP979 is shown to be applicable to papers containing rosin, glue, starch, oxidizable fillers and lignin, and to pulps containing natural resins in any amount. As the method depends upon the estimation of each cellulose fraction by oxidation with dichromate, and as the sizing materials are all oxidizable, the manner of making corrections for these materials is described in detail. The alpha-cellulose values so obtained are shown to be in good agreement with those of a gravimetric method for a wide range of pulps and papers. The relative shortness of the volumetric procedure is especially apparent when the papers contain mineral fillers or lignin, as these are removed when necessary rather than estimated and corrected for.

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I. INTRODUCTION

A volumetric method for the determination of alpha-, beta-, and gamma-cellulose was described in a previous article.[1] In this method the three cellulose fractions are separated in the usual manner, in that the alpha-cellulose is filtered from a mixture of the ground sample and sodium hydroxide solution, and the beta-cellulose is allowed to settle in the acidified filtrate before a portion of the gamma-cellulose is removed. The amount of cellulose in each fraction is determined by quantitative oxidation with dichromate. The small size of the test sample, 0.3 g, the elimination of the usual moisture and ash determinations, and various other simplifications resulted in a relatively rapid procedure. The method was shown to give results

[1] Herbert F. Launer. J. Research NBS 18, 333 (1937) RP979.

for alpha-cellulose which were practically identical with those obtained by a gravimetric procedure. The data presented were obtained for: soda, chemically refined sulfite and bleached sulfate pulps, also washed new and old rags, and new-rag paper containing 8 percent of clay. None of the samples contained sizing materials or more than 0.2 percent of resin, the values for which were determined using ethyl alcohol-hydrochloric acid [2] solution.

The purpose of the present article is to show that the method is applicable to samples containing rosin, glue, and starch sizes, inorganic fillers, large amounts of lignin, or natural resins in any amount.

The method of study was that previously employed. Each material was analyzed both volumetrically and gravimetrically for alpha-cellulose, using the gravimetric results as the standard for comparison.

II. ANALYTICAL PROCEDURE

In the gravimetric method a 2-g sample was employed. The proper corrections for moisture, ash, and filler materials, resin, glue, starch, or lignin were made upon both the ground sample and the alpha-cellulose, which was filtered through cloth on a 7.5-cm Büchner funnel.

The volumetric method was slightly changed. A small disk of 80-mesh copper or bronze screen was placed in the Gooch crucible. This greatly facilitated filtration, especially in the testing of papers made from old rags with high beta-cellulose content. The screen was allowed to remain in the 12 *M* sulfuric acid until adhering fibers were dissolved, but was removed before the dichromate solution was added. This procedure was found by blank experiments to introduce no detectable error.

Aside from the adoption of the screen as a permanent part of the volumetric method, no other changes in procedure were introduced for papers containing glue, starch, and rosin, for which corrections are applied in the calculations.

However, when a paper contains lignin or an oxidizable filler, as for example, zinc sulfide, it is a much more rapid process to eliminate these materials than to determine their percentage content and correct for them.

It was found that the effect of lignin upon the volumetric results could be satisfactorily eliminated by the following procedure. The separation of alpha-cellulose was carried out on newsprint, sample 7 in table 1, in the usual manner, after which the alpha-cellulose was thoroughly macerated in 50 ml of 12 *M* sulfuric acid and allowed to stand for 30 minutes with occasional stirring. The greater part of the lignin remained undissolved and was then removed by filtration through a Büchner funnel 7.5 cm in diameter provided with an 80-mesh copper screen supporting a layer of asbestos. Fifty milliliters more of 12 *M* acid was used for rinsing, after which dichromate was added and the determination was completed in the usual manner. The amount of lignin which dissolved in the acid had only a negligible

[2] Herbert F. Launer, *Simplified determination of resin in pulps and papers*, J. Research NBS **18**, 227 (1937) RP973. RP973 also defines the terms "resin" and "rosin," as used in the present work.

effect upon the results and was in any event compensated by the small amount [3] of lignin in the beta-plus-gamma fraction. This is seen from a comparison with the gravimetric results (table 1), in which careful determinations of the lignin in the alpha-cellulose and in the ground sample had been made and corrections applied. The volumetric value for alpha-cellulose with the lignin not removed was 93.7 percent.

Of the usual filler materials, zinc sulfide presents by far the greatest difficulties in the analysis of papers. Nevertheless, the effect of zinc sulfide on the results could also be easily eliminated. Approximately one-third of the zinc sulfide present [4] enters the beta-plus-gamma portion as a suspension and must be removed. This was accomplished in sample 6 by carrying out the separation in the usual manner, except that the filtrate was received in a 100-ml beaker and the alpha-cellulose was rinsed with 20 instead of 35 ml of water. To remove the suspended zinc sulfide, the beta-plus-gamma portion was then filtered through a Gooch crucible, provided with a thick asbestos mat, directly into a 100-ml volumetric flask. The determination was carried out in the usual manner from this point. It was not found necessary to remove the filler from the alpha fraction. Results [5] obtained with other samples of paper with and without zinc sulfide indicated that the effect upon the gamma-cellulose values is negligible. In some analyses in which the zinc sulfide was not removed from the beta-plus-gamma portion the alpha-cellulose value was 78.7 percent, instead of 80.8 percent, as shown in table 1.

III. COMPARISON OF THE VOLUMETRIC AND GRAVIMETRIC RESULTS FOR ALPHA-CELLULOSE

The materials listed in table 1, column 1, together with those materials studied previously, represent a wide range of types encountered in paper chemistry.

A comparison of the alpha-cellulose values, obtained by each method, shows that entirely acceptable values for alpha-cellulose are obtained by the volumetric method. In calculating the results of the volumetric method, corrections for the sizing materials were made but the lignin and the inorganic fillers were neglected, because they had been essentially eliminated in the analytical procedure. The gravimetric results were in all cases corrected for these materials. The average deviation of the individual values from the means is 0.13 percent for the volumetric and 0.19 percent for the gravimetric results, which indicates somewhat better reproducibility in the case of the volumetric method.

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[3] The amount of lignin which dissolved in the alkali was 2.7 percent, since it was found that of the 22.7 percent of lignin in the ground sample, 20.0 percent remained with the alpha-cellulose. For lignin determination, see Paper Trade J. **87**, 61 (1928) and modification by Willets, Tech. Assn. Papers **15**, 116 (1932).

[4] This was found to be the case upon analyzing the alpha-cellulose obtained by the gravimetric procedure and the ground sample for zinc sulfide by TAPPI tentative standard T438m-36.

[5] Not shown in table 1.

TABLE 1.—*Volumetric and gravimetric percentages of alpha-cellulose compared, and the percentages of gamma-cellulose*

Samples [a]	Paper stock	Sizing materials, etc.		Alpha-cellulose by volumetric method		Alpha-cellulose by gravimetric method		Gamma-cellulose
		Kind	Amount					
			Percent	*Percent*	*Percent* (mean)	*Percent*	*Percent* (mean)	*Percent*
1a	New-rag [b]	Resin	1.9	95.2 95.2 95.0	95.1	95.6 95.2 95.0	95.3	2.8 2.4 2.8
1b	do	Resin Glue	1.9 1.6	95.9 96.2 96.3	96.2	96.2 96.2 96.1	96.2	2.1 1.9 2.1
2a	Old-rag	Resin	1.0	82.9 82.8 82.9	82.9	83.2 83.2 83.2	83.2	1.8 1.8 1.9
2b	do	Resin Glue	1.0 5.9	88.3 88.4 87.9	88.2	88.5 88.3 87.6	88.1	2.5 2.6 2.5
2c	do	Resin Starch	1.0 2.6	85.4 85.3 85.3	85.3	84.8 84.8 85.2	84.9	1.5 1.7 1.6
2d	do	Resin Starch [c]	1.1 0.7	86.7 86.4 86.2	86.4	86.0 85.4 85.9	85.8	2.0 1.9 1.9
2e	do	Resin Starch [c] Glue	1.1 0.7 3.4	89.8 89.7 90.3	89.9	90.0 89.7 89.2	89.6	2.4 2.4 2.5
3	Sulfite pulp	Resin	0.7	82.9 82.8 82.6 82.8	82.8	82.0 81.9 82.1	82.0	12.7 12.5 12.7 12.5
4	Sulfite paper	Resin	2.5	79.4 79.2 79.4	79.3	78.6 78.4 78.4	78.5	13.9 ------- 14.2
5	Soda-sulfite (1:1) paper	Resin TiO_2 $BaSO_4$	1.1 3.2 6.6	72.4 72.3 71.9	72.2	71.3 72.3 71.7	71.8	7.3 7.1 7.1
6	Rag-sulfite (1:1) paper	ZnS	3.9	81.1 80.3 80.9	80.8	81.2 80.8 81.0	81.0	------- ------- -------
7	Newsprint	Resin, etc. [d] Lignin	1.2 22.7	91.7 91.7 91.5	91.6	92.4 92.6 92.6	92.5	8.3 8.3 8.5
8	Unbleached sulfate (kraft) paper.	Resin	1.0	85.2 85.0 84.9	85.0	85.4 84.7 85.8	85.3	14.8 15.0 15.1

[a] All papers bearing identical numbers were made from fibrous materials from the same sources; the letters indicate a difference in amount and kind of other materials present.

[b] The new-rag paper was made from No. 1 white shirt-cuttings. The old-rag paper was made from "twos and blues" and No. 1 old white rags in the proportion 1:1.

[c] This starch had been added in the beater, otherwise the glue and starch were surface sizes.

[d] In this instance, the resin content was determined using benzene-alcohol (2:1) solution, instead of ethyl alcohol-hydrochloric acid solution.

IV. CORRECTIONS FOR THE SIZING MATERIALS

In order to apply corrections for resin, glue, and starch, it is necessary to know the amounts of these materials in the various fractions and also the dichromate equivalent of each.

1. DICHROMATE EQUIVALENTS OF THE SIZING MATERIALS

The dichromate equivalents of resin, glue, and starch were determined as nearly as possible under test conditions. Small amounts of materials, corresponding to the quantities in 0.3-g samples, were weighed out and dissolved in water,[6] after which 50 ml of concentrated sulfuric acid, 2.50 ml of dichromate solution, corresponding to the amount which usually remains after oxidation of the beta-plus-gamma

[6] Saturated sodium carbonate solution was used to dissolve the rosin.

cellulose, and enough water to make a total volume of 100 ml, were added, and maintained at a temperature of 140 to 150° C for 10 minutes. The results are given in table 2.

TABLE 2.—*Dichromate equivalents for resin, glue, and starch*

Material	Weight taken	Dry weight	Volume of 1.835 *N* dichromate solution used	Dichromate equivalent. Grams of material per milliliter of 1.835 *N* dichromate solution
	g	g	ml	
Rosin (papermakers' grade *F*)	0.0066	0.0066	1.01	0.0065
	.0060	.0060	0.89	.0067
Average				0.0066
Glue [1]	0.0160	0.0139	0.91	0.0153
	.0165	.0144	.92	.0156
Average				0.0154
Starch	0.0160	0.0142	1.09	0.0130
	.0114	.0101	0.79	.0128
Average				0.0129

[1] The glue in the samples analyzed was a high-grade hide glue and was listed as No. 4 in table 1 of the publication, *Use of glue in coated paper*, by Hamill, Gottschalk, and Bicking, Tech. Pap. BS **20** (1926); T323. Other samples of glue, listed in the same table, were No. 1, a medium-grade hide glue; No. 3, a high-grade bone glue; and No. 6, a low-grade bone glue. These gave dichromate values of 0.0137, 0.0142, and 0.0140 g per ml respectively. The average of the four values is 0.0143, which, if used instead of 0.0154, would have caused a difference of 0.1 and 0.4 percent in the alpha cellulose percentages for samples 1b and 2b, respectively.

Precision higher than 2 to 3 percent should not be expected in such experiments, but it is interesting to note that the value for starch is in fair agreement with the theoretical value 0.0124, based upon the empirical formula $C_6H_{10}O_5$. The value for rosin, 0.0066, after dividing by 0.001 835, the number of oxidation equivalents in 1 ml of 1.835 *N* dichromate, gives an equivalent weight of 3.6, which is in good agreement with the value (3.63) obtained when using much larger quantities of rosin.[7]

2. DISTRIBUTION OF THE SIZING MATERIALS AMONG THE THREE CELLULOSE FRACTIONS AND THE METHOD OF APPLYING THE CORRECTIONS

(a) ALPHA FRACTION

For the purpose of determining the amounts of resin, glue, and starch in the alpha fraction, 5-g samples of each kind of paper listed in table 1 were treated with the usual proportions of sodium hydroxide solution and water. The alpha-cellulose was removed by filtration through an 80-mesh copper screen on a Büchner funnel, 7.5 cm in diameter, and analyzed for resin, glue, or starch.[8] The quantities remaining with the alpha-cellulose, based upon the oven-dry weight

[7] J. Research NBS **18**, 230 (1937) RP973. In this article it is also shown that the natural resins in soda and sulfite pulps have approximately the same equivalent weight and, therefore, the same dichromate equivalent as papermakers' rosin, grade *F*.

[8] Glue and starch were determined by use of TAPPI standards T418m (corrected May 15, 1935) and T420m (corrected March 15, 1934), respectively.

of the original sample, were found to be on the average as follows: Glue, 0.25 percent; [9] starch, 0.2 percent; and resin, 0.1 percent. The last value is applicable only when all the resin has been added in the form of rosin. In the case of natural resins, the amount remaining with the alpha-cellulose is 0.3 percent.

The manner of applying the corrections is illustrated by calculation of the alpha-cellulose content of sample 2e, table 1. The alpha-cellulose fraction, to which 25.00 ml of dichromate had been added, required after oxidation, 23.37 ml of ferrous ammonium sulfate, 1 ml of which solution was equivalent to 0.2485 ml of dichromate. The dichromate consumed was, therefore,

$$25.00-(23.37\times 0.2485)=19.19 \text{ ml.}$$

One-half of the beta-plus-gamma fraction, to which 5.00 ml of dichromate had been added, required after oxidation, 13.57 ml of ferrous ammonium sulfate. The dichromate consumed by the beta-plus-gamma fraction was, therefore,

$$2[5.00-(13.57\times 0.2485)]=3.26 \text{ ml.}$$

Rosin, glue, and starch were present in the beta-plus-gamma portion in the amounts of 1.0, 3.15, and 0.5 percent, respectively, which values were obtained by subtracting the amounts remaining with the alpha-cellulose from the values given in column 2 of table 1. From this, from the dry weight of the sample, 0.28 g, and from the corresponding factors given in table 2, column 5, the corrections in terms of dichromate solution are obtained as follows:

$$\text{For rosin: } \frac{0.28\times .01}{0.0066}=0.42 \text{ ml;}$$

$$\text{for glue: } \frac{0.28\times .0315}{0.0154}=0.57 \text{ ml; and}$$

$$\text{for starch: } \frac{0.28\times .005}{0.0129}=0.11 \text{ ml.}$$

The total correction is, therefore, 1.10 ml, and the corrected dichromate value for the beta-plus-gamma portion is 2.16 ml. After similar corrections, the corresponding value for the alpha portion is 19.06, and the alpha-cellulose content is

$$\frac{19.06}{19.06+2.16}\times 100=89.8 \text{ percent.}$$

(b) GAMMA FRACTION

The distribution of sizing materials among the beta and gamma fractions is best determined by comparing the gamma-cellulose values of a series of papers made from the same base paper but having variations in the kind and amount of sizing materials. On the assumption that the glue remains in solution with the gamma-cellulose

[9] Previous work at this Bureau gave values that were somewhat lower for glue. See Burton and Rasch, BS J. Research 6, 603 (1931) RP295. Those experiments were performed on alpha-cellulose from a gravimetric procedure, in which much larger amounts of wash water had been used. No results for starch were obtained.

and is oxidized, the latter was corrected for glue in paper 2b, table 1. The agreement with the gamma-cellulose value of paper 2a is fair, whereas, if the correction had not been made, the gamma-cellulose value would have been 7.6 percent, which obviously is too high. For starch, the same reasoning may be applied, for if the correction for the 2.4 percent of starch in the beta-plus-gamma portion of sample 2d were not applied, the gamma-cellulose value would be 4.1 percent, which obviously is too high, whereas, after making the correction, the value obtained is in good agreement with that of 2a. On the other hand, rosin would be expected to precipitate rather completely with the beta-cellulose, under the conditions of acidity specified in the method (approximately 0.4 *N* in H_2SO_4). This is indicated by the results for samples 1a and 1b, table 1, where, if the resin correction of 0.76 ml had been applied, the values for the gamma-cellulose would have become negative, since the correction would have been greater than the uncorrected dichromate value for the gamma portion. A large number of experiments, performed [10] in another connection, further substantiate this. On a series of papers made from a chemically refined sulfite pulp, and having resin contents of 0.2, 1.1, 1.6, 1.7, and 1.9 percent, the gamma-cellulose values, without applying corrections for resin, were 5.6, 5.4, 5.8, 7.0, and 6.6 percent, respectively. If corrections are applied, the values become low: 5.6,[11] 3.4, 2.9, 3.9, and 3.0 percent, respectively. Consequently, although some resin may occasionally enter the gamma portion, better results, on the whole, are obtained by neglecting it. Thus, the glue and starch but not the resin are corrected for in the gamma portion.

V. DICHROMATE EQUIVALENTS FOR CELLULOSE AND LIGNIN

By combining the gravimetric and volumetric data for any given pulp or paper, in this article and the preceding one, it is possible to calculate the cellulose-dichromate value. The results are given in table 3 for materials relatively free from pentosans.[12] The average value agrees well with the theoretical value 0.01239, the weight in grams of cellulose oxidized by 1 ml of 1.835 *N* dichromate solution, calculated on the basis of the chemical equation for the oxidation of cellulose by dichromate:

$$C_6H_{10}O_5+4Cr_2O_7^{--}+32H^+=6CO_2+21H_2O+8Cr^{+++}$$

This constitutes an additional substantiation of the various steps involved in the analyses.

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[10] This work was done by C. I. Pope.

[11] No corrections are applicable to this particular value as natural resins to the extent of 0.3 percent or less remain with the alpha-cellulose, as previously explained.

[12] Pentosans present in the usual amounts do not affect the cellulose-dichromate value appreciably, however, since the pentosan-dichromate value, calculated on the basis of the formula for pentosans, $C_5H_8O_4$, is similar, 0.01212 g per milliliter of 1.835 *N* dichromate solution. This explains the fact that pentosans, no matter how they are distributed among the three cellulose fractions, do not seriously affect the results obtained by the volumetric method for alpha-cellulose. In a previous publication (see footnote 1) the pentosan-dichromate value was incorrectly calculated to be 0.0220, which necessitated the assumption that pentosans must be distributed among the three cellulose fractions in the same manner as cellulose itself, in order to explain the agreement between gravimetric and volumetric results for alpha-cellulose. There is, therefore, no longer a basis for this assumption.

TABLE 3.—*Dichromate equivalent for the cellulose in the various materials*

Sample	Material	Dichromate equivalent: Grams of cellulose per 1 ml of 1.835 *N* dichromate	Sample	Material	Dichromate equivalent: Grams of cellulose per 1 ml of 1.835 *N* dichromate
[1] 1009	No. 1 old white rags	0.01241	2a	Old-rag paper	.01223
1008	No. 1 new white rags	.01246	2b	Old-rag paper	.01248
988	Refined [2] sulfite pulp	.01246	2c	Old-rag paper	.01235
1a	New-rag paper	.01243	2d	Old-rag paper	.01245
1b	New-rag paper	.01248	2e	Old-rag paper	.01241
				Average	0.01242

[1] The first three materials are dealt with in the preceding article.
[2] Sulfite pulp which had been subjected to additional chemical purifying processes by the manufacturer.

It is of interest to calculate the dichromate value for lignin, using the following data for newsprint. The complete analysis of the newsprint, necessary in the gravimetric method for alpha-cellulose, permits the calculation of the amounts of materials in a 0.3-g sample.

	Grams
Moisture	0.0293
Ash	.0030
Resin, fats, etc	.0032
Lignin	.0614
Cellulose	.2030

A 0.300-g sample of newsprint consumed 23.55 ml of dichromate. Subtracting the resin correction, 0.49 ml, obtained as previously illustrated, and the cellulose "correction" .2030/.0124=16.37 ml from this, the volume of dichromate consumed by the lignin was 6.69 ml. This gives the lignin-dichromate value of 0.0092, which is in approximate agreement with the theoretical value 0.0072, based on the formula [13] $C_{43}H_{42}O_{14}$, and on the assumption of complete oxidation to CO_2. The value found is to be regarded as an upper limit, strictly speaking, but suffices to indicate that lignin is more oxidized than rosin but less so than cellulose or papermakers' glue and starch.

VI. SUMMARY

The main results of the present work and that described in the previous article are as follows:

1. A relatively rapid and simple method for the determination of alpha-, beta-, and gamma-cellulose in pulps and papers has been developed. A 0.3-g sample, which need not be weighed accurately, is employed. The separation of the alpha from the beta and gamma fractions is performed in a Gooch crucible provided with a disk of 80-mesh copper or bronze screen, which permits very rapid filtration for all types of materials.

2. The entire alpha fraction, and unusually large aliquot parts, one-half and one-fourth, of the filtrate are taken for the analysis of the beta-plus-gamma and the gamma fractions, respectively, thus minimizing the multiplication of errors. The amount of each cellulose fraction is determined volumetrically by oxidation with potassium

[13] From an article by Walter M. Fuchs, *The chemical nature of lignin*, Paper Trade J. **102**, 33 (1936). The agreement with the theoretical value is not close enough to substantiate the formula given. It merely shows that the order of magnitude is correct.

dichromate solution, the strength of which need not be known accurately, as the concentrations of the oxidimetric solutions do not enter into the calculations.

3. By comparison with the results obtained by a gravimetric procedure, the method is shown to be applicable to a wide range of materials, including soda, sulfite, chemically refined sulfite, and bleached sulfate pulps, also new rags and old rags, and papers made from various pulps, pulp mixtures, rags, rag mixtures, and wood-pulp rag mixtures.

4. Corrections may be made for natural resins and rosin, glue, and starch in the alpha-and gamma-cellulose portions in a manner described in detail.

5. Neither moisture nor ash determinations are made on the alpha-cellulose or on the ground sample, in fact, no precision weighings are involved. This constitutes a saving of time in the analysis of papers containing clay, titanium dioxide, or barium sulfate, and is particularly advantageous when the fillers are either zinc sulfide, calcium carbonate, or calcium sulfite, which change upon ignition.

6. The analysis of pulps or papers containing large amounts of lignin is greatly simplified as no knowledge of the lignin content is necessary.

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