Relation of Certain Infrared Bands to Cellulose Crystallinity and Crystal Lattice Type.   Part II.   A New Infrared Ratio for Estimation of Crystallinity in Celluloses I and II*

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Synopsis

A new infrared ratio, $a_{1372\ cm.}{}^{-1}/a_{2900\ cm.}{}^{-1}$, is proposed for measuring crystallinity in cellulosic materials.   The advantage of this ratio over others which have been used is that it can be applied to both celluloses I and II and, therefore, to samples containing a mixed lattice.   Two series of samples, encompassing a wide range of crystallinity, were prepared from highly crystalline celluloses I and II.   The infrared ratios of these samples were compared with crystallinity values from x-ray diffractograms and density measurements, and with accessibility data from moisture sorption.   It was shown that the new infrared ratio ranks samples of both lattice types, as well as partly mercerized cottons, in the same order as do x-ray, density, and moisture sorption data.   The correlation of the new infrared ratio with accessibility, derived from moisture regain, is better than with crystallinities from either x-ray or density measurements.   Reasons for this are suggested.

INTRODUCTION

In Part I[1] the infrared spectra of highly crystalline celluloses I, II, and III were compared qualitatively with one another and with the spectrum of amorphous cellulose.   Particular attention was directed to those spectral bands which have been used by other workers to assess crystallinity, lateral order, and extent of lattice transformation.   From this comparison it became apparent that these bands were related to both crystallinity and lattice type (i.e. celluloses I or II), hence their utility as criteria of either parameter was severely limited.

It was also shown in the first phase of this study that a group of bands in

the 1200–1400 cm.$^{-1}$ region (assigned to C–H and O–H bending and CH$_2$ wagging motions) appeared to be related to crystallinity and not to lattice type.   Of these, the one at 1372–1375 cm.$^{-1}$ (C–H bending) was chosen as being most suitable for indicating crystallinity.   A quantitative study of the relationship between the ratio of the intensity of this band and one at 2900 cm.$^{-1}$ (C–H stretching), and three other types of measurement of crystallinity, was undertaken.   Both cellulose I and cellulose II samples were included, in an attempt to find a criterion which could be applied to both lattice types.

MATERIALS AND METHODS

The choice of materials covering a wide range of crystalline content poses some problems.   A series of samples of cellulose II varying widely in crystallinity is relatively easy to obtain, since regenerated celluloses can supply low to medium crystalline contents and the higher levels can be prepared by removing some of the disordered material by partial acid hydrolysis.   A suitable series of materials with the native cellulose I lattice is more difficult to secure.   Most native celluloses are fairly highly crystalline; at least, they are all in the same range.   Some increase can be obtained by partial acid hydrolysis; but when attempts are made to decrease the crystallinity below that in the naturally occurring cellulosic materials, trouble is encountered.   This is because "chemical" decrystallization treatments— swelling in alkali, strong acids, or ethylamine—tend to produce a lattice transformation, so that it is not possible to be sure that the decrystallized sample does not contain some cellulose II or III.   Mechanical decrystallization by long grinding in a ball mill[2] or shorter grinding in the more vigorous vibratory ball mill presumably does not cause lattice transformation, although upon recrystallization of severely ball-milled material some cellulose II is formed.   The major part of this study, therefore, is based on two vibratory ball-milled series (one for cellulose I, the other for cellulose II), supplemented by several rayons and some cottons and their hydrocelluloses.

Cotton samples studied were a commercial lot of kier-boiled yarn which was alcohol-extracted in the laboratory; a completely mercerized yarn prepared from the preceding stock lot by treatment with 20% sodium hydroxide at 0 °C.; two partly mercerized yarns prepared by treatment with 11 and 12% sodium hydroxide at room temperature; and two samples of lint cotton (S × P and Hopi Acala varieties) known to be slightly lower than normal in crystallinity.   Three rayons were used: Fortisan, XL (a tire cord type), and Fiber 40 (low wet-modulus type).

Hydrocelluloses were prepared from the stock lot of purified cotton and the completely mercerized cotton by refluxing for 30 min. in 4N hydrochloric acid followed by appropriate washing.   Hydrocelluloses were prepared from the rayons by refluxing for 15 min. in 4N hydrochloric acid followed by washing with ammonia in aqueous ethanol and then with ethanol to prevent formation of a horny mass upon drying.

The two vibratory ball-milled series were prepared from the materials of highest available crystallinity for cellulose I and II; that is, from the cotton hydrocellulose and the Fortisan hydrocellulose. These were milled for various lengths of time in a steel vibratory mill using steel balls.

Infrared spectra were obtained with a Beckman IR-7 spectrophotometer by use of the potassium bromide pellet technique.[3] Spectra of five samples were obtained with a Perkin-Elmer Model 221 spectrophotometer. Fibrous samples were reduced to small pieces before mixing with potassium bromide, either by grinding in a Wiley mill to pass a 20-mesh screen or by cutting with scissors to very short lengths. Both techniques seemed equally satisfactory and avoided decrystallization by more severe disintegrative methods. Hydrocelluloses were already fine powders and did not require cutting or grinding before incorporating in potassium bromide pellets.

X-ray diffractograms were obtained on the vibratory ball-milled series with a General Electric Model XRD-5 x-ray diffractometer equipped with a proportional counter. All other samples were run with a Norelco high-angle precision x-ray diffractometer equipped with proportional counter and pulse-height analyzer. Both instruments were equipped with copper target and nickel filter to produce Cu Kα radiation. Crystallinity indexes were calculated from the diffractograms by two methods—the correlation method of Wakelin et al.,[4] and an empirical one based on that of Segal et al.[5]

The Wakelin correlation method requires the use of diffractograms from two standard samples of (presumably) 100% crystalline and 100% amorphous cellulose, respectively. The diffractograms of the experimental samples are then evaluated by a point-by-point comparison of the curves with those of the standard samples according to the correlation procedure described by Wakelin et al. This method thus rates samples on a scale whose upper and lower ends are fixed by the crystalline content of the experimental materials chosen as the 100 and 0% standards. The fact that, for cellulose, a 100% crystalline material is unattainable does not detract from the usefulness of this technique for rating samples for purposes of comparison. The values obtained, however, will not be expected to agree in magnitude with those obtained by other methods. For this study the hydrocelluloses prepared from cotton and Fortisan were chosen as the crystalline standards for cellulose I and cellulose II, respectively, and the vibratory ball-milled materials ground for the longest times were used for the amorphous standards.

In the empirical method, the diffractogram height at the position of the 002 peak ($2\theta = 22.6°$ for cellulose I, $2\theta = 21.7°$ for cellulose II) and at suitable locations for the amorphous background ($2\theta = 19.0°$ for cellulose I, $2\theta = 16.0°$ for cellulose II) were used to calculate the percentage of crystalline material, Cr, from the relation,

$$\% \, Cr = \frac{I_{002} - I_{am}}{I_{002}} \times 100$$

Since for cellulose II considerable diffracted intensity from the $10\bar{1}$ peak extends over the region of $2\theta = 19°$, this location (which was used for estimating amorphous background for cellulose I) cannot be used for cellulose II. Instead, the position at $2\theta = 16.0°$, which is approximately at the minimum between the peaks at $2\theta = 12.0°$ and $2\theta = 20.0°$, was used.

This empirical method, like the Wakelin method, gives only a relative set of values, but is useful in rating a series of samples with respect to one another.

Density was measured by the technique of Orr et al.[6] in density-gradient columns containing a mixture of carbon tetrachloride and heptane. The liquid in the column and the sample were carefully dried before each determination. Each density value reported is the average of at least three separate determinations. Those cotton samples which were in the form of yarns or loose fibers were placed in the gradient column without cutting. A loose knot was tied in the yarns or fibers to hold them together. The hydrocelluloses and the ball-milled series were fine powders which were placed in the column in that form. The unmilled hydrocelluloses and the material milled for the longer times usually made rather narrow layers in the tubes but material milled for 2 and 5 min. generally was spread over a wide band. This was believed to indicate a considerable range of density values in these samples due to some portions having received more mechanical action than others during the very short milling periods. The value where the greatest concentration of the powdered sample occurred was recorded; in some cases, the average of the upper and lower edges of the band was used. As an experimental method of getting a single density value rather than an average of values for these samples, portions of the pressed pellets prepared for use in the x-ray diffractometer were placed in the density gradient tubes along with the powdered material. This method was not successful under the conditions used since these pellets were usually of lower apparent density—sometimes considerably lower—than any portion of the unpressed powder. When the pellets were allowed to stand in the tubes for long periods of time, their densities sometimes would approach or become equal to that of the powder. This behavior was interpreted as indicating the formation during the pressing operation of void spaces in the pressed pellets which were inaccessible to the liquid in the gradient column. A similar situation was encountered when attempts were made to measure densities of some of the rayon fibers. These gave absurdly low values, due undoubtedly to voids in the fibers, as others have reported.[7] These values were rejected as not being valid, and hence are not reported.

In calculating crystallinity, density values for crystalline and amorphous cellulose are required. For the density of crystalline material, the theoretical value calculated from unit-cell dimensions was used; that is, 1.592 g./cc. for cellulose I, 1.583 g./cc. for cellulose II.[8] A suitable value for the density of completely amorphous cellulose is more debatable. Those in the literature range from 1.455 g./cc.[7] to 1.50 g./cc.[9] Three different values

were tried in preliminary calculations; that of Hermans[9] (1.50 g./cc.) was finally somewhat arbitrarily selected.   The crystalline fraction, Cr, was calculated from the relation,

$$Cr = (V_x - V_{am})/(V_{cr} - V_{am}),$$

where V_x, V_{am}, V_{cr} are the specific volumes of the sample, of amorphous cellulose, and of crystalline cellulose, respectively.

Accessibility was estimated from the moisture regain at 65% R. H. and 21°C. by Valentine's[10] relation, $F_{Am} = $ S.R./2.60, where F_{Am} is the "amorphous" fraction (i.e., accessibility) and S.R. is the sorption ratio (the ratio of the moisture sorption of the experimental sample to that of a purified standard cotton at the same relative humidity).   The moisture regains were determined in humidity chambers kept at constant temperature, with constant humidity maintained by saturated sodium nitrite solution.[11]

RESULTS

The x-ray diffractograms of the unmilled and ball-milled samples (Fig. 1) show that the original unmilled materials (cotton hydrocellulose and Fortisan hydrocellulose) were highly crystalline.   Milling produced progressive reductions in crystallinity until an apparently completely amorphous state was reached, as judged by the absence of crystalline diffraction peaks
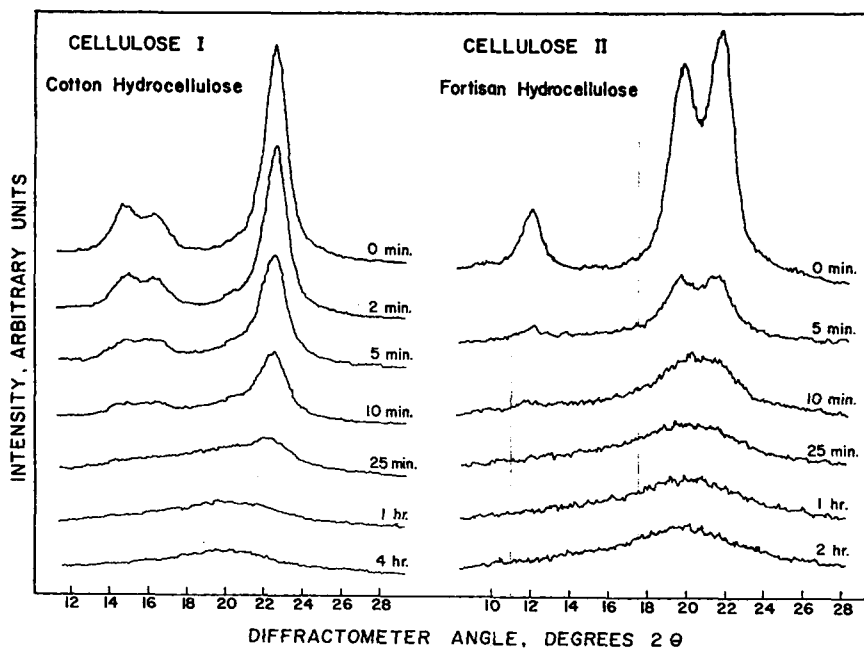

Fig. 1. X-ray diffractograms of cellulose I and cellulose II showing the effect of vibratory ball-milling for different lengths of time.

TABLE I

Crystallinity, Accessibility, and Infrared Index Data on Various Samples

| Sample | X-ray crystallinity index, % | | Density, g./cc. | Crystallinity from density, %[b] | Accessibility from moisture regain | Infrared ratio a_{1429}/a_{893}[c] | Infrared ratio a_{1372}/a_{2900}[d] |
	Empirical[a]	Wakelin					
Cellulose I							
Cotton hydrocellulose, milled 0 min.	88	(100)-Std.	1.550	56	0.34	4.30	0.84
2 min.	85	86	1.548	54	0.36	4.00	0.81
5 min.	74	65	1.544	49	0.43	3.08	0.78
10 min.	63	44	1.532	36	0.54	1.94	0.68
25 min.	16	15	1.515	17	0.80	1.21	0.49
1 hr.	0	0	1.507	8	—	0.78	0.43
4 hr.	0	(0)-Std.	1.502	2	0.98	0.81	0.44
Cotton yarn, purified	83	—	1.550	56	0.38	—	0.90
Cotton lint, S × P	84	80	1.544	49	0.41	3.44	0.71
Cotton lint, Hopi Acala	83	73	1.548	54	0.42	3.05	0.62

Cellulose II							
Fortisan hydrocellulose, milled 0 min.	85	(100)-Std.	1.542	52	0.46	0.34	0.75
5 min.	58	34	1.533	41	0.58	0.41	0.64
10 min.	43	26	1.522	28	0.71	0.56	0.45
25 min.	24	4	1.516	20	0.89	0.61	0.37
1 hr.	19	0	1.512	15	0.93	0.62	0.32
2 hr.	20	(0)-Std.	1.514	18	0.93	0.67	0.34
Fortisan rayon	80	74	—	—	0.58	—	0.68
XL rayon	64	35	—	—	0.80	—	0.54
Fiber 40 rayon	65	~42	—	—	0.73	—	0.60
Fortisan hydrocellulose	88	(100)	—	—	0.47	—	0.76
XL hydrocellulose	81	75	—	—	0.50	—	0.72
Fiber 40 hydrocellulose	87	~83	—	—	0.50	—	0.67
Fully mercerized cotton	66	51	1.534	42	0.61	0.43	0.54
Partly mercerized cotton (50% cellulose II)	62	—	1.534	40	0.52	1.03	0.59
Partly mercerized cotton (70% cellulose II)	58	—	1.537	44	0.54	0.78	0.58

[a] Empirical formula: $\% \; Cr = (I_{002} - I_{am})/(I_{002})$.
[b] Based on theoretical values for density of crystalline cellulose and on density of amorphous = 1.50 g./cc.
[c] "Crystallinity index" of O'Connor et al.,[16] "lateral order index" of Hurtubise and Krässig.[17]
[d] Proposed crystallinity ratio.

and by the fact that no further change in the diffractogram was produced by additional milling. The cotton hydrocellulose was reduced to this x-ray-amorphous state by 1 hr. of grinding while the Fortisan hydrocellulose seemed by the above criteria to be completely amorphous after about 25 min. Other data subsequently indicated an appreciable residual crystallinity in the last three samples of the ball-milled cellulose II series.

Table I gives the x-ray crystallinity indexes calculated from the diffractograms by the empirical formula (column 2) and by the Wakelin correlation method (column 3). The empirical values range from 88 to 0% for the cellulose I series, while for the cellulose II series they range from 85 to 19–20%, even though qualitatively the diffractograms of the last two samples appear completely amorphous. This may be due to the empirical nature of the formula, but there is some evidence from density and moisture sorption measurements to suggest that these samples are not completely amorphous. Values calculated by the Wakelin method for the cellulose I series range from 86 to 0%, and agree moderately well with the empirical ratings, although there are 9 and 19% discrepancies for the 5- and 10-min. samples, respectively. The agreement is much poorer for the cellulose II series, where the Wakelin values are lower than the empirical values by 17 to 24%. This is most probably due to a residual crystalline content, noted above, in the sample milled for the longest time, which was arbitrarily chosen as the amorphous standard in the Wakelin method. Since one method uses an empirical relation and the other method rates samples on an arbitrary scale, good agreement would scarcely be expected.

Density data and crystallinity percentages calculated from them using $d_{Am} = 1.50$ g./cc. are given in columns 4 and 5 of Table I. It will be noted that the crystallinity values so obtained are quite low, ranging from 2% to a maximum of 56%. Two factors contribute to produce such low values. One is the choice of Hermans' estimate of 1.50 g./cc. for the density of the amorphous fraction. If Tyler and Wooding's value of 1.455 g./cc. is used, the range becomes 36–71%, which shows higher values for all samples but a narrower range. Another factor tending to give low values is that experimentally determined densities of cellulosic fibers are affected by the extent to which the immersion liquid can penetrate the submicroscopic structure. Wahba and Aziz[12] have recently summarized the published data on this subject with the statement that "the apparent specific volume of any sample of cellulose measured in nonswelling fluids is greater the larger the size of the molecules of fluid." He quotes Davidson's[13] data which had shown that the specific volume of cotton fibers is about the same in such liquids as chloroform, carbon tetrachloride, benzene, nitrobenzene or toluene but that the volume in these liquids is about 1% higher than in helium. Wakeham[14] had found that dioctylphthalate, with a molecular size about three times that of benzene, gives 1–2% greater volumes for cotton than when benzene is used. Thus, due to the method of measurement, the densities in Table I are likely to be too low relative to the crystalline densities calculated from unit cell dimensions, and hence will yield relative crystal-

linities that are too low.   Since the purpose of the measurements was to aid in intercomparison of samples in the present series only, their utility should not be seriously impaired by the above considerations so long as it is recognized that they are not absolute values.

Accessibilities derived from moisture regain data are given in column 6 of Table I.   These values represent the fraction of the OH groups which are accessible, and would include not only those in the disordered and partially disordered regions but also those OH groups on the surfaces of the crystallites.   Thus for two celluloses of the same crystallinity but different crystallite size one would expect the sample with the smaller crystallites to exhibit the higher moisture regain and, hence, accessibility.   Such an effect can be seen in the data of Table I.   Fortisan and cotton hydrocelluloses (the materials used for the two ball-milled series) are of high crystallinity. The x-ray and density data suggest that they are approximately equal in crystalline content, but the accessibility values are appreciably different— 0.46 for unmilled Fortisan hydrocellulose, 0.34 for the corresponding cotton hydrocellulose.   It is well known that Fortisan contains smaller crystallites than cotton.   Morehead[15] reported approximate average dimensions as $334 \times 27 \times 50$ A. for the former and $1440 \times 50 \times 64$ A. for the latter. The calculated ratios of surface to volume (disregarding the end surfaces of crystallites) are 0.114 and 0.071, respectively, which indicates that Fortisan crystallites have 1.60 times as much surface per unit of volume as cotton crystallites.   The ratio of the accessibility values for the two materials is 1.35.

By ball-milling, the crystallites of both materials are eventually destroyed so that crystallite size should not influence the relative magnitude of the accessibility.   Indeed, it is seen that after prolonged milling, the accessibility for samples of both series becomes nearly equal to unity, as should be the case if these are almost completely amorphous materials.   The more gradual destruction of the crystalline phase in the cotton cellulose I material
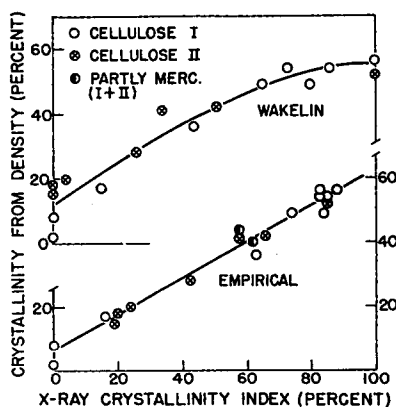

Fig. 2. Relation between crystallinity values calculated from density data and those calculated from x-ray diffractograms.
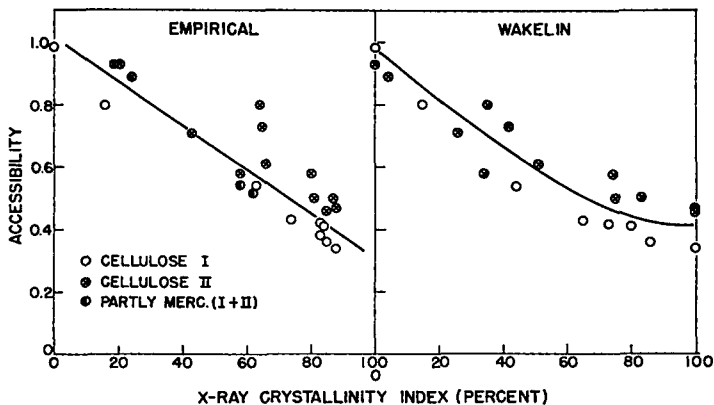
Fig. 3. Relations between the accessibility derived from moisture regain and crystallinity values calculated from x-ray diffractograms by the empirical method (left) and by the Wakelin method (right).
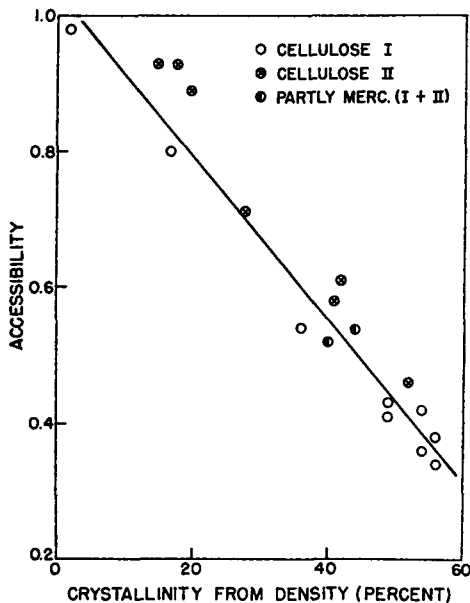

Fig. 4. Relation between accessibility and crystallinity calculated from density.

at early stages of grinding, already noted when examining the x-ray data, is again apparent in the accessibility values.

Before discussing the infrared data, intercomparisons of x-ray, density, and accessibility values are appropriate. Figure 2 shows the relation between crystallinity values calculated from density data and those derived from x-ray diffractograms by both methods. The Wakelin x-ray values give a slightly curvilinear plot with some scattering of cellulose I and cellu-
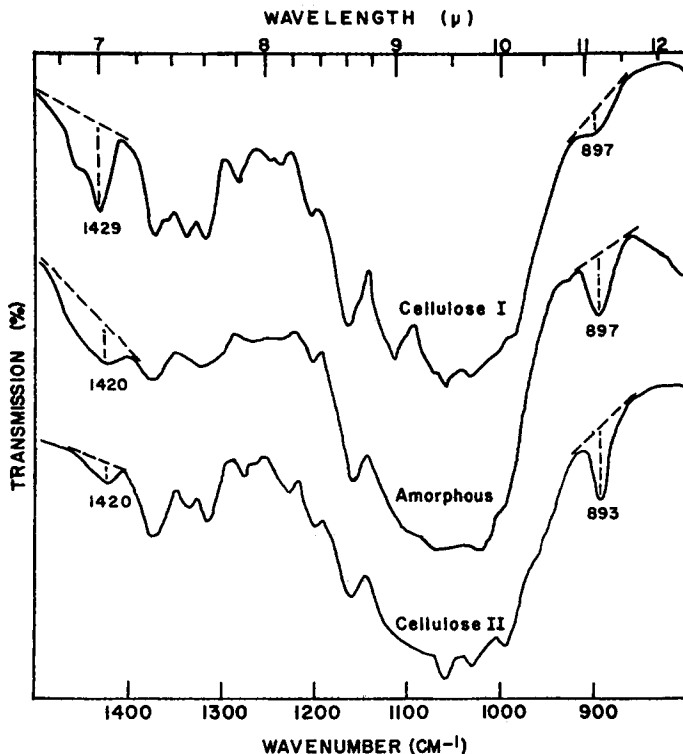
Fig. 5. Portions of infrared spectra illustrating crystallinity (or lateral order) index, $a_{1429 \text{ cm.}}{}^{-1}/a_{893 \text{ cm.}}{}^{-1}$, for highly crystalline cellulose I, amorphous cellulose, and highly crystalline cellulose II.

lose II values at the lower end, while the values derived by the empirical formula fall along a straight line about which points representing both lattice types are fairly uniformly distributed. The correlation coefficient of this line is 0.99.

In Figure 3 the accessibility data are plotted against x-ray crystallinities calculated by both the empirical method and the Wakelin method. The points representing x-ray crystallinity indexes show considerable scatter (correlation coefficient of empirical line, -0.91), with the cellulose I and cellulose II data more or less segregating into separate groups. As noted earlier, accessibility is affected by crystallite size, and most of the cellulose II samples are rayons which have smaller crystallites—hence more accessible OH groups on their surfaces—than the cellulose I samples derived from cotton cellulose.

The relation between accessibility values and crystallinities calculated from density is shown in Figure 4. Accessibility and density values show a considerably closer correlation (correlation coefficient, -0.97) than accessibility and empirical x-ray values.

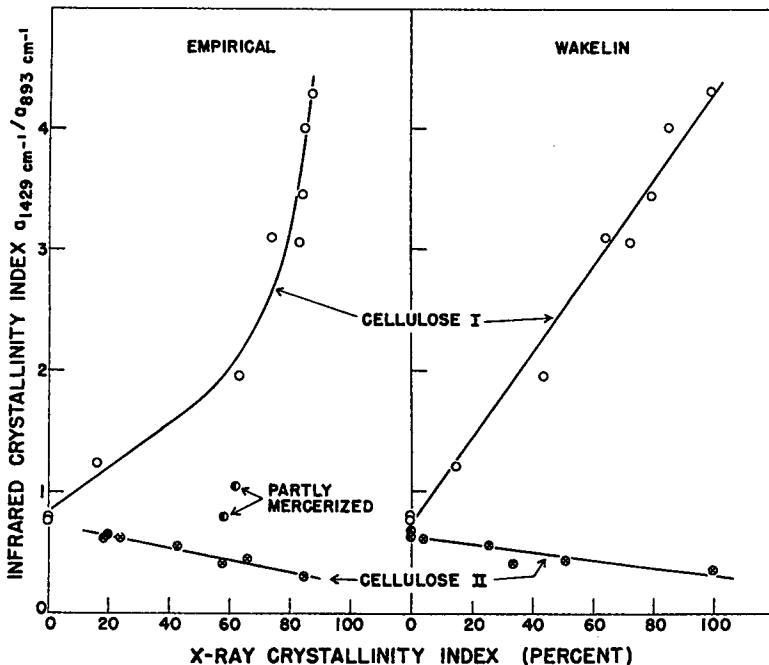The infrared data consist of two sets of ratios: (1) the "crystallinity

EMPIRICAL WAKELIN

INFRARED CRYSTALLINITY INDEX $a_{1429\ cm.^{-1}}/a_{893\ cm.^{-1}}$

CELLULOSE I

PARTLY MERCERIZED

CELLULOSE II

X-RAY CRYSTALLINITY INDEX (PERCENT)

Fig. 6. Relations between infrared crystallinity (or lateral order) index, $a_{1429\ cm.}{}^{-1}/$ $a_{893\ cm.}{}^{-1}$, and empirical (left) and Wakelin (right) x-ray crystallinities.

index" of O'Connor et al.[16] ("lateral order index" of Hurtubise and Krässig[17] and (2) a new ratio which is being proposed as a better measure of crystallinity, particularly for samples of cellulose II and for those that contain both type I and type II lattice. O'Connor's infrared crystallinity index is the ratio of the absorptivities at 1429 and 893 cm.$^{-1}$. Figure 5 shows the portions of the infrared spectra involved. O'Connor et al. noted that this index could not be applied to mercerized cellulose, while Hurtubise and Krässig showed that it changed regularly with extent of swelling in caustic. It was of interest to examine the values of this index for the present series of samples. These are given in column 7 of Table I. A graphical comparison with the empirical and the Wakelin x-ray crystallinities is shown in Figure 6. The values for the cellulose I samples fall on a straight line for the Wakelin values, and on a curved line for the empirical data. The cellulose II data, on the other hand, fall on entirely separate lines from the cellulose I data, with very small slopes of the opposite sign from the corresponding curves for cellulose I. The two partly mercerized samples are of particular interest. According to the empirical x-ray data, these samples are of moderate crystallinity (58 and 62%), yet the low values of the infrared crystallinity index would indicate a very low degree of crystallinity. It is for evaluating samples such as these, frequently encountered in textile finishing, that another infrared index is needed.
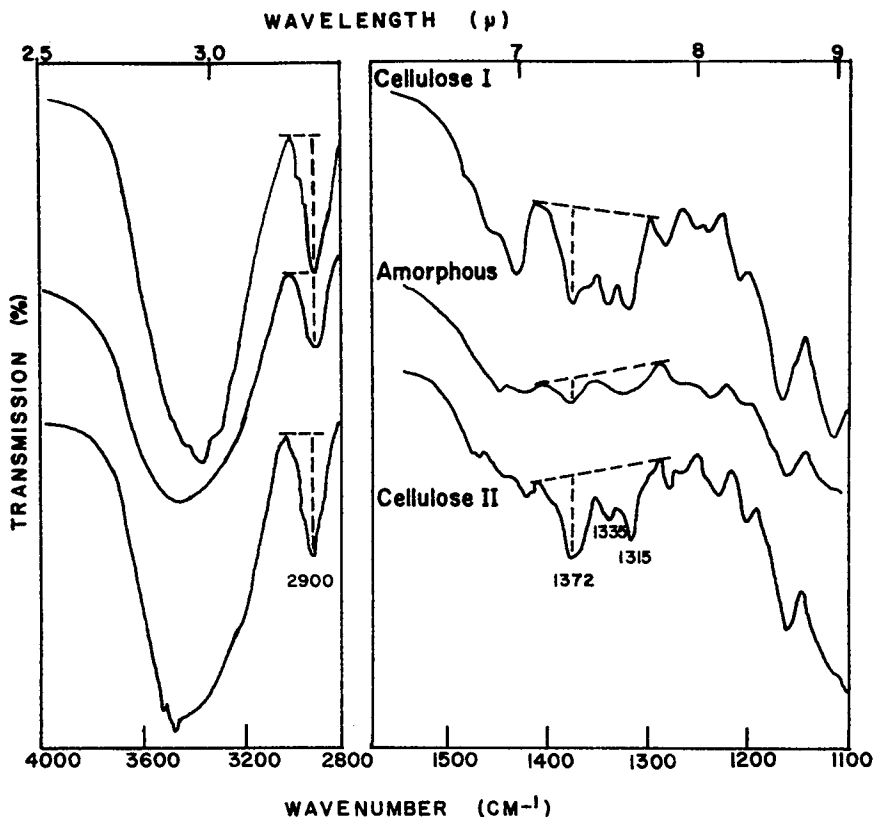
Fig. 7. Portions of infrared spectra illustrating proposed infrared crystallinity ratio, $a_{1372 \text{ cm.}^{-1}}/a_{2900 \text{ cm.}^{-1}}$.

In Part I[1] it was noted that the region between 1200 and 1400 cm.$^{-1}$ contained several bands which appeared to be affected by the amorphous content of the sample rather than by the lattice type, since admixture of highly crystalline cellulose II with cellulose I did not change the relative intensities appreciably whereas admixture of amorphous cellulose did. This region also appeared to show similar progressive changes with extent of ball-milling of both cellulose I and II.   The strongest bands showing the greatest changes were those at about 1372, 1335, and 1315 cm.$^{-1}$.   Of these, the one at 1372 cm.$^{-1}$ was selected.   This band is assigned to a C–H bending mode and hence should not be affected by differences in amount of water adsorbed onto the cellulose, whereas the adjacent band at 1335 cm.$^{-1}$, assigned to O–H in-plane bending, could be.   The band at 1315 cm.$^{-1}$ is tentatively assigned to CH_2 wagging motion and could be affected to some extent by a change in lattice type for the same reason that the band at 1429 cm.$^{-1}$, attributed to the CH_2 scissoring motion, is affected.

The absorptivity of the 1372 cm.$^{-1}$ band was first tried as a measure of crystallinity but was found to give rather poor correlations with other param-
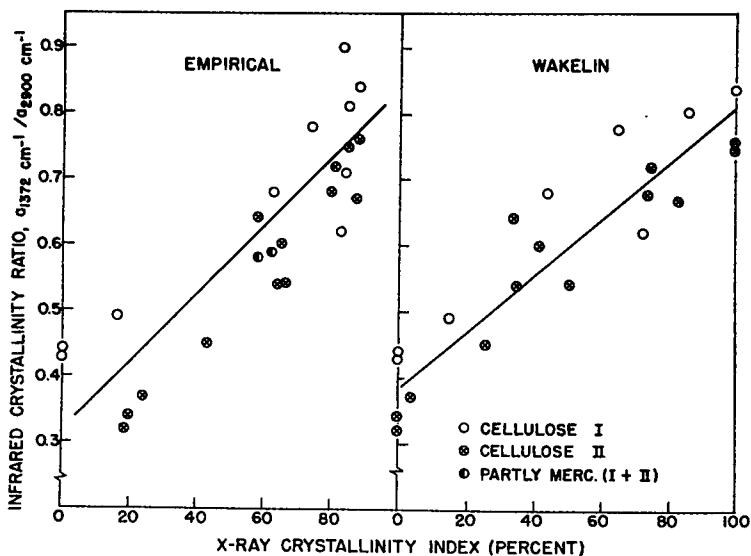
Fig. 8. Relations between proposed infrared crystallinity ratio, $a_{1372 \text{ cm.}}{}^{-1}/a_{2900 \text{ cm.}}{}^{-1}$, and x-ray crystallinity indexes.

eters. This was due partly to the uncertainty in actual sample concentration in the heterogeneous mixture of fiber particles and potassium bromide in the sample pellet, and probably to a greater extent to the uncontrollable variation in scattered light from one sample to another. It seemed better, therefore, to use a ratio of this band intensity to that of another band which was unaffected by changes in crystallinity, thus providing a kind of internal standard to compensate for the sources of variation mentioned. Such a band of constant intensity cannot logically be expected to exist; however, certain bands showed much less change than others. Of these, the strongest band of the group centered at 2900 cm.$^{-1}$ (C-H and CH$_2$ stretching) was chosen. Figure 7 shows the appearance of the spectra of cellulose I, cellulose II, and amorphous cellulose in the two regions of interest. The methods of drawing the baselines are indicated. For the band at 2900 cm.$^{-1}$ the intensity at the adjacent shoulder near 3000 cm.$^{-1}$ was chosen as the base. In the type of instrument used, there is a break in the spectrum at 2800 cm.$^{-1}$ which makes if difficult to construct the usual type of baseline between transmission maxima on either side of the band. For the band at 1372 cm.$^{-1}$ a line was drawn between the maxima at approximately 1290 and 1410 cm.$^{-1}$, giving a common baseline for the group of three bands which occur close together in this region and which are changing simultaneously.

Values of this ratio are listed in the last column of Table I and are plotted (Fig. 8) against the empirical and the Wakelin x-ray crystallinity indexes. In Figure 9 the proposed ratio is plotted against crystallinity from density and against accessibility. The points representing cellulose II samples

show the same general trend as the cellulose I samples in all four plots, in contrast to the complete separation of points for the two lattice types seen in Figure 6. More importantly, data for the partly mercerized samples fall into line with values for the pure lattice types. This indicates that the proposed infrared ratio could be used in studying the natural cellulosic fibers during stages of textile processing which involve alkali treatments.

The data in Figures 8 and 9 show considerable scatter about the regression lines, as indicated by correlation coefficients of 0.86 for the empirical x-ray data, 0.88 for density data, and −0.92 for accessibility. Except for accessibility, these coefficients are lower than any of those for the intercomparisons of the three latter parameters. The rather poor correlation of the
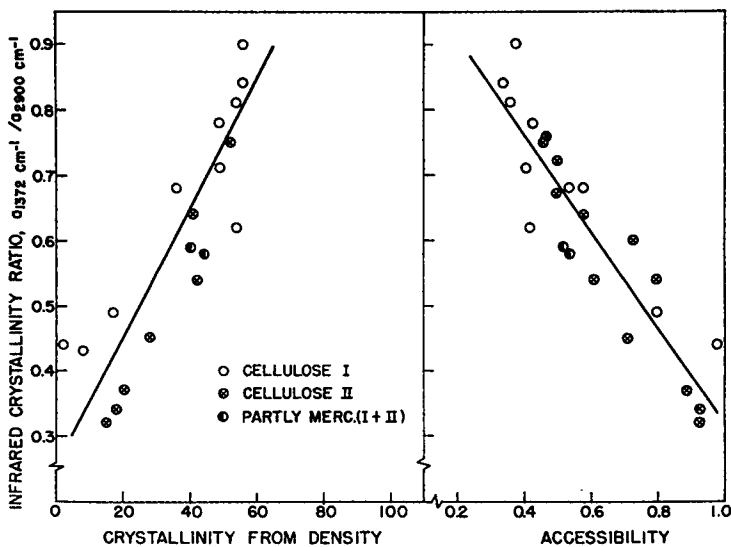

Fig. 9. Relations between proposed infrared crystallinity ratio, $a_{1372\ \text{cm.}}{}^{-1}/a_{2900\ \text{cm.}}{}^{-1}$, and crystallinity from density (left) and accessibility (right).

infrared ratio with crystallinities from x-ray and density data can be partly explained if one considers that the infrared ratio is dependent upon the environment of individual molecules and reflects the freedom of vibration of the atomic groups in the molecules whereas x-ray and density methods of assessing the fine structure are dependent upon the quantity and size of larger units of submicroscopic structure, the crystallites. Thus, for detection of molecular order by x-ray diffraction, the crystallites must be larger than certain minimum dimensions; both the dimensions and the presence of imperfections in the crystallites will affect the measurements. Density measurements, likewise, are dependent on the average degree of order of larger volume-units of the cellulose, since the immersion liquid cannot penetrate into some regions of intermediate order. The similarity in fine structural properties measured by x-ray diffraction and by density is

emphasized when it is recalled that a correlation coefficient of 0.99 was found for these two types of data.

The better correlation of infrared ratios with accessibility data is logical if one considers that moisture sorption, like infrared absorption bands, is dependent upon the environment of atomic groups in the molecules. Accessibility from moisture sorption measurements indicates how many hydroxyl groups are sufficiently free from neighboring molecules to allow absorption of water vapor, while the intensity of infrared bands can be affected by the closeness of packing of adjacent molecules which would interfere with vibrations of atomic groups. Thus the criterion of fine structure for accessibility and infrared data is at the molecular level rather than at the level of the larger subunits, the crystallites, as is the case for x-ray and density data.

CONCLUSIONS

The proposed infrared crystallinity ratio, $a_{1372cm.^{-1}}/a_{2900cm.^{-1}}$, ranks samples of cellulose I and cellulose II and those containing a mixed lattice in the same order as crystallinity parameters derived from x-ray diffraction, density measurements, and moisture sorption data. The correlation of the infrared ratio with the first two parameters is not as good as might be desired, but reasons have been advanced for the poor correlation. The closer relation of the infrared ratio to accessibility from moisture regain indicates that they are both measuring degree of order at the same level of organization of fine structure. It is suggested that this new ratio should have considerable application in studies of natural cellulosic fibers which are subjected to caustic treatments during purification or in the course of textile finishing operations.

Use of trade names does not imply endorsement by the United States Department of Agriculture over other similar products or instruments.

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Résumé

On a proposé un nouveau rapport infra-rouge, $a_{1372 \text{ cm}^{-1}}/a_{2900 \text{ cm}^{-1}}$, pour mesurer la cristallinité dans des matériaux cellulosiques. L'avantage de cette relation en comparaison avec d'autres qui ont été employées est qu'elle peut être appliquée aux celluloses I et II, ainsi qu'aux échantillons qui contiennent des réseaux mixtes. À partir des celluloses I et II de haute cristallinité, on a préparé deux séries d'échantillons, employant un large domaine de cristallinité. Les rapports infra-rouges de ces échantillons ont été comparés avec les valeurs de cristallinité obtenues par des diffractogrammes aux rayons-X et avec les données accessibles obtenues par la sorption d'humidité. On a démontré que les nouveaux rapports infra-rouges comprennent des échantillons des deux types de réseau, aussi bien que des cotons partiellement mercérisés dans le même ordre que ceux donnés par les rayons-X, la densité et la sorption d'humidité. La corrélation du nouveau rapport infra-rouge avec l'accessibilité, déduite en gain d'humidité, est meilleure que celle avec les cristallinités obtenues par rayons-X ou les mesures de densité. On suggère des raisons à ce phénomène.

Zusammenfassung

Als mass für die Kristallinität von Celluloseproben wird ein neuer Infrarorquotient, $a_{1372 \text{ cm}^{-1}}/a_{2900 \text{ cm}^{-1}}$, vorgeschlagen, dessen Vorteil gegenüber anderen in Verwendung stehenden Quotienten darin besteht, dass er sowohl auf Cellulose I als auch auf Cellulose II und somit auf Proben mit gemischtem Gitter anwendbar ist. Aus hochkristalliner Cellulose I und II wurden zwei Reihen von Proben hergestellt, die einen weiten Kristallinitätsbereich umfassten. Die Infrarotquotienten dieser Proben wurden mit den aus Röntgenbeugungsdiagrammen und Dichtemessungen bestimmten Kristallinitätswerten sowie mit den aus der Feuchtigkeitssorption ermittelten Zugänglichkeitsdaten verglichen. Die auf Grund dieses Infrarotquotienten aufgestellte Reihenfolge der Proben beider Gittertypen sowie teilweise mercerisierter Baumwolle stimmt mit der auf Grund von Röntgenbeugungs-, Dichte- und Feuchtigkeitssorptionsdaten aufgestellten Reihenfolge überein. Die Korrelation des neuen Infrarotquotienten mit der aus der Feuchtigkeitsaufnahme bestimmten Zugänglichkeit ist besser als diejenige mit der aus Röntgenbeugungs- oder Dichtemessungen bestimmten Kristallinität. Gründe dafür werden angegeben.