

X-Ray Investigations on Cellulose II and Mixtures of Cellulose I and II

1. A Method for Characterizing and Determining the Relative Contents of the two Modifications

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The previously reported method for characterizing samples of cellulose I by width and position of the peaks in the X-ray diffractograms is extended to include cellulose II and mixtures of cellulose I and II. Procedures for determination of the ratio between the two modifications as well as an estimate of their crystalline order is described. The methods are based on measurements of intensity and width of the (10 $\bar{1}$) and (002) diffraction lines of cellulose II and the (002) line of cellulose I.

In a previous paper¹ it was shown that for the same crystalline modification of cellulose, variations in the state of order is clearly reflected in a corresponding change in width of the peaks in X-ray diffractograms of the samples. This suggests the width of the predominating lines in the diffractograms to be the most convenient X-ray parameters describing the state of order in the specimens, as previously utilized² for samples of cellulose I. However, the height and the shape of a peak will be strongly influenced by the presence of other modifications, since in this case a superposition of peaks takes place. Mixtures of the most common cellulose modifications, I (native) and II (regenerated), frequently occur both in commercially dissolving pulps³ and after treatment of native cellulose with swelling reagents. In the hitherto reported X-ray methods for determining the relative contents of the different cellulose modifications no attention has been paid to the state of order in the sample³⁻⁵. It is the purpose of the present paper to demonstrate how an estimate of crystalline order and a determination of the ratio between the two modifications may be obtained from X-ray diffractograms of the samples, where in the ratio determination the degree of order is taken into account.

The main goal has been to establish a procedure based on parameters which lend themselves readily to measurements. It has been found most practical

to employ the intensity distribution in the region $2\theta = 18^\circ$ to 24° (referred to $\text{CuK}\alpha$ radiation) which usually displays two peaks. The one at $2\theta = 20^\circ$, consists of the $(10\bar{1})$ -line of cellulose II and the (021) -line of cellulose I, the other at $2\theta = 22^\circ$ — 22.7° receives contributions from the (002) -lines of both modifications. For simplicity we shall designate the two peaks $(10\bar{1})$ and (002) .

As parameters sensitive to composition both the centre of gravity of the two peaks and the ratio between the peak intensities ($I_{10\bar{1}}/I_{002}$) have been tried. These two parameters display, however, essentially the same features. In the following we shall restrict ourselves to the peak intensity ratio, as this quantity is the one which is most readily measured.

The peak intensity ratio as well as the centre of gravity will to some extent depend on the degree of orientation in the specimens, particularly due to the (021) -reflection of cellulose I. Hence measurements have been carried out both on unoriented samples and pressed sheets. The latter type of specimens has been found most convenient in practice, especially for pulp samples which usually are presented as sheets. Pressed specimens have therefore mainly been used in the experiments.

EXPERIMENTAL PROCEDURE

Transmission diffractograms of the samples were prepared in the manner described previously². For the pressed samples the applied pressure was about $2\,500\text{ kg/cm}^2$. A microphotometer curve for a mixture of cellulose I and II is reproduced in Fig. 1, displaying the cellulose II $(10\bar{1})$ -peak and the composite (002) -peak. The sharp peak at 20.88° is the quartz (100) reference line. The parameters used for characterization of the samples are indicated in the figure. The angles refer to $\text{CuK}\alpha$ radiation.

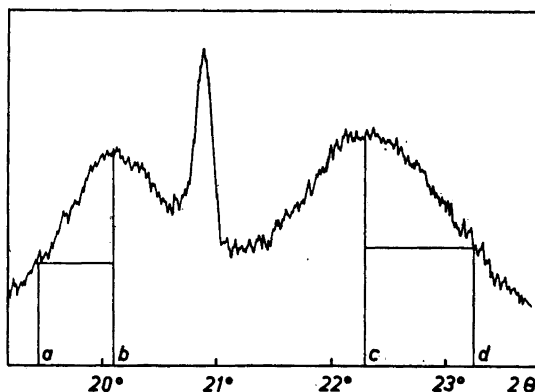


Fig. 1. Microphotometer curve for a sample consisting of a mixture of cellulose I and II. The letters a, b, c, and d indicate the $(10\bar{1})$ inner half value intersection, the $(10\bar{1})$ peak position, the (002) peak position, and the (002) outer half value intersection respectively.

RESULTS

The investigations included two different qualities of each of the two modifications I and II, a number of laboratory mixtures prepared from these samples in known ratios, and finally a series of cotton samples treated with hydrochloric acid for 1 to 4 h. The results are given in Table 1.

Table 1. Peak angles, half value intersections and peak intensity ratio $I_{10\bar{1}}/I_{002}$. CuK α radiation.

Specimen	No. of samples	(10 $\bar{1}$), cellulose II		(002), cellulose I & II		$I_{10\bar{1}}/I_{002}$	
		peak angle (degrees)	half value intersection (degrees)	peak angle (degrees)	half value intersection (degrees)	pressed sheets	unoriented sample
<i>Cellulose II</i>							
1. Mercerized cotton treated with 39% HCl for 3 h	4	20.08	19.46	22.16	22.72	1.20	1.16
2. Mercerized acetate grade wood pulp	4	20.16	18.73	21.59	23.14	1.26	1.23
<i>Cellulose I</i>							
3. Surgical cotton treated with H ₂ SO ₄	6			22.71	23.42	0.41	0.31
4. Acetate grade wood pulp	5			22.55	23.63	0.64	0.55
<i>Laboratory mixtures</i>							
5. 20% 1. 80% 3	3	20.06	19.40	22.16	22.97	1.09	1.055
6. 40% 1. 60% 3	3	20.08	19.44	22.23	23.26	0.95	0.905
7. 60% 1. 40% 3	4	20.15	19.43	22.47	23.41	0.795	0.67
8. 80% 1. 20% 3	3	20.26	19.39	22.67	23.42	0.575	0.495
9. 20% 2. 80% 4	4	20.22	18.63	21.74	23.42	1.165	1.14
10. 40% 2. 60% 4	4	20.29	18.52	22.04	23.54	1.055	1.00
11. 60% 2. 40% 4	4	20.39	18.1	22.36	23.70	0.90	0.87
12. 80% 2. 20% 4	3	20.58		22.48	23.62	0.73	0.695
<i>Surgical cotton treated with 39% HCl</i>							
13. for ½ h	3	20.26		22.58	23.65	0.87	0.79
14. » 1 »	3	20.14	18.6	22.37	23.59	0.97	0.93
15. » 2 »	2	20.07	19.32	22.18	23.23	1.10	1.03
16. » 3 »	2	20.06	19.49	22.19	23.07	1.10	1.08
17. » 4 »	2	20.04	19.43	22.17	23.16	1.06	1.01

From the 47 samples of specimen 1–12 the following mean standard deviations were found: Peak angles 0.035°, half value intersections: 0.03°, intensity ratio: 0.02.

DISCUSSION

The composition-sensitive parameter $I_{10\bar{1}}/I_{002}$ is seen to depend not only on the contents of cellulose I and II but also on the crystalline order in the two modifications. Corrections for the dependence on crystalline order must therefore be applied in order that the peak intensity ratio can be used for composition determination. Such a correction may apparently be based on the half widths of the peaks. For reasons which will be explained below, the angular position of the half value intersections (see Fig. 1) was preferred.

In Fig. 2 the (002) outer intersection is plotted *versus* the peak intensity ratio. As an approximation straight lines through points corresponding to the same composition with respect to crystalline modification may be considered representative for the specific composition. The plot clearly illustrates the magnitude of the corrections which have to be applied to the measured intensity ratio in order to obtain the correct value for the contents of the two cellulose modifications. For samples containing a high percentage of cellulose II the (10 $\bar{1}$) half value intersection can be used as ordinate in the calibration chart. It has to be emphasized that the measurements used for constructing the calibration chart in Fig. 2 refer to samples with comparable crystalline order in the two modifications. Measurements on mixtures where the two components differ widely in crystalline order indicate that the correction method applies as well when cellulose I is the most crystalline fraction. When the cellulose II fraction is much more ordered than the cellulose I-fraction, the correction parameter appears to be measured too low, leading to an over-estimation of the cellulose II-contents.

Fig. 2 has been used as a calibration chart to determine the cellulose II-contents of the acid-treated samples 13—17, leading to the values given in the first line of Table 2.

Table 2. Contents of cellulose II and estimated half widths for the samples 13—17.

Sample	13	14	15	16	17
per cent cellulose II, pressed sheets	38	50	76	79	73
per cent cellulose II, unoriented samples	39	50	72	81	72
Half width (10 $\bar{1}$), degrees	>2.5	2.5	1.5	1.20	1.35
» » (002), »	<1.75	<1.75			

Fig. 2A plot very similar to Fig. 2 except for a translation to the left of the straight lines was obtained from peak intensity ratios measured for unoriented specimens. Cellulose II-contents for samples 13—17 determined by means of this plot and peak intensity ratios for unoriented specimens of these samples are given in the second line of Table 2.

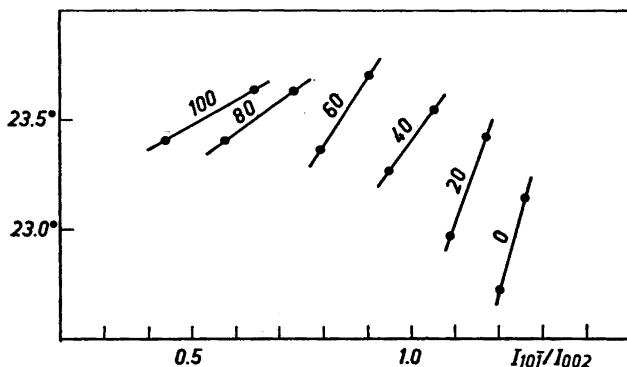


Fig. 2. The (002) outer half value intersection plotted as a function of the peak intensity ratio $I_{10\bar{1}}/I_{002}$ for series of mechanical mixtures of cellulose I and II (See Table 1). The numbers in the figure indicate the percentage of cellulose I in the samples.

An estimation of the half width of the diffraction lines for the major constituent in the mixture may also be done. From Fig. 2 it is seen that the (002) half value intersection for samples of cellulose with the same degree of crystalline order vary very slowly with composition when cellulose I is the main fraction. A similar feature is displayed by the (10 $\bar{1}$) half value intersection for samples with cellulose II as the greater part. The position of the peaks, on the other hand, is very sensitive to composition. Thus it appears most reasonable to calculate half widths from the measured intersections and the peak angles corresponding to pure samples of cellulose I and II. This idea is also supported from studies of composite theoretical profiles. It is found that a neighbouring peak will produce a rather small displacement on the half value intersection at the side furthest away from the interfering peak. For instance will the displacement vanish for the outer half value intersection of two Cauchy peaks separated through a distance equal to their half widths. This corresponds fairly to the influence of the cellulose II (10 $\bar{1}$)-peak on the (002)-peak of cellulose I for samples 9–12. The influence of neighbouring peaks on the same side as the intersection may, however, be considerable. Thus it is seen that measurement of cellulose II (10 $\bar{1}$) half value intersection may be worthless and in some cases even impossible due to the influence of the neighbouring (101) and (10 $\bar{1}$) peaks for cellulose I (samples 11 and 12).

From such considerations the half widths given in Table 2 for samples 13–17 have been estimated, taking the cellulose II (10 $\bar{1}$) and cellulose I (002) reflection angles to be 20.08° and 22.70° respectively. Due to great difference in line width between the two components in samples 13 and 14 the (002) line width for cellulose I is probably overestimated, the correct value may not be greater than the value 1.54° found for native cellulose². The half widths of the (10 $\bar{1}$) and (002) lines for pure cellulose II samples can be obtained in a similar way, leading to the values 1.18° and 1.13° for the acid treated samples, and 2.78° and 2.70° for the mercerized sample.

CONCLUSION

In the present paper the previously reported method² for characterizing samples of cellulose I by width and position of the lines in their X-ray diffractograms is extended to include cellulose II and mixtures of cellulose I and II. The application so far indicate that the method is well suited to detect and to describe structural differences between samples within the same modification as well as the ratio between cellulose I and cellulose II in mixtures. When mixtures of the two modifications are considered, a reliable line width parameter indicating the state of order in the sample can only be ascribed to the major constituent, and there will be some ambiguity for mixtures close to 50–50 %.

The interpretation of the measured widths must take into account both the lateral dimensions and crystalline order of the microfibril. At least for the mercerized samples the crystalline order seems to be the more important factor. The lateral order in cellulose II will be dealt with in a subsequent paper⁶. A thorough discussion of the hydrolysis experiments is given elsewhere⁷.

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REFERENCES

1. Gjønnnes, J., Norman, N. and Viervoll, H. *Acta Chem. Scand.* **12** (1958) 489.
2. Gjønnnes, J. and Norman, N. *Acta Chem. Scand.* **12** (1958) 2028.
3. Ellefsen, Ø., Tønnesen, B. A., Wang Lund, E and Øien, K. *Norsk Skogind.* **11** (1957) 284.
4. Rånby, B. G. *Acta Chem. Scand.* **6** (1952) 101, 116.
5. Rasch, O. A. and McCarthy, J. L. *Norsk Skogind.* **8** (1954) 329.
6. Gjønnnes, J. and Norman, N. *Acta Chem. Scand.* **14** (1960) 639.
7. Ellefsen, Ø., Gjønnnes, J. and Norman, N. *Norsk Skogind.* **13** (1959) 411.

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