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The Use of Half Width and Position of the Lines in the X-Ray Diffractograms of Native Cellulose to Characterize the Structural Properties of the Samples

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Measurements of the position and half width of the (002)-reflexion for different samples of cellulose I (native) have been carried out. The values of the half widths have been compared with the degree of amorphity determined from a separation of the observed intensity into an amorphous and a crystalline part, and it is shown that this factor increases monotonically with the half width. The structural interpretation of the half width parameter is ambiguous, but its value should be related to the diameter and state of order of the microfibrils.

In a previous paper [1] it has been demonstrated that the X-ray diffractograms of cellulose I (native) to a fair degree of approximation can be interpreted as a superposition of broad crystalline reflexions, each reflexion having the shape of a Cauchy distribution. The normalized intensity distribution can thus be written

$$I(s) = \sum K_j \frac{\alpha_j}{\alpha_j^2 + (s - s_{oj})^2} \qquad (1)$$

where

$s = \frac{4\pi}{\lambda} \sin \Theta$

s_{oj} = peak position
$2\alpha_j$ = half width of the j'th reflexion
K_j = constant depending on the structure factor of the j'th reflexion

Each sample of cellulose I is in this way characterized by the parameters in equation (1). Of these the α_j and s_{oj} can be measured from the diffractograms.

The intensity distribution below $s = 2$ is dominated by the four reflexions (101), (10$\bar{1}$), (02$\bar{1}$) and (002). (101), (10$\bar{1}$) and (002) are of special interest as

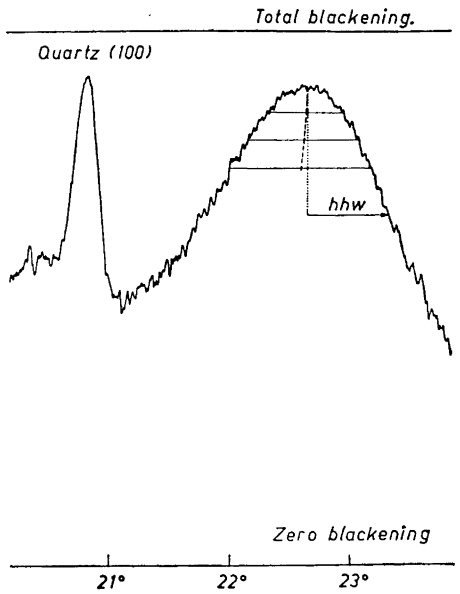

Fig. 1. Part of microphotometer curve. Residue of H_2SO_4 treated surgical cotton.

they give informations about dimensions and lattice distortions in directions normal to the fibre axis. As an accurate determination of the position and half width of (101) and (10$\bar{1}$) is impeded by the superposition of the two peaks, the investigations were restricted to the measurement of the peak position and half width of the (002)-reflexion.

EXPERIMENTAL PROCEDURE

Powder patterns of the investigated samples were prepared in a Guinier vacuum camera using Cu $K\alpha$-radiation. For accurate determination of the (002) peak position the samples were mixed with quartz (15 % by weight) and pressed into thin sheets in a briquetting machine. From the diffractograms film density curves were obtained by means of a recording microphotometer, the angular scale of the diffractograms being determined from the zero mark and the position of the quartz reflexions.

Fig. 1 shows a typical microphotometer curve. The peak abscissa was determined by bisecting horizontal cords and extrapolating to the peak level, as indicated in the figure. The half half-width was measured from the peak abscissa towards the high-angle side of the peak, as the low-angle side is strongly influenced by the (021)-reflexion, especially for samples with low order. The ordinates were read from zero film blackening, *i. e.* no coherent or incoherent background was subtracted.

RESULTS

11 different qualities of cellulose I were investigated. Half widths and peak positions were measured for five samples of each quality, and the mean values are listed in Table 1.

Table 1. (002)-peak position and half width for samples of cellulose I. Degree of amorphity determined by the method of Ellefsen *et al.*[2]

	Samples	Peak position $2\Theta°$	Half width in degrees	Degree of amorphity
1.	Surgical cotton	22.72	1.54	
2.	» » treated with H_2SO_4, residuum	22.71	1.32	0.37
3.	» » » » » peptized	22.68	1.40	0.36
4.	Cotton linters	22.71	1.40	0.41
5.	Acetate grade wood pulp	22.55	2.12	0.49
6.	Super cord grade wood pulp	22.52	2.44	0.53
7.	Viscose grade wood pulp	22.48	2.52	0.52
8.	Bleached sulfite pulp	22.40	2.80	0.56
9.	Surgical cotton ground in agate ball mill 1 h	20.2	8.8	
10.	» » » » » » » 3 »	19.9	9.8	
11.	» » » » » » » 8 »	19.8	11.0	1.00 *

* by definition

Based on the 40 diffractograms for samples 1—8, the standard deviation in peak position and half width for the average values in Table 1 were found to be 0.015° and 0.03°, respectively. For the ground samples the errors are appreciably higher.

DISCUSSION

Owing to the overlap of the reflexions, the correct values of the parameters α and s_0 can only be obtained when the line profile is corrected for neighbouring peaks and the structure independent scattering. In order to carry out such corrections the intensity distribution would have to be normalized, and more thorough considerations be made about line shapes. As the corrections will involve a considerable amount of work and in no case alter the sequence in which the samples can be placed on the basis of half width or peak position, such corrections were omitted. The error in the measured width was estimated from eqn. (1) using the parameters from the previous article [1]. The widths in Table 1 were found to be 5 % and 8 % too high for the cotton and acetate pulp samples, respectively.

The results in Table 1 seem to be in consistency with the technological knowledge of the cotton and pulps involved. A narrow width corresponds to a well crystalline material, a broad peak to a sample of less order, herein included small particle size.

In order to compare the results with other measurements, the Degree of amorphity determined by the method of Ellefsen, Wang Lund, Tønnesen and Øien [2] was calculated for 7 of the samples. The numbers are given in the last column in Table 1. In Fig. 2 the Degree of amorphity is plotted *versus* measured half width, and it can be seen that it increases monotonically with the half width. This result is by no means surprising since the calculated Degree of amorphity is proportional to the normalized intensity at $s = 1.32$ ($2\Theta = 18.6°$) where the adjusted intensity curve for the amorphous material touches

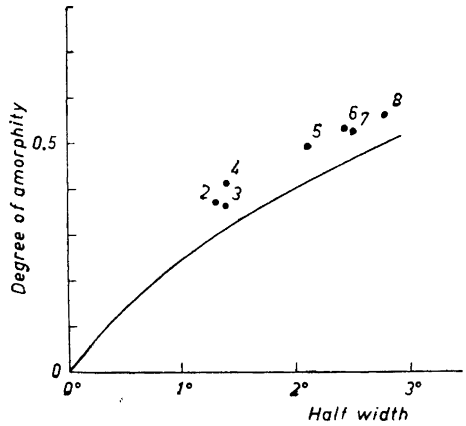

Fig. 2. Degree of amorphity *versus* half width for samples of cellulose I. The numbers correspond to the sample numbers in Table 1. The full drawn curve is based on the calculated intensity from eqn. (1) at $s = 1.32$.

the total intensity curve. Assuming eqn. (1) to be valid and the widths of the four significant (101), (10$\bar{1}$), (021) and (002) peaks to be interdependent in accordance with earlier results [1], an estimate of the total intensity at $s = 1.32$ can be made. The calculations led to the values of the Degree of amorphity represented by the full-line curve in Fig. 2, and it is seen that the plotted values in the same figure follow the trend of this curve.

The data in Table 1 seem to indicate a connection between half width and peak position, an observation which is illustrated in the graphical plot in Fig. 3. The reason for the almost linear decrease in the position of the (002)

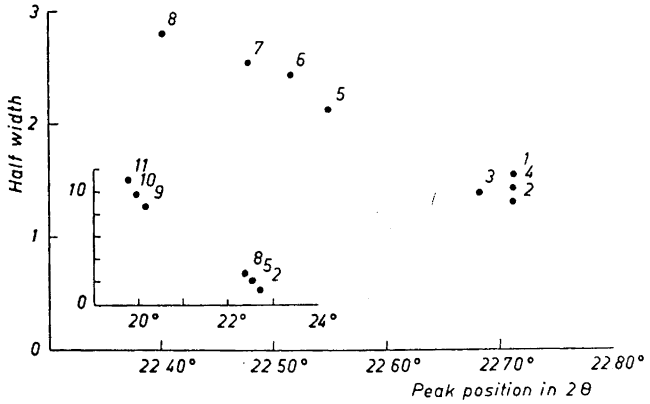

Fig. 3. Half width and position of the (002)-peak for samples of cellulose I. The numbers correspond to the sample numbers in Table 1.

peak with increasing half width may be found in an increase in the average interplanar spacing, though such a conclusion is highly uncertain since shifts in the position of the peak of the observed magnitude may be due to the influence of the other crystalline reflexions.

It is a question whether the measured half width can be associated more directly with structural parameters like the dimensions and intrinsic order of the microfibrils. Also here it is necessary to be cautious as the interpretation of line widths to a certain extent is arbitrary when only one order of the reflexions from a set of lattice planes can be measured. If the broadening of the line is attributed to small particle size only, calculations give a mean particle diameter of 60 Å for cotton and 30 Å for sulfite pulp. These dimensions should be taken as lower limits.

Finally the influence of the experimental technique should be considered. In pressing the samples the fibres are preferentially oriented with their axes in the plane of the sheet. This will for instance lead to a much higher intensity of the (021) peak compared with the (101), (10$\bar{1}$) and (002) peaks in a diffractogram of a sample in a symmetrical transmission set up than in a symmetrical reflexion set up. The position and half width of the (002)-reflexion from some pressed samples were therefore also measured in the Bragg-Brentano focusing set up with a proportional counter. The determination of half widths was further carried out on unoriented samples in the Guinier camera. For the counter measurements it was found a systematic shift of magnitude 0.05° towards higher angles in the peak position, and the half widths decreased 5 to 10 %. The half width determined from the film diffractograms of the unoriented samples led to values between the counter readings and the data in Table 1. When different samples are compared, the same technique should therefore be used in order to obtain the best result.

CONCLUSION

The present X-ray method gives an expedient and accurate prodecure to describe differences in the structural properties of samples of cellulose I. For measuring half widths it is not necessary to add a standard substance, and the line width can be read directly from a microphotometer trace or a counter diffractogram. The interpretation of the half width is somewhat arbitrary, but its value depends on the dimensions and lateral order of the microfibrils.

When the specimen also contains cellulose II, the influence of the new reflexions has to be considered. Further work on cellulose II and of mixtures of cellulose I and II is in progress.

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