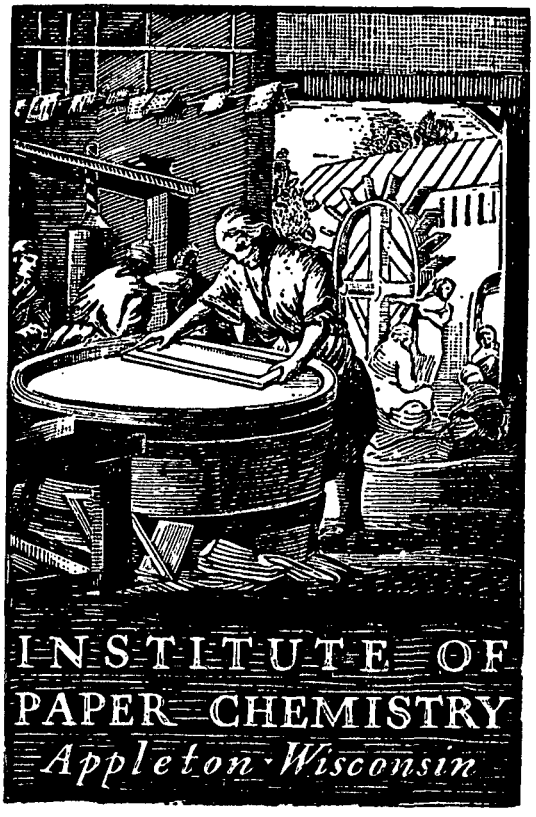
Roger Van Geem



CHARACTERIZATION OF PULPS FOR PAPERMAKING

A COMPARISON OF SOME FIBER MEASUREMENT TECHNIQUES

Project 2406

Report Four

A Progress Report

to

MEMBERS OF GROUP PROJECT 2406

November 30, 1966

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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THE INSTITUTE OF PAPER CHEMISTRY

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CHARACTERIZATION OF PULPS FOR PAPERMAKING

A COMPARISON OF SOME FIBER MEASUREMENT TECHNIQUES

SUMMARY

This report describes a study by comparison and analysis of variance of various approaches to the measurement of three interrelated properties of a population of fibers: average length, number of fibers per gram (mass), and coarseness. Methods representing direct and indirect approaches on macro- and microscales were selected for comparison.

Fiber length measurements were determined by:

(a) Measurement of projected fiber images with a curvimeter (Projection Technique).

(b) Direct measurement on a microscope stage.

(c) Calculation from intersections per fiber against a ruled grid (Grid Count Technique).

Fiber mass determinations, presented as number of fibers per gram, were made by:

(a) Reduction of a weighed quantity of fibers in suspension by serial dilution to a concentration such that fibers deposited on slides prepared from a given volume could be readily counted with a microscope (Serial Dilution Method).

(b) Calculation from the weight of the undyed fraction of fibers and the number of dyed fibers removed from a dried aliquot of a suspension containing a known percentage (by weight) of dyed fibers (Dyed Fraction Method).

(c) Quantitative measurement of the concentration of oxidation products of the reaction of a counted population of fibers with potassium dichromate through the use of a colorimeter (Oxidation Technique).

Coarseness was determined indirectly by calculation from mass and fiber length data obtained by the above methods and calculated directly from the average number of fiber intersections with a superimposed scan line of known length on a very thin sheet prepared from a weighed quantity of fibers.

The pulp fibers used in this work were a laboratory-prepared Douglas-fir/springwood pulp and Weyerhaeuser Bleached Sulfite Grade W. Both pulps are bleached and have been used previously in other phases of this program. Other pulps, also bleached, were tested as a means of indicating the range of applicability and differentiation of some of the "nonstandard" tests.

The variations between test methods for a given property were substantial, the differences in results being attributed to test variability and specificity of various methods for certain fractions of the pulp fibers. An analysis of variations was run on the test results of a program of replicated grid count-oxidation fiber length and mass determinations. This analysis indicated an overall test variation of 11.7% in the determination of the number of fibers per gram. The variation in the oxidation method of mass determination was 9.1%, the variation in fiber counting was 1.8%, and the variation in the sampling of dilute fiber suspensions with an 8-mm. I.D. eyedropper was 9.0%. An overall variation of 9.2% was found in the fiber length determination by the grid count method.

Good agreement was obtained between the results of the grid count-oxidation method and the scan line-very thin sheet method as used in the analysis of variations. An analysis of variations in the scan line-very thin sheet method for coarseness and the number of fibers per gram, using the grid count technique to determine average fiber length, indicated an overall test variation of 5.4% in the measurement of coarseness with a sampling variation of 2.6%. An overall variation of 8.7% was obtained in the determination of the number of fibers per gram from the coarseness and average fiber length. The substantial difference between the variations in the grid count-oxidation method and the scan line-very thin sheet method was accounted for by the differences in sampling variation and it was concluded that these differences represented an increase in precision with sample size.

INTRODUCTION

The mensuration of individual fibers can be carried out with reasonable accuracy through the use of the microscope with techniques and equipment such as the IPC Compacted Fiber Dimension Apparatus, microtoming, and comparator eyepieces. Measurements on individual fibers, however, do not reflect the properties of a population of fibers unless a statistical sample is measured. The purpose of this work was to use various techniques for determining the average fiber length, mass, and coarseness of a population of fibers in order to assess the factors that influence the accuracy and reproducibility of results.

The determination of fiber length, mass, and coarseness for a population of fibers relies upon either direct measurement techniques or indirect techniques with the assumption of some sort of statistical distribution. Direct measurement methods include such techniques as microweighing of individual fibers on a quartz balance, fiber measurements with a microscope and a micrometer stage or a comparator eyepiece, counting of individual fibers, and weighing of macrosamples which can be reduced (by techniques such as serial dilution) to populations of fibers that can be treated individually. Indirect methods involve such techniques as fiber measurement based upon the distribution of fibers against a grid or scan line of known dimensions (these might be better termed quasidirect methods as they involve measurement by division into unit distances but on the basis of a random distribution) and chemical techniques whereby fibers are chemically reacted and the concentration of the products is compared with the concentration of the reaction products of known quantities of fiber.

Each of these methods or techniques requires some sort of sampling and sample preparation technique. These can include weighing samples of wet or dry pulp, dispersion of fibers initially dry or wet in water, sampling of fiber

suspensions with large eyedroppers or graduated cylinders, and deposition of fibers on supporting media such as microscope and lantern slides or filter paper or formation of very thin sheets [produced in the manner of the so-called 2-D sheets of Kallmes and Corte (4)].

Another approach to the measurement and counting of fibers utilizes the resistance change produced by the presence of suspended fibers in an electrolyte flowing between two electrodes. The pulse change in resistance activates an electronic counter, the duration of the pulse is related to the fiber length and the magnitude of the pulse can be equated to the fiber volume. The modification of a Coulter particle counter for the purpose of measuring fiber length has been reported by Valley and Morse (1). Instrumentation for this type of analysis is not available at the Institute at the present time.

There are other approaches using techniques based upon the classification of pulps by retention on screens of varying mesh size which yield results related to fiber dimensions. However, the relations are complex and involve other factors such as fiber flexibility so that the results of a screen classification test cannot be used to calculate directly the fiber dimensions. For this reason classification techniques were not considered in this study although they may be of later use in fines removal or fractionation of fibers for selective studies such as the relationship between fiber length and coarseness for a given pulp.

Coarseness is a property related to fiber mass and fiber length. It is expressed as the mass per unit length of a fiber (TAPPI Coarseness is expressed in mg./100 m). It can be determined directly or it can be calculated from the average length and number of fibers per gram. Inasmuch as the mass of a fiber is the product of the solid volume and its density it is apparent that coarseness is

actually the product of the cross-sectional area of the fiber and its bulk density. It is interesting to note that no matter how much a fiber is shortened or brushed out by beating and refining, as long as neither separation nor removal of material from the surface takes place the coarseness is unchanged. In addition, the product of the average coarseness of a fiber and its external specific surface is its average cross-sectional perimeter. The interrelations between fiber length, coarseness, and specific surface could no doubt provide substantial insight into the character of a pulp, both as a means of comparison and as an indication of response to treatment, providing that values representative of these properties could be determined quickly and accurately.

Previous work concerned with the measurement of the mass and dimensions of fiber populations was done by Lloyd White under the aegis of Project 2210 (5) and a general discussion of fiber dimensions has been presented in an "informal note" by Robert Holm entitled "A Review of Fiber Dimensions and Their Use in Pulp Characterization".

DISCUSSION OF APPROACHES

FIBER LENGTH

Average fiber length is the mean value of a distribution of fiber lengths, often with ranges of lengths having ratios of the order 25:1. It can be used as a representative length for properties dependent upon the total length of a population of fibers (e.g. coarseness) but it does not represent the distribution, which is seldom symmetrical. Weighting techniques have been used to express fiber length in terms less affected by the very short fractions, comprised mainly of fines and debris. One such method of weighting is to divide the individual lengths of a population into intervals and determine the weighted average length from the square of the average length of each interval times its frequency divided by the product of the average length of each interval and its frequency. Weighting may or may not provide a better representation of the length of a fiber population; however, skewed distributions cannot be described by a single number.

Three techniques from which the average fiber length of a population of fibers could be determined were compared. The first two also indicate the length distribution, the third does not. These techniques were termed: fiber length by projection, direct measurement, and the grid count technique.

Fiber Length By Projection

This is an Institute method based upon the technique of Ilvessalo-Pfäffli and V. Alfthan (2) where fibers dyed with Congo Red were dried on one by three inch slides, projected to a magnification of 50X on a translucent screen, and measured individually with a curvimeter connected to electronic counters which record the number of fibers in 0.2-mm. intervals.

Direct Measurement

The procedure used in this method was to measure approximately 400 fibers individually by aligning each fiber on the stage of a microscope with a dissecting needle and noting its length at a magnification of 23X with a comparator eyepiece. A distribution of lengths was obtained by recording and grouping the fiber lengths in 0.2-mm. increments. This is one of the most straightforward means of determining fiber length but it is also one of the most tedious.

Fiber-Grid Intersections

The grid count technique utilizes the relationship between the length of a fiber and the number of intersections it makes with a ruled grid of known spacings. The statistical relation between length and the number of intersections of a straight line dropped with random orientation on a grid relates to the Buffon needle problem whereby the intersections of a needle of given length were used to determine the value of π. This technique was used by Brady, Berzins, and Clark (3) to determine average fiber length with the equation (their notation):

$$L = N_{av} \, W \left[\frac{\pi}{4}\right] \qquad (1)$$

where: L = average fiber length

N_{av} = average number of grid crossings per fiber

W = spacing between grids (for a square-ruled grid)

In some work [e.g., Kallmes and Corte (4)] it was considered necessary to apply a correction factor for the curvature of the fiber in the form of an average ratio of the perimeter of the curved fiber and the straight line distance

between the two ends. White (5) used this correction in his work initially and later revised his calculations when he found the correction unnecessary and erroneous. That the number of grid crossings is related to the actual fiber length for fibers bent less than π radians can be easily verified experimentally by randomly dropping a straight piece of thin wire on a ruled grid a number of times and comparing the average number of crossings to a repeat experiment where the same wire is bent into a semicircle.

FIBER MASS

The mass of a population of fibers is expressed in terms of the number of fibers in one gram of fibers. Basically, there are two problems involved in obtaining this number; the first is to count the fibers and the second is to determine the mass of the counted fibers. As the accuracy and precision of the solution of one problem increases the other falls off, i.e., neglecting statistical requirements one fiber can be counted accurately but is difficult to weigh while the weight of one million fibers is easy to determine if you know you have one million fibers. Thus, there are two approaches; a large sample can be weighed then reduced by sampling to a population that can be counted accurately and conveniently or a small sample can be counted then weighed by some micro-weighing technique. In this work three methods involving one or the other of these approaches were used. They were the dilution method, the dyed fraction method, and the colorimetric determination of oxidation products.

Dilution Method

This method is based upon the technique devised by Graff (6) in which one-half gram of ovendry dyed fiber is suspended in one liter of water and diluted in successive stages using 100-ml. aliquots to a concentration of one-one hundred-thousandth of a gram per ml. A 5-ml. sample of the final suspension is dried on a lantern slide and the fibers counted under a microscope at a magnification of 20X.

Dyed Fraction Method

The dyed fraction method used in this work was devised at the Institute by R. H. Van Eperen and W. A. Wink. In this method, approximately one gram of fibers comprised of an accurately weighed dyed fraction (3 to 5% of the total fibers) and an accurately weighed fraction of undyed fibers is dispersed in 20 liters of water. Approximately 100 ml. of the suspension is removed and dried. The dyed fibers are counted as they are removed and the remaining undyed fraction is weighed on a microbalance. Assuming the ratio of dyed to undyed fibers had not changed, the number of fibers per gram can be calculated. The use of this method was reported and described by White (5) in his work under Project 2210.

Colorimetric Determination of Oxidation Products

The use of the potassium dichromate oxidation technique for the quantitative determination of the β and γ content of pulp titrating with sodium thiosulfate using starch and potassium iodide as an indicator is described in TAPPI Method T203 os-61. The use of a colorimetric method to analyze oxidized pulp solutions is described by Ohlsson (7) and by Barton and Prutton (8). Kitson and Mellon (9) studied the transmittancy of potassium dichromate-acid solutions and showed only minor effects at 600 nm. resulting from changes in pH and sulfuric acid concentration with 100% transmittancy below 9M and 97% above 11M sulfuric acid solutions.

Although this technique had been previously applied strictly to the cellulose components of pulp it was felt that the total oxidizable material in a given pulp would be in constant ratio to the mass of the pulp and possibly in a constant ratio for certain groups of pulps. Thus, a standard absorbency-concentration curve could be derived for oxidized solutions of a pulp and used to determine concentrations of oxidized solutions made from a known number of fibers. The possibilities of this method were suggested by Dr. Browning.

An alternate to this method is the Anthrone method for determining colorimetrically the amount of carbohydrate in a pulp sample. This method was used by Jentzen (10) for the quantitative determination of wood fibers. It involves the dissolution of the sample in concentrated sulfuric acid followed by reaction with the anthrone reagent in much the same manner as the oxidation method. However, the anthrone method requires careful control of the reaction temperature and the reaction time and the stability of the reaction products with time and exposure to light is questionable according to the procedures of Helbert and Brown (11). In contrast, the oxidation method seems to give reasonable accuracy with no special control other than good quantitative laboratory practice and colorimeter measurements on oxidized solutions exposed to room lighting in glass-stoppered flasks for several days indicated no appreciable change.

COARSENESS

As stated earlier, coarseness can be calculated from the average fiber length and the average fiber weight of a population of fibers. It can also be determined directly as the total length of a population of fibers of known total mass. The total length of a random network of fibers can be related to the number of fibers crossing a line of known length or from the intersections on a grid of known spacing providing the fibers are distributed in a plane.

Kallmes and Corte (4) defined a two-dimensional sheet as a network of so few fibers that less than 1% of the area of the sheet is covered by more than two fibers. Applying this concept in terms of very thin sheets, a distribution of fibers can be obtained in which individual fibers can be readily observed and counted under relatively low magnification. In their work with spruce pulp Kallmes and Corte found that their two-dimensional criterion was met and the

forming process was random when 0.05 g. of pulp was used to form a sheet by the TAPPI Standard T 220 m-58 method. Using a network of randomly distributed straight lines as a model they derived a number of equations describing the geometry of the network and an equation expressing the number of fibers in the sheet in terms of the intersections on a scan line of given length (their notation):

$$N_f = \frac{\pi A \bar{\tau}}{2 \bar{\lambda}} \left(\frac{N}{L} \right) \qquad (2)$$

where: N_f = number of fibers

A = sheet area

$\bar{\tau}$ = average curl factor

$\bar{\lambda}$ = average fiber length

N = number of fibers intersecting the scan line

L = length of the scan line

By dividing this equation by the weight of the sheet ω the number of fibers can be expressed in terms of fibers per gram; subsequently multiplying by the average fiber length and omitting the curl factor (see above discussion on grid count technique) an equation for coarseness can be written:

$$C = \frac{\pi A}{2 \omega} \left(\frac{N}{L} \right) \qquad (3)$$

where C is the average coarseness as mass per unit length.

The determination of coarseness by this method is similar to the TAPPI Coarseness Method T.234 su-64 in which a weighed sample of dyed fibers is deposited on a filter paper in a TAPPI sheet machine then transferred onto a warm gelatin coated slide, the coarseness being determined from scan line crossings as observed by projection or with a microscope.

A method using a grid instead of scan lines is the now superceded TAPPI Coarseness Method T 234 sm-60 where a sample of pulp suspension is dried on a lantern slide then projected against a grid.

COMPARISON OF TECHNIQUES

Basically the problems in measuring average properties consist of: (1) Testing a sample of fibers somewhere in number between one and infinity that is representative, (2) testing in a manner that does not favor or discriminate against certain fractions of the sample, (3) actually testing for the desired property, (4), (5) and (6), accuracy, precision, and reproducibility. Other factors such as cost, complexity, and speed influence the utility of a test. There being no absolute scale or standard pulp fiber for evaluation of measurement techniques, it would seem that the best recourse for assessing the deficiencies and attributes of various techniques would be through a comparison of techniques, with the desired result being not necessarily proof of the superiority of a specific method but an indication of an approach that could provide a best compromise of the above problems. A similar approach was used by White (5) in his evaluation of a single fiber weighing technique applied to Paraña pine.

Douglas-fir/springwood (the fraction retained on a 28-mesh screen in a Bauer-McNett classifier) and Weyerhaeuser Bleached Sulfite, Grade W (mostly western hemlock) pulps were chosen for the comparison study. The Douglas-fir was selected in order to maintain continuity with other phases of activity in this project. The source and the cooking procedure used in its production is described in Project 2406, Report One. The Weyerhaeuser Bleached Sulfite was picked because of its common use in this project and at the Institute for laboratory beater calibration. Samples of eucalyptus and birch fibers were also tested by the scan line--very thin sheet method to obtain a rough indication of its range of applicability and differentiation.

The test methods employed in the comparison were:

1. Fiber length by projection
2. Serial dilution
3. Dyed fraction
4. TAPPI Coarseness T.234 sm-60
5. Grid count--oxidation
6. Scan line--very thin sheet

The first four methods are recognized methods in general use at the Institute. Descriptions of procedures for these methods, test data and methods of calculation are appended to this report (Appendix I). In this section the grid count technique, the oxidation technique, and the very thin sheet technique procedures used are described and the results are compared with the results of the recognized methods.

GRID COUNT TECHNIQUE

Preparation of Slides

Samples of fibers were dispersed in accordance with TAPPI Method T 401 m-60; however, in preparing slides from these dispersions (0.05% consistency) it was found that the quantity of fibers deposited on a slide was more than could be conveniently counted and the dispersion was diluted to about half the original concentration. Slides were prepared by depositing a quantity of the dispersion with a medicine dropper from which the tip had been removed. The one by three inch slides were warmed on a hot plate and tapped with a dissecting needle to keep the fibers from agglomerating until dry.

Counting and Measurement of Fibers

A prepared slide was aligned on a ground-glass grid with 1/4-inch square rulings so that it covered a series of squares numbered from 1 to 48. The grid and slide were placed under a binocular microscope at 10X to 23X magnification. The number of fibers were counted using the squares to divide the slide into easily counted regions and the number of fiber-grid line crossings were counted. The counts were tabulated on two push-button counters. The average fiber length was then determined from Equation (1).

OXIDATION TECHNIQUE

Standard curves were derived for Weyerhaeuser Bleached Sulfite Grade W pulp, a sample of Douglas-fir/springwood (dyed with Congo red), and a sample of eucalyptus fibers by measuring the absorbency at 600 nm. of oxidized solutions of known concentrations against blanks containing equivalent amounts of potassium dichromate and sulfuric acid. These measurements were taken in a Coleman Jr. Spectrophotometer using two 25 x 105-mm. round cuvettes. (Some measurements were taken in a Beckman Model DU Spectrophotometer using one centimeter cells. Although the Beckman unit is a more accurate instrument, its lack of ready availability made the Coleman Jr. more desirable. Moreover, the greater light path of the Coleman cuvettes offset to a large degree the differences in instrument accuracies.) Samples of the pulps, ranging from 0.15 to 0.26 g., dried overnight at 105°C., were weighed on an analytical balance and placed in a volumetric flask. Two-tenths of a milliequivalent of potassium dichromate per milligram of pulp were added in the form of a 1N solution. The sample was allowed to soak in the $K_2Cr_2O_7$ solution for five minutes, then 100 ml. of concentrated sulfuric acid was added and the materials were allowed to react for 15 minutes. At the end of the reaction period the solution was cooled in a beaker of cold water and diluted to 200 ml.

These solutions, ranging in concentration from 1.0 to 1.5 mg. per ml. were further diluted by diluting aliquots taken with a pipet in a 25-ml. volumetric flask to concentrations ranging from 0.021 to 0.120 mg. per ml. with 10 to 15 ml. of concentrated H_2SO_4 and water. Blanks were prepared for each dilution by making up solutions of $K_2Cr_2O_7$ and H_2SO_4 containing equivalent volume concentrations computed on the basis of the quantities of acid and $K_2Cr_2O_7$ used in preparing the sample solutions. The standard curves obtained with these samples are shown in Fig. 1.

Mass determinations were run on samples of 1000 to 2500 fibers; this required several slides as the number of fibers per slide ranged from 150 to 800, most having about 300 fibers per slide. The fibers were washed from the slides with distilled water and a rubber "policeman" into a small beaker. The dispersed sample was boiled dry with care that the fibers did not become charred and a quantity of 0.1N $K_2Cr_2O_7$ was added at a ratio of 0.5 milliequivalent per milligram of fiber on the assumption of 3 million fibers per gram. After five minutes, 10 ml. of concentrated sulfuric acid were added, and after a 15-minute reaction period the solution was cooled and transferred to a 25-ml. volumetric flask and diluted with washings from the reaction beaker to 25 ml. The optical absorbency of the solution was determined in the spectrophotometer and the mass was calculated from the standard curve.

VERY THIN SHEET TECHNIQUE

Preparation of Very Thin Sheets

Weyerheauser Bleached Sulfite, Douglas-fir/springwood, and eucalyptus fibers were used to form very thin handsheets. Sheets were formed in a standard $6\frac{1}{2}$-in. sheet mold using 0.05 g. of ovendry pulp (0.025 in the case of the Douglas-fir pulp which was difficult to count at the higher weight). The pulp

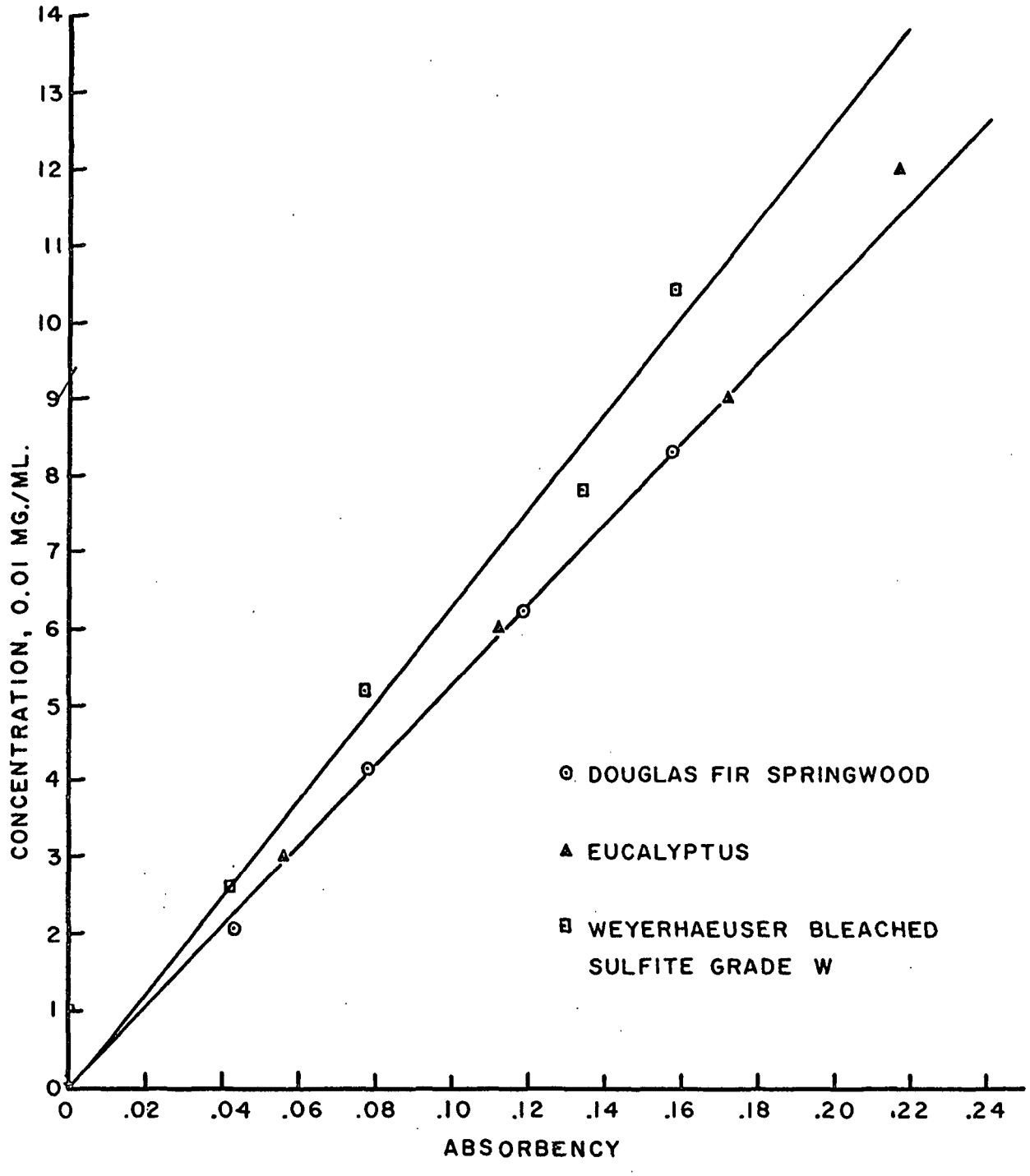

Figure 1. Standard Absorbency Curves for Three Oxidized Pulp Fibers at 600 nm.

specimens were dispersed by shaking with water in a test tube with two glass beads when the pulp was difficult to disintegrate (birch and eucalyptus). Dilution in the sheet mold was to 7 liters (7.1×10^{-4} and 3.6×10^{-4}% consistency for 0.05 and 0.025 g. of pulp, respectively). The sheets were formed on a 100-mesh nylon screen with exception of the birch fiber sheets which were formed on a 200-mesh nylon screen. After forming, the sheets were transferred to $6\frac{1}{4}$-inch diameter chromeplated sheet metal disks by placing the nylon screen upside down on the disk and pressing with blotting paper against the bottom side of the screen to approximately two pounds total force for thirty seconds to $1\frac{1}{2}$ minutes. The transferred sheets were allowed to air dry. The metal disks were used after attempts to transfer the sheets to colored blotting paper were unsuccessful.

Scan-Line Counting

The disks supporting the sheets were placed under a binocular microscope and illuminated at an angle of approximately thirty degrees. Counting was done at 40X using an eyepiece reticle which superimposed a line 2.5-mm. long on the fiber network. The number of fiber intersections with the line was counted. Twenty counts were made in random fashion about the sheet. The coarseness was then calculated from Equation (3). The average fiber length was determined by means of the grid counting method with slides prepared from samples of fibers taken directly from the sheets. The product of the coarseness and average fiber length was then converted to the number of fibers per gram.

RESULTS

A comparison of averaged results of the various test methods applied to the Weyerhaeuser Bleached Sulfite and the Douglas-fir/springwood is shown in Table I. Typical data obtained and calculations for the various methods are presented in Appendix I. The variation in the results obtained with the

TABLE I

COMPARISON OF TEST RESULTS

(AVERAGE VALUES FOR THREE DETERMINATIONS EXCEPT WHERE NOTED)

Test Method	Average Fiber Length, mm.	Number of Fibers Per Gram, millions	Coarseness, mg./100 m.
Weyerhaeuser Bleached Sulfite, Grade W			
Grid count--oxidation (pulp sample)[a]	1.64	2.70	22.6
Grid count--oxidation (projection sample)[b]	1.46	2.24	30.5
Dyed fraction	1.83	1.82	30.0
Dilution	-	2.78	29.7
Projection	1.21	-	
Scan line--very thin sheet	1.83	2.16	25.3
TAPPI coarseness T 234 sm-60	-	-	22.3
Douglas-Fir/Springwood			
Grid count--oxidation[c]	2.72	1.85	19.8
Dyed fraction	2.46	1.95	20.9
Scan line--very thin sheet	2.81	1.82	19.6

a Fibers obtained directly from pulp sample.

b Dyed fibers on slides from fiber length by projection determination, average of 2 determinations.

c Average of 4 determinations.

Weyerhaeuser Bleached Sulfite is considerable while, except for average length, reasonable agreement was obtained for the three tests performed on the Douglas-fir. The significance of the differences between the test results depends not only upon the specificity of the test for certain fiber fractions but also upon variations within the test. In the case of specificity it is easy to speculate that one might expect low fibers per gram counts and high average fiber lengths by the dyed fraction method due to the omission of short fractions and fines in the visual selection of fibers; likewise one might expect the same effects in the scan line--very thin sheet method due to loss of fines and short fractions in forming the network. The test results seem to bear this out, with the possibility of the loss of short fiber fractions being further borne out by comparison of the fiber length values by the grid count--oxidation versus scan line--very thin sheet methods where the grid count technique for fiber length was employed in both cases. Methods where sampling is done by eyedropper techniques may favor shorter fiber fractions. This would not account for the grid count--oxidation versus scan line--very thin sheet differences because eyedropper sampling was used in both cases for fiber length but it could account for the differences between the grid count--oxidation and the dyed fraction results and also for differences between the dyed fraction and scan line--very thin sheet results.

Sample size is a factor that can affect variability within a test. It is closely related to sampling techniques, test method, and distribution of fibers. The effect of sample size in relation to distribution may be attributable to the differences in the variations in test results with the Weyerhaeuser and Douglas-fir pulps by recalling that the Douglas-fir sample consisted of the fiber fraction retained on a 28-mesh screen and would therefore have a narrower range of fiber length distribution.

In order to assess the import of the range of variations observed in these comparisons, two substantially different pulps were tested by the scan line--very thin sheet method and compared to the test results with the Weyerhaeuser and Douglas-fir pulps as shown in Table II. The eight-point range of variation in coarseness by different methods noted with the Weyerhaeuser pulp is greater than the range of three of the four pulps tested by the same method. This would tend to indicate that coarseness obtained by two different methods cannot be used to differentiate between two pulps.

TABLE II

FIBER PROPERTIES CALCULATED BY SCAN LINE AND GRID COUNT TECHNIQUES ON VERY THIN SHEETS

Pulp	Average Fiber Length, mm. by grid count	Coarseness by Scan Line Technique, mg./100 m.	Calculated Fibers Per Gram, millions
Weyerhaeuser Bleached Sulfite Grade W	1.83	25.3	2.16
Douglas-fir/springwood	2.81	19.6	1.82
Birch	1.35	12.0	6.15
Eucalyptus	1.20	18.5	4.51

ANALYSIS OF VARIATIONS IN THE GRID COUNT--OXIDATION METHOD

Before proceeding further with comparisons of methods and approaches it seemed that the next logical step would be an analysis of the variations that could occur within a test. Subsequently, an analysis of variations was run on the grid count--oxidation test method using the classified Douglas-fir/springwood.

Fifteen slides were prepared by sampling a dilute slurry of fibers with an 8-mm. I.D. glass dropper, applying approximately 1 ml. of slurry to each slide. The number of fibers and the number of fiber-grid intersections were counted with six replications. The counting was done against a ground glass etched with a 1/4-inch square-ruled grid under a binocular microscope at 23X. The average fiber length for each slide was calculated by means of Equation (1).

The slides were divided into five samples of three slides each and the total mass of each sample was determined by the oxidation--colorimetric method. The fibers were washed from the slides into a beaker, boiled down, oxidized and dissolved in potassium dichromate and sulfuric acid and compared against a blank on a Coleman Jr. Spectrophotometer at 600 nm. The potassium dichromate was added in a 0.1N solution at a ratio of 0.5 meq. per mg. of fiber estimated on the assumption of 3×10^6 fibers/g. Five milliliters of concentrated sulfuric acid were added to dissolve the fibers and the oxidized solution was diluted to 10 ml. in a volumetric flask. (In previous work a 25-ml. dilution was used as it was thought that this was the minimum quantity that could be tested in the particular cuvettes available. This was not entirely satisfactory inasmuch as the solution concentrations were often in a region of questionable accuracy and sensitivity on the colorimeter. A little experimentation showed that as little as 10 ml. of solution could be tested thereby increasing concentrations by a factor of 2.5.) The blanks were prepared in the same manner as the samples.

Coefficients of variation (standard deviation expressed as percent of the mean) were calculated for the replicated counts of fibers and fiber-grid intersections and for the ratios of intersections to fibers. These results are summarized in Table III and typical data and calculations are shown in Appendix II. The average coefficients of variation in fibers counts and intersection counts from this data were 1.8 and 3.2%, respectively. Since the ratio of crossings to fibers is determined from these counts the coefficient of variation in the crossings to fibers ratio is related by the equation

$$\nu_{cf}^2 = \nu_f^2 + \nu_c^2 \qquad (4)$$

where: ν_{cf} = coefficient of variation due to counting for the number of intersections per fiber

ν_f = coefficient of variation due to counting for the number of fibers

ν_c = coefficient of variation due to counting for the number of fiber-grid intersections

The coefficient of variation in counting intersections per fiber was 3.7% as calculated by this relation while the average observed value was 3.2%. In later calculations the larger value was used.

The variation in the ratio of intersections to fibers between slides is equal to the sum of counting variations and the sampling variations between slides as shown by the relationship

$$\nu_o^2 = \nu_{\frac{cf}{6}}^2 + \nu_s^2 \qquad (5)$$

where: ν_o = overall coefficient of variation in number of crossings per fiber for all slides

ν_s = coefficient of variation in number of crossings per fiber due to sampling differences between slides

The overall coefficient of variation ν_o was determined for the fifteen slides using the average values from replicated counts (see Appendix II). This was found to be 9.2%. From this the coefficient of variation in sampling was calculated to be 9.04%.

The results of the fiber mass determinations in terms of fibers per gram are presented in Table IV along with the average fiber lengths for each sample. Also shown in Table IV is the coarseness of each sample calculated from the product of average fiber length and fibers per gram. The number of samples used in the mass determinations is statistically small thereby reducing the exactness of the coefficient of variation. For example, the square of the coarseness variation should equal the sum of the squares of the average fiber length and fiber mass variations which it apparently does not. Were the coarseness variation in Table IV taken as fact along with the fiber length (the latter is based upon 15 samples and 90 observations) the coefficient of variation in the fiber mass determination would be 9.1% compared to the 11.7% observed.

The component variations in the fiber mass determination are related by the following equation:

$$\nu_{fg}^2 = \nu_m^2 + \frac{\nu_s^2}{3} + \frac{\nu_f^2}{6} \qquad (6)$$

where: ν_{fg} = coefficient of variation in number of fibers per gram

ν_m = coefficient of variation in oxidation--colorimetric fiber mass determination

TABLE III

COEFFICIENTS OF VARIATION IN INDIVIDUAL SLIDE OBSERVATIONS FOR SIX REPLICATE COUNTS

Sample 2406-5-2387-	Slide	Number of Fibers, %	Number of Crossings, %	Crossings per Fiber, %
57	1	1.53	3.23	3.09
	2	1.95	2.15	3.06
	3	1.16	1.74	1.75
58	1	1.34	6.63	5.50
	2	1.94	2.80	1.83
	3	1.92	4.59	4.47
60	1	2.53	2.73	4.62
	2	3.15	3.88	1.94
	3	4.29	4.84	5.81
61	1	0.87	3.13	3.01
	2	1.94	1.87	1.35
	3	1.74	2.16	1.47
63	1	0.70	5.16	5.40
	2	1.05	2.02	2.01
	3	1.42	1.80	2.49
Average		1.84	3.25	3.19

TABLE IV

VARIATIONS IN FIBER LENGTH, FIBER MASS,
AND COARSENESS DETERMINATIONS

Sample 2406-5-2387-	Average Fiber Length, mm.	Fibers Per Gram, millions	Calculated Coarseness, mg./100 m.
57	2.42	1.46	28.3
58	2.58	1.46	26.6
60	2.28	1.82	24.1
61	2.53	1.68	23.5
63	2.46	1.87	21.8
Mean	2.45	1.66	24.9
Variance	0.0148	37,893	6.66
Coefficient of variation	5.0%	11.7%	10.4%

Using the observed value for the variation in the fibers per gram test and the previously determined sampling and fiber counting variations the expected variation in the oxidation--colorimetric test is 10.5%.

Summarizing, the expected variations in the determination of the number of fibers per gram by this test can be broken down into the sources listed in Table V.

TABLE V

SUMMARY OF VARIATIONS IN GRID COUNT--
OXIDATION METHOD FOR A SINGLE TEST

Source	Coefficient of Variation, %
Overall--fibers per gram	11.7
Overall--fiber length	9.2
Mass determination	9.1
Fiber counting	1.8
Fiber-grid intersection counts	3.2
Sampling	9.0

The mass determination test involves several operations involving sample handling, preparation, volumetric dilutions, instrument precision, calibration, and read-out. Each of these operations are subject to variation and contribute to the total variation so that it is not surprising that the overall variation in this test is somewhat greater than less complex measurements such as the counting of fiber-grid intersections.

Of the component measurement and operation variations contributing to an overall test variation the sampling of fibers had the greatest variation. There would seem to be two sources of variation in the sampling technique used in this work: 1. The sampling technique itself in which variations can be ascribed to flocculation and fiber classification during the sampling process, and, 2. The distribution of the fiber population which may be such that the samplings are too small to be representative. Although the effect of this variation can be reduced by multiple sampling the reduction is paid for by redundant testing.

ANALYSIS OF VARIATIONS IN THE SCAN LINE--VERY THIN SHEET METHOD

As indicated by the previous analysis, sampling is of critical importance to reproducibility. The sampling technique is subject to some variation; however, the magnitude of variation experienced with the "eyedropper" technique is greater than would be expected thus suggesting the possibility of variations between samplings due to insufficient quantities to provide a cross section of a fiber population. The very thin sheet technique requires samples many times larger; thus, it was felt that an analysis of variations in the scan line--very thin sheet method would provide an indication of the effect of sample size. The Weyerhaeuser Bleached Sulfite, Grade W, was used in this analysis; it was not classified and would therefore have a greater distribution in comparison with the classified Douglas-fir fraction used previously.

Very thin sheets were formed in a TAPPI standard sheet mold from nominally 0.05 g. per sheet of ovendry pulp weighed to 0.0001 g. on a 200-mesh nylon screen. During the course of the work it was determined that measurements could be taken with the scan line without removing the sheets; possibly this could yield better results since the transfer operation required in the earlier described method in which the sheets were tested on chrome-plated disks would be eliminated. Both methods were analyzed to test for differences.

The cumulative count of fiber intersections with a scan line 2.50-mm. long superimposed by a microscope at 40X in ten random areas of the sheet was termed an observation, six such observations being made per sheet. Ten sheets were made; five were tested on the nylon screens and five were transferred to chrome-plated disks and tested. Three microscope slides were prepared from samplings of each of the sheets and average fiber length measurements were made by the grid crossing method with a single fiber and intersection count per slide.

The coarseness and fiber length data were set up in a hierarchic classification (12) to provide a breakdown of the component variances. The results are summarized in Table VI and a typical classification and treatment of the replicated data is shown in Appendix III.

Variations in the estimated variance between samples and within samples for tests on the chrome-plated disks resulted in impossible estimates of sampling and testing variances by the hierarchic method [this does not imply that the data itself was highly variable; for amplification see Davies (12), p. 100-108]. Only overall estimates of variance were obtained for the samples tested on the chrome-plated disks.

Although the mean results of the tests were nearly equal, the overall variation experienced in testing the sheets on the disks was substantially greater than the overall variation for tests on the screens. A "t" test (see Appendix III) applied to the grand mean coarseness values indicated a real difference at a 95% confidence level. The difference may have been the result of incomplete transfer of the sheets to the disks during the pressing operation and the possibility of scan line crossing counting errors due to the reflection of fibers by the chrome surfaces of the disks. Because of its apparent advantage, only the technique of testing on the screens will be considered in the remainder of the discussion.

Comparison of the results presented in Table VI with the scan line--very thin sheet results in Table I for the same pulp reveals that the earlier work (Table I) shows greater coarseness, fewer fibers per gram, and a longer average fiber length. Recalling that a 100-mesh screen was used in the earlier work while a 200-mesh screen was used in the more recent work, the differences can be attributed to greater losses of fines and short fiber fractions with the 100-mesh screen. The finer screen would be preferable for any further use of this method.

TABLE VI

RESULTS OF COARSENESS, AVERAGE FIBER LENGTH, AND FIBERS PER GRAM DETERMINATIONS ON VERY THIN SHEETS

Sample 2406-5-2387-110-	Coarseness,[a] mg./100 m.	Average Fiber[b] Length, mm.	Calculated Number of Fibers per Gram, millions
Sheets transferred to disks:			
1	22.52	1.59	2.78
2	23.12	1.74	2.50
3	22.12	1.55	2.92
4	21.69	1.77	2.61
5	22.06	1.84	2.47
Mean	22.30	1.70	2.66
Coefficient of variation-			
Overall	7.47%	14.00%	7.25%[d]
Sampling	--[c]	--[c]	
Testing	--[c]	--[c]	
Sheets tested on screens:			
6	21.97	1.70	2.68
7	23.74	1.68	2.51
8	22.96	1.75	2.49
9	23.22	1.53	2.81
10	23.83	1.52	2.75
Mean	23.14	1.64	2.65
Coefficient of variation-			
Overall	5.41%	8.50%	5.11%
Sampling	2.62%	4.80%	
Testing	4.73%	7.00%	

a. Average for six scan line observations.
b. Mean value for three slides tested by the grid count method.
c. Variation in the estimated variance between samples and within samples was too large to provide an estimate of the standard deviations in sampling and testing (see Appendix III).
d. Variation in five samples of values calculated from mean coarseness and fiber length values for each of five samples.

The hierarchic classification of fiber length data for sheets tested on the screens resulted in an estimated sampling variation of 4.80%, an estimated testing variation of 7.00%, and an estimated overall variation of 8.50%. Using a test schedule of three slides tested per sheet (as was done in this work) reduces the testing variation by the square root of three so that average fiber length can be determined for each sheet with an estimated variation of 6.26%.

The calculation of the number of fibers per gram from the coarseness and average fiber length has a coefficient of variation equal to the square root of its components in the equation:

$$\nu_{fg}^2 = \nu_s^2 + \nu_c^2 + \nu_{fl}^2 \qquad (7)$$

where: ν_{fg} = coefficient of variation in the determination of the number of fibers per gram

ν_c = coefficient of variation in the determination of coarseness

ν_s = coefficient of sampling variation (more precisely the coefficient of variation between sheets)

ν_{fl} = coefficient of variation in the determination of fiber length

The expected coefficient of variation for the computed number of fibers per gram from the results of a single determination would then be 8.7%. The estimated coefficients for a single scan line--very thin sheet test are summarized in Table VII.

TABLE VII

SUMMARY OF VARIATIONS IN SCAN LINE TECHNIQUE FOR A SINGLE TEST

Source	Coefficient of Variation, %
Overall--coarseness	5.4
Overall--fiber length (3 slides tested per sheet)	6.3
Overall--fibers per gram	8.7
Scan line counting	4.7
Sampling	2.6

None of the techniques used in this method is destructive to the fibers and a single test for coarseness can be performed in one-half hour. The speed and nondestructive nature of the scan line technique means that it would be practicable to reduce substantially the variations in the method by repeated tests on more than one sheet. For example, the coefficient of variation for number of fibers per gram expected for single tests on duplicate sheets would be 6.2% which is comparable to the 6.1% variation that could be expected for three determinations by the grid count--oxidation method. Duplicate tests on duplicate sheets would further reduce the coefficient of variation for number of fibers per gram to 4.5%.

The apparent small sampling error, which may be attributed to the use of samples sufficiently large to be representative of a fiber population, along with procedural simplicity and speed makes the scan line--very thin sheet approach an attractive one. When used to determine coarseness this technique is similar to the TAPPI coarseness method T 234 su-64 with the exception of the transfer step in the TAPPI method where the fibers in the sheet are sampled for scan line measurements with a gelatin coated slide. The transfer step introduces another source of variation and the use of a slide restricts the field over which random measurements can be taken, in effect reducing the sample size.

CONCLUSIONS

The differences observed between the test methods compared can be accounted for to some extent (aside from individual test variation) by the specificity of a given test for a range less than the actual distribution of the fibers. For example, it is reasonable to expect low fibers per gram counts and high average fiber lengths by the dyed fraction and scan line--very thin sheet methods because of fines omission in the visual selection of fibers in the case of the dyed fraction method and fines loss during formation in the very thin sheet method. Comparison with other methods seemed to bear this out, although none of the methods is without criticism in terms of selectivity. Methods involving the sampling of fiber suspensions with eyedroppers or scoops can favor shorter fractions due to classification while mechanical treatment in the form of agitation during the preparation of fiber suspensions can result in fiber breakage.

Sampling variation was found to be the largest factor affecting the reproducibility of the grid count--oxidation method. It was postulated that the technique of sampling a small quantity of fibers from a dilute suspension with an eyedropper did not provide samples representative of the population sampled. This was supported by the fact that the variations due to sampling were much less in the very thin sheet technique where samples sufficiently large to be weighed on an analytical balance were used. From this it is concluded that in terms of reproducibility it is better to perform random replications of a test on a large sample than to perform single tests on a number of very small samples. The scan line--very thin sheet method seems to be the most desirable approach for this reason. In addition, it was the simplest, quickest, and most straightforward test for coarseness of all the tests considered.

An extension of the very thin sheet technique worth consideration lies in the possibility of forming random fiber distributions of sufficiently low areal densities that direct grid count fiber length observations can be made using the forming screen as the grid. In this manner the variations introduced in sampling the sheets for the preparation of grid count slides would be eliminated.

GENERAL DISCUSSION

Before any measurement technique can be applied uniformly to pulps and pulp fibers a criterion must be adopted that defines a pulp fiber in terms of testable properties. Pulps generally contain materials other than fibers in the form of debris, cell wall material and anything else that may have fallen into the digester. These nonfiber materials can occur in significant quantities, especially in hardwoods. To apply a test of a property such as length or coarseness defined in terms of a fiber to a material that is not a fiber is clearly illogical. There are two alternatives for testing a pulp that is not 100% fibers. Tests can be redefined or new tests innovated that encompass by definition the fiber and nonfiber components, or the nonfiber materials can be segregated from the pulp fibers and tested separately. The latter alternative seems to be the more reasonable and future efforts should probably be directed toward the development of techniques of separation and quantitative description of the nonpulp fiber components. For unbeaten pulps the differences are by and large apparent and visual resolution between fibers and nonfibers can be made. However, in the case of beaten pulps the resolution becomes occluded by the generation of fines and fragments. It is here that a clear criterion is needed that would be the basis of what constitutes a fiber, i.e., does a split fiber become two fibers, what becomes of a fiber broken transversely or a pulverized fiber? If fiber fragments or split fibers are not to be considered whole fibers, should they be considered fractions of fibers (if so, how does one sum them) or should they be considered nonfibers? Essentially the question to be solved is whether such properties as coarseness and fiber length are constant-valued properties of a pulp species or properties of a given pulp in a given state.

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APPENDIX I

STANDARD TEST PROCEDURES AND DATA

DILUTION METHOD

This is a standard Institute test based upon the dilution method of Graff (6) with slight changes in sample conditioning and final sampling. The pulp sample is conditioned to 72°F., 50% R.H. One-half gram is soaked in 50 ml. of distilled water and rolled between the fingers to disintegrate it. The suspension is diluted to 500 ml., heated to 50°C., 5 ml. of 0.2% Congo Red solution is added; after boiling for ten minutes 0.5 g. of soda ash and 5 g. of sodium sulfate is added and boiling is continued for an additional ten minutes. The suspension is cooled and diluted to one liter. Ten 100-ml. portions are each diluted to one liter and from these ten 100-ml. portions are diluted to 500 ml. Ten 100-ml. portions of the 500-ml. dilutions are then combined to produce one liter of suspension at a concentration of 0.00001 g./ml. The final suspension is poured back and forth between a 1000-ml. graduate and a 2-liter beaker. The suspension is then sampled from the 2-liter beaker with a 150-ml. beaker and a 5-ml. portion is immediately taken by pouring into a 11-mm. I.D. 5-ml. graduate made from a 10-ml. graduate. The sample is transferred to a clean glass plate and allowed to dry.

Fibers, fiber fragments, and ray cells greater than 0.1 mm. in length were counted at 20X with a binocular microscope equipped with an eyepiece micrometer. The following counts were made on the Weyerhaeuser Bleached Sulfite Grade W pulp.

Sample	Fibers + Parenchyma and Ray Tracheid Cells >0.1 mm.	Fibers Only >0.1 mm.
1	254	138
2	243	148
3	223	132
Av.	240	139

Average number of fibers, parenchyma and ray tracheids >0.1 mm. = 240 x 20,000 = 4,800,000 fibers per gram.

Average number of fibers only >0.1 mm. = 139 x 20,000 = 2,780,000 fibers per gram.

FIBER LENGTH BY PROJECTION

This is an Institute method based upon the method of Ilvessalo-Pfäffli and V. Alfthan (2). The projection method involves the measurement of fiber length by projecting a one by three-inch slide prepared from a Congo Red-dyed sample of fiber onto the back side of a translucent screen at 50X and measuring and counting individual fibers. The measurement and counting is done with a curvimeter connected to electronic counters which record the number of fibers counted in intervals of 0.2 mm. The fiber length distribution data for the Weyerhaeuser Bleached Sulfite Grade W is shown in Table VII.

DYED FRACTION METHOD

In this method, devised by R. H. Van Eperen and W. A. Wink, a sample of fibers dyed in boiling water with Congo Red and a sample of undyed fiber is conditioned to 72°F., 50% R.H. Approximately 0.04 g. of dyed fibers and 1.0 g. of undyed fibers are weighed to 0.0001 g., mixed and dispersed in 20 liters of distilled water. Approximately 100 ml. of the suspension is removed, dried, and the undyed fibers are weighed to 0.00001 g., while the dyed fibers are counted and measured with a comparator eyepiece in a microscope at 23X. Tests were run on Weyerhaeuser Bleached Sulfite Grade W and Douglas-fir/springwood. The fiber

TABLE VII

FIBER LENGTH BY PROJECTION

(Fiber Length Distribution Data for Weyerhaeuser Bleached Sulfite Grade W)

Interval, mm.	Frequency	(a) Frequency, %	(b) Average Length, mm.	(a)(b)	$(a)(b)^2$
0-0.1	3	0.2	0.05	0.01	0.001
0.1-0.3	196	13.5	0.2	2.70	0.540
0.3-0.5	352	24.2	0.4	9.68	3.872
0.5-0.7	160	11.0	0.6	6.60	3.960
0.7-0.9	89	6.1	0.8	4.88	3.904
0.9-1.1	67	4.6	1.0	4.60	4.600
1.1-1.3	58	4.0	1.2	4.80	5.760
1.3-1.5	67	4.6	1.4	6.44	9.016
1.5-1.7	53	3.6	1.6	5.76	9.216
1.7-1.9	45	3.1	1.8	5.58	10.044
1.9-2.1	53	3.6	2.0	7.20	14.400
2.1-2.3	45	3.1	2.2	6.82	15.004
2.3-2.5	49	3.4	2.4	8.16	19.584
2.5-2.7	35	2.4	2.6	6.24	16.224
2.7-2.9	42	2.9	2.8	8.12	22.736
2.9-3.1	35	2.4	3.0	7.20	21.600
3.1-3.3	28	1.9	3.2	6.08	19.456
3.3-3.5	22	1.5	3.4	5.10	17.340
3.5-3.7	18	1.2	3.6	4.32	15.552
3.7-3.9	14	1.0	3.8	3.80	14.440
3.9-4.1	7	0.5	4.0	2.00	8.000
4.1-4.3	5	0.3	4.2	1.26	5.292
4.3-4.5	7	0.5	4.4	2.20	9.680
4.5-4.7	3	0.2	4.6	0.92	4.232
4.7-4.9	-	--	4.8	----	-----
4.9-5.1	1	0.1	5.0	0.50	2.500
5.1-5.3	1	0.1	5.2	0.52	2.704
	1455			121.49	259.657

Arithmetic average fiber length $\Sigma ab/100=1.21$ mm.

Weighted average fiber length $\Sigma ab^2/\Sigma ab=2.14$ mm.

length measurements are summarized in 0.2-mm. increments in Tables VIII and IX and the dyed fraction test results are shown in Table X.

TAPPI COARSENESS

The TAPPI coarseness was run according to TAPPI Suggested Method T234 sm-60. With this method a sample of 0.1 g./liter pulp suspension is poured into a 4.5 x 10 cm. vessel with 5 to 8 mm. sides constructed from a large glass slide and weighed to 0.001 g. subtracting the tare of the cell. The water is evaporated on a warming plate and the cell containing the dried fibers is placed in a projector capable of projecting a 10 x 10 mm. field to 8 x 8 in. A region of the cell selected at random is projected onto a sheet of white paper ruled with an 8 x 8-in. grid of lines at one-inch intervals. The magnification of the projector is set by projecting a clear plastic millimeter scale onto the grid and adjusting the magnification until 5 mm. on the scale coincided with 4 inches on the grid.

The number of fiber image-grid crossings are counted for eight randomly selected fields and the coarseness is calculated by the relation:

$$C = \frac{(0.1W)\ (0.0156\ F\ G^2)\ (10^5)}{(\pi/4)\ (S)\ (N)\ (A)}$$

where: $\underline{A}$ = area of the cell (45 cm.^{2})

$\underline{F}$ = number of fields examined (8)

$\underline{N}$ = total number of fiber image-grid crossings in $\underline{F}$ fields

$\underline{W}$ = weight of 0.1 g./liter suspension added to the cell, grams

$\underline{G}$ = length of the side of a grid (8 inches)

$\underline{S}$ = spacing of grid lines relative to the cell (1.25 mm.)

$\underline{C}$ = coarseness value, mg./100 meters

TABLE VIII

DYED FRACTION METHOD

(Summary of Fiber Length Measurements on Weyerhaeuser Bleached Sulfite, Grade W)

Interval, mm.	(b) Average Length, mm.	Frequency	(a) Frequency, %
0-0.2	0.1	2	0.47
0.2-0.4	0.3	12	2.81
0.4-0.6	0.5	38	8.90
0.6-0.8	0.7	27	6.32
0.8-1.0	0.9	35	8.20
1.0-1.2	1.1	30	7.03
1.2-1.4	1.3	37	8.67
1.4-1.6	1.5	27	6.32
1.6-1.8	1.7	24	5.62
1.8-2.0	1.9	22	5.15
2.0-2.2	2.1	25	5.86
2.2-2.4	2.3	24	5.62
2.4-2.6	2.5	17	3.98
2.6-2.8	2.7	15	3.51
2.8-3.0	2.9	18	4.22
3.0-3.2	3.1	21	4.92
3.2-3.4	3.3	12	2.81
3.4-3.6	3.5	17	3.98
3.6-3.8	3.7	10	2.34
3.8-4.0	3.9	5	1.17
4.0-4.2	4.1	2	0.47
4.2-4.4	4.3	5	1.17
4.4-4.6	4.5	1	0.23
4.6-4.8	4.7	0	0
4.8-5.0	4.9	1	0.23
		427	

Arithmetic average fiber length = $\Sigma ab/100$ = 1.83 mm.

Weighted average fiber length = $\Sigma ab^2/\Sigma ab$ = 2.42 mm.

TABLE IX

DYED FRACTION METHOD

(Summary of Fiber Length Measurements on Douglas-fir/Springwood)

Interval, mm.	(b) Average Length, mm.	Sample 1 (a) Frequency	Sample 1 (a) Frequency, %	Sample 2 (a) Frequency	Sample 2 (a) Frequency, %
0.2-0.4	0.3	1	0.26	--	----
0.4-0.6	0.5	1	0.26	--	----
0.6-0.8	0.7	4	1.05	1	0.24
0.8-1.0	0.9	5	1.31	4	0.96
1.0-1.2	1.1	10	2.62	12	2.89
1.2-1.4	1.3	16	4.20	10	2.41
1.4-1.6	1.5	7	1.84	16	3.86
1.6-1.8	1.7	17	4.46	25	6.02
1.8-2.0	1.9	28	7.35	27	6.51
2.0-2.2	2.1	37	9.71	47	11.33
2.2-2.4	2.3	43	11.29	44	10.60
2.4-2.6	2.5	35	9.19	59	14.22
2.6-2.8	2.7	43	11.29	43	10.36
2.8-3.0	2.9	46	12.08	41	9.88
3.0-3.2	3.1	39	10.24	35	8.44
3.2-3.4	3.3	24	6.30	28	6.75
3.4-3.6	3.5	18	4.72	14	3.37
3.6-3.8	3.7	5	1.31	6	1.45
3.8-4.0	3.9	2	0.52	2	0.48
4.0-4.2	4.1	--	----	1	0.24
		381		415	

Arithmetic average fiber length = $\Sigma ab/100$

Sample 1: 2.46 mm.
Sample 2: 2.45 mm.

Weighted average fiber length = $\Sigma ab^2/\Sigma ab$

Sample 1: 2.65 mm.
Sample 2: 2.61 mm.

TABLE X-A

DYED FRACTION METHOD

(Dyed Fraction Test Results)

	Douglas-fir/Springwood		Weyerhaeuser Bleached Sulfite, Grade W
	Sample 1	Sample 2	
Dyed fibers, %	3.573	3.573	4.417
Number of dyed fibers	381	415	427
Number of undyed fibers	10,282	11,200	9,240
Wt. of undyed fibers, mg.	5260	5730	5080
Average fiber length, mm.	2.46	2.45	1.83
Sample average	2.46		
Average fiber wt., mg.	0.512	0.512	0.550
Sample average	0.512		
Fibers per gram	1,953,000	1,953,000	1,818,000
Sample average	1,953,000		

The following determinations were made on the Weyerhaeuser Bleached Sulfite Grade W pulp:

	Coarseness, mg./100 meters	
	Fibers Only	Fibers + Parenchyma and Ray Tracheid Cells
Trial 1	21.4	19.5
Trial 2	23.2	21.9
Av.	22.3	20.7

It should be noted that this is a TAPPI suggested method and it has been revised and superceded by TAPPI suggested method T 234 su-64. In this revision the fibers are dyed, deposited on a filter paper in a TAPPI sheet machine and couched onto a heated gelatin coated slide. The slide is then projected onto a grid or observed with a microscope as it is moved through the field of view with a mechanical stage. The number of fibers in a field and the number of fibers crossing a set of lines a known distance apart and having a known total length are recorded. Knowing this and the weight per unit area of the fibers deposited on the filter paper, the coarseness value can be calculated.

APPENDIX II

ANALYSIS OF VARIATIONS IN GRID COUNT--OXIDATION METHOD

TABLE XI

TYPICAL GRID COUNT DATA FOR FIBER COUNTING

Sample 2406-5 - 2387-60

		Number of Fibers		
	Trial	Slide 1	Slide 2	Slide 3
	1	519	466	275
	2	558	486	272
	3	542	494	271
	4	530	480	265
	5	544	470	255
$\underline{n} = 6$	6	531	451	246
		3224	2847	1584
		1,733,286	1,352,089	418,816
Mean, $\bar{x} = \frac{\Sigma x}{n}$		537	474	264
Variance, $Vx = \frac{\Sigma x^2 - \frac{(\Sigma x)^2}{n}}{n-1}$		184.7	237.5	128.0
Standard deviation, $\sigma = Vx^{1/2}$		13.60	15.43	11.32
Coefficient of variation, $v = 100\frac{\sigma}{\bar{x}}$		2.53%	3.15%	4.29%

TABLE XII

TYPICAL GRID COUNT DATA FOR FIBER-GRID INTERSECTIONS

Sample 2406-5 - 2387-60

	Trial	Slide 1	Slide 2	Slide 3
	1	255	217	118
	2	239	226	115
	3	243	233	112
	4	247	230	115
	5	256	213	103
$\underline{n} = 6$	6	245	214	117
		1485	1333	680
		367,765	296,519	77,216
Mean, $\bar{\underline{x}} = \frac{\Sigma \underline{x}}{\underline{n}}$		247	222	113
Variance, $\underline{Vx} = \frac{\Sigma \underline{x}^2 - \frac{(\Sigma \underline{x})^2}{\underline{n}}}{\underline{n}-1}$		45.5	74.2	29.9
Standard deviation, $\sigma = \underline{Vx}^{1/2}$		6.75	8.62	5.47
Coefficient of variation, $\nu = 100 \frac{\sigma}{\bar{\underline{x}}}$		2.73%	3.88%	4.84%

TABLE XIII

TYPICAL GRID COUNT DATA FOR CROSSINGS PER FIBER

Sample 2406-5 - 2387-60

	Trial	Slide 1	Slide 2	Slide 3
	1	0.491	0.466	0.429
	2	0.428	0.465	0.423
	3	0.448	0.472	0.414
	4	0.466	0.479	0.434
	5	0.470	0.453	0.404
$\underline{n} = 6$	6	0.461	0.474	0.476
		2.764	2.809	2.580
		1.275546	1.099266	1.112514
Mean, $\bar{\underline{x}} = \frac{\Sigma \underline{x}}{\underline{n}}$		0.461	0.468	0.430
Variance, $\underline{Vx} = \frac{\Sigma \underline{x}^2 - \frac{(\Sigma \underline{x})^2}{\underline{n}}}{\underline{n}-1}$		0.000453	0.000082	0.000623
Standard deviation, $\sigma = \underline{Vx}^{1/2}$		0.021	0.009	0.025
Coefficient of variation, $v=100 \frac{\sigma}{\bar{\underline{x}}}$		4.62%	1.94%	5.81%

TABLE XIV

VARIATIONS IN RATIO OF GRID INTERSECTIONS
TO FIBERS FOR ALL SLIDES

Sample 2406-5 - 2387-	Slide	Grid Intersections Per Fiber[a]
57	1	0.466
	2	0.497
	3	0.505
58	1	0.467
	2	0.516
	3	0.570
60	1	0.461
	2	0.468
	3	0.430
61	1	0.476
	2	0.523
	3	0.514
63	1	0.451
	2	0.557
	3	0.408
Mean		0.487
Variance		0.00199
Coefficient of variation		9.16%

a. Average of six replicate determinations.

APPENDIX III

CLASSIFICATION AND TREATMENT OF SCAN LINE--VERY THIN SHEET DATA

HIERARCHIC CLASSIFICATION OF COARSENESS DATA FOR SHEETS TESTED ON FORMING SCREENS, mg./100 m.

Sample 2406-5 - 2387-110-

Observation	6	7	8	9	10		
1	21.42	25.28	21.80	23.95	22.63		
2	21.20	24.65	22.55	24.25	25.08		
3	23.95	23.35	23.50	23.53	24.62		
4	21.75	21.82	22.55	22.08	23.87		
5	20.75	22.82	22.82	22.08	24.32		Grand
6	22.73	24.50	24.55	23.40	22.48	Total	Mean
Sum, $\underline{S}$	131.80	142.42	137.77	139.29	143.00	694.28	
Mean, $\underline{x}$	21.97	23.74	22.96	23.22	23.83		23.14
Crude sum of squares, $\Sigma \underline{x}^2$	2902.1368	3389.0382	3167.9499	3237.9387	3413.8574	16,110.9210	
Correction, $\underline{S}^2/6$	2895.2067	3380.5761	3163.4288	3233.6174	3408.1667	16,080.9957	
Sum of squares about sample mean, $\Sigma \underline{x}^2 - \underline{S}^2/30$	6.9301	8.4621	4.5211	4.3213	5.6907	29.9253	
Degrees of freedom	5	5	5	5	5	25	

Variance within samples, $\underline{V}_{\underline{x}} = \frac{29.9253}{25} = 1.197$

Correction for grand mean, $\underline{St}^2/6 = \frac{694.28^2}{30} = 16{,}067.4906$

Sum of squares between samples, $\Sigma \underline{S}^2/6 - \underline{St}^2/30 = 13.5051$

Total sum of squares, $\Sigma \underline{x}^2 - \underline{St}^2/30 = 43.4304$

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Quantity Estimated by the Mean Square
Between samples	13.5051	4	3.376	$\sigma_o^2 + 6\,\sigma_1^2$
Within samples	29.9253	25	1.197	σ_o^2
Total	43.4304	29	1.498	

$\sigma_o = 1.09 \quad \sigma_1 = 0.61$

Coefficient of variation in sampling, $\nu_1 = 100\,\frac{0.61}{23.14} = 2.62\%$

Coefficient of variation in testing, $\nu_o = 100\,\frac{1.09}{23.14} = 4.73\%$

Coefficient of variation in overall test, $\nu_t = (\nu_1^2 + \nu_o^2)^{\frac{1}{2}} = 5.41\%$

HIERARCHIC CLASSIFICATION OF FIBER LENGTH DATA FOR SHEETS TESTED ON FORMING SCREENS, mm.

Sample 2406-5 - 2387-110-

Slide Number	6	7	8	9	10		
1	1.552	1.766	1.795	1.458	1.723		
2	1.820	1.615	1.796	1.599	1.417		
3	1.735	1.655	1.657	1.539	1.434	Total	Grand Mean
Sum, $\underline{S}$	5.107	5.036	5.248	4.596	4.574	24.561	
Mean, $\underline{\bar{x}}$	1.702	1.678	1.749	1.532	1.525		1.637
Crude sum of squares, $\Sigma \underline{x}^2$	8.731329	8.466006	9.193290	7.051086	7.032974	40.474685	
Correction, $\underline{S}^2/3$	8.693816	8.453765	9.180501	7.041072	6.973825	40.342979	
Sum of squares about sample mean, $\Sigma \underline{x}^2 - \underline{S}^2/3$	0.037513	0.012241	0.012789	0.010014	0.059149	0.131706	
Degrees of freedom	2	2	2	2	2	10	

Variance within samples, $\underline{V}_{\underline{x}} = \frac{0.131706}{10} = 0.0131706$

Correction for grand mean, $\underline{St}^2/15 = \frac{24.561^2}{15} = 40.216181$

Sum of squares between samples, $\Sigma\, \underline{S}^2/3 - \underline{St}^2/15 = 0.126798$

Total sum of squares, $\Sigma \underline{x}^2 - \underline{St}^2/15 = 0.258504$

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Quantity Estimated by The Mean Square
Between samples	0.126798	4	0.03170	$\sigma_o^2 + 3\,\sigma_1^2$
Within samples	0.131706	10	0.01317	σ_o^2
Total	0.258504	14	0.01846	

$\sigma_o = 0.1147 \quad \sigma_1 = 0.0787$

Coefficient of variation in sampling, $\nu_1 = 100\,\frac{0.0787}{1.637} = 4.80\%$

Coefficient of variation in testing, $\nu_o = 100\,\frac{0.1147}{1.637} = 7.00\%$

Coefficient of variation in overall test, $\nu_t = (\nu_1^2 + \nu_o^2)^{\frac{1}{2}} = 8.50\%$

TEST FOR DIFFERENCE BETWEEN GRAND MEAN COARSENESS VALUES FOR SHEETS TESTED ON FORMING SCREENS AND TRANSFERRED TO DISKS.

	Estimated Standard Deviation
On disks	1.22
On screens	1.67
Average	1.44

Standard Error of the Difference in Mean Values:

$$\text{S.E.}\ (\bar{x}_s - \bar{x}_d) = \pm 1.44\sqrt{\frac{1}{30} + \frac{1}{30}}$$

$$= \pm 0.372$$

For 95% confidence limits based upon $\varphi = 58$ degrees of freedom, $t = 2.00$ [Davies (12) p. 366]

95% confidence limits for difference in mean values $= \pm (2.00)\ (0.372) = \pm 0.744$

Thus, the difference in the mean values can be estimated with 95% confidence to be $(23.14\text{-}22.30) \pm 0.74$ or a real difference ranging from 0.10 to 1.58 mg./100 m.