

# Determination of Cellulose Accessibility by Differential Scanning Calorimetry

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## Synopsis

The thermal behavior of various cellulose samples with different degrees of crystallinity as measured by X-ray diffraction techniques was studied with a differential scanning calorimeter (DSC). The broad endothermic peak which appears between 110 and 160°C is due to loss of absorbed (bound) water. Since a direct relationship was observed between the area of this peak and the crystallinity of the sample, a new procedure for estimating cellulose accessibility (which is related to crystallinity) was proposed and developed. DSC curves obtained on cellulose samples preconditioned at certain constant relative humidities were used to determine sample accessibilities by the proposed method. The accessibility values obtained by DSC showed excellent agreement with crystallinity values determined by more traditional techniques. Completely amorphous cellulose was obtained by anhydrous deacetylation of cellulose triacetate and was used as the standard amorphous cellulose material.

## INTRODUCTION

Cellulose, the major structural component of plant cell walls, exists as long fibers composed of smaller structural units called microfibrils, which, in turn, consist of aggregates of elementary fibrils. The size of the microfibrils varies with the degree of aggregation of elementary fibrils which depends largely on the source of cellulose. Although many models have been proposed to explain the structure of cellulose, no one model can account for all of the observed properties of the microfibrils.<sup>1</sup> Nevertheless, all such theories assume the existence of two distinctly different regions within the microfibril: one of highly-ordered cellulose molecules called the crystalline area, and the other of less highly-ordered cellulose molecules called the amorphous area. There are probably no sharp boundaries between the areas of high molecular order and the less-ordered amorphous fractions, but rather a gradual transition from the highly crystalline regions to the completely amorphous areas.

Cellulosic materials from all natural sources have the same cellulose crystalline structure, which is called cellulose I or native cellulose. However, when the crystalline structure of native cellulose is destroyed by some dissolving or swelling treatment, the regenerated cellulose usually presents a different crystalline pattern. In nature, cellulose microfibrils are highly, although not completely, crystalline: about 70–80% of cellulose in cotton and about 60–70% of cellulose in wood is crystalline. Most aqueous reagents penetrate only the amorphous areas of cellulose fibers. Therefore, these amorphous or noncrystalline regions are also called the accessible regions of cellulose. Hence, the concepts of crystallinity and accessibility of cellulose

are closely related. Many physical and chemical techniques have been developed to estimate cellulose crystallinity and accessibility.

Cellulose molecular cohesion is due to the large number of hydroxyl groups forming intramolecular hydrogen bonds between adjacent glucose units of the chain and intermolecular hydrogen bonds between different chains. These hydrogen bonds are responsible for the fibrillar and crystalline structure of cellulose. However, a considerable number of free hydroxyl groups are also present in cellulose fibers, primarily in the noncrystalline regions of cellulose. Therefore, as the capacity of cellulose fibers for water absorption depends largely on the availability of free hydroxyl groups, it is generally considered that water absorption (equivalent to bound water) occurs almost entirely in the amorphous regions of cellulose, neglecting the free hydroxyl groups that may be present on the surfaces of the crystallites. It has been shown that crystalline areas of cellulose only absorb small amounts of water,<sup>2,3</sup> although about 28% of the hydroxyl groups present on the perimeter of microfibrils are available to form hydrogen bonds and absorb water. For highly crystalline celluloses water adsorbed on crystal surfaces cannot be neglected. Crystal surfaces for highly crystalline materials contribute significantly to cellulose accessibility. In our study, however, we concentrated on more amorphous materials for which the assumption of relatively little water adsorbed on crystal surfaces is a good assumption.

The thermal degradation of cellulosic materials has also been extensively studied. As noted by Shafizadeh et al.,<sup>9-12</sup> cellulose thermal decomposition proceeds through complex simultaneous and consecutive chemical reactions which lead to cellulose pyrolysis and further combustion. Most of these reactions do not occur below 200°C. However, all these thermal-physical changes and chemical reactions are highly dependent on the composition and physical nature of the cellulosic material, the ambient atmosphere, and the time of heating.<sup>9,10,13</sup> Therefore, one would not expect perfect agreement in the results of different workers, and indeed, some differences do exist. Although it was shown that cellulose degradation reactions are more extensive in air or oxygen than in inert atmospheres such as nitrogen,<sup>13</sup> these differences begin to be significant only at long heating times. It is known that, at moderate temperatures over short periods of time, cellulose is relatively stable.<sup>9</sup> Under experimental conditions of rapid heating using a differential thermal analyzer, Shafizadeh and co-workers<sup>11,12</sup> studied the thermal behavior of wood and its primary components: cellulose, xylan, and lignin. They detected a common endotherm occurring in the range of about 80–150°C with a peak of about 110°C which was attributed to dehydration, or loss of absorbed water.

Therefore, as water sorption occurs almost totally in the amorphous areas of cellulose, the area of the endothermic peak due to loss of absorbed water is directly related to the amorphous fraction of cellulose. Using this fact, we propose a DSC procedure to estimate cellulose accessibility to water which correlates well with crystallinity. The ability to measure cellulose accessibility accurately in samples with a very low degree of crystallinity as estimated by X-ray methods is the principal advantage of this new method. Furthermore, some research laboratories may have greater access to DSC equipment than to X-ray diffraction equipment.

## EXPERIMENTAL

### Anhydrous Deacetylation of Cellulose Triacetate

Completely amorphous cellulose was obtained by saponification of cellulose triacetate according to the Cumberbirch and Harland procedure.<sup>14</sup> Finely cut cellulose triacetate sheets (Kodacel TA 401) were used. Approximately 0.7 g of sample was first thoroughly moistened with ethanol, and the ethanol was then removed. The sample was dissolved in 18 mL methylene chloride, working under a hood and stirring the solution with a rod for about 30 min until all the sample was completely dissolved. The dissolved sample was then diluted with 75 mL pyridine. The saponification was performed by adding the following materials while vigorously shaking the solution: 60 mL 0.1N NaOH, 90 mL acetone, and 180 mL 1.0N NaOH/ethanol (50/50, v/v) solution. After standing overnight, the precipitated cellulose was filtered off, washed with anhydrous ethanol, and air dried.

### BALL MILLING TREATMENT

Cellulose samples with different degrees of crystallinity were prepared by a mechanical procedure. Cotton linter pulp sample SR-210 from Buckeye Cellulose Corp. was used as the starting material. The material was first finely ground in a Wiley mill to pass a 0.5 mm mesh screen and was then ground in a ball mill for varying periods of time.

### CRYSTALLINITY INDEX MEASUREMENT

In order to estimate the crystalline–amorphous ratio of all cellulose materials, duplicate X-ray diffractograms of each of the samples were taken using a General Electric XRD-6 Diffractometer. The X-ray diffractograms from all the samples were analyzed by using the empirical procedure of Segal et al.<sup>15</sup> This method consists of estimating a crystallinity index which is defined as

$$\text{Cr.I. (\%)} = \frac{I_{002} - I_{\text{am}}}{I_{002}} \times 100 \quad (1)$$

where  $I_{002}$  is the maximum intensity (in arbitrary units) of the diffraction from the (002) plane at  $2\theta = 22.8^\circ$ , and  $I_{\text{am}}$  is the intensity of the background scatter measured at  $2\theta = 18^\circ$  in the same units. As mentioned, the procedure of Segal is empirical and not an absolute technique. Therefore, it is not frivolous to develop additional techniques for measuring cellulose accessibility particularly for highly amorphous cellulose samples for which Segal's procedure is of little value.

### CELLULOSE ACCESSIBILITY MEASUREMENT BY A PROPOSED DSC METHOD

*Energy Change Measurement.* While a differential thermal analyzer records the difference in temperature between the sample and an inert

reference substance, a differential scanning calorimeter (DSC) measures the power required to maintain a temperature difference of zero between the sample and the reference. Therefore, since DSC measures energy flow directly, it is possible to use this technique for quantitative purposes.<sup>16,17</sup>

In a typical differential scanning calorimeter curve of our cellulose samples, an endothermic peak appears between about 110 and 160°C with a maximum near 145°C. This peak is assumed to be due to loss of absorbed water. The area of this peak is directly proportional to the endothermic heat flow caused by the physical change(s) in the sample: water desorption from cellulose and evaporation (dehydration). Therefore, the energy changes produced during cellulose dehydration can be calculated by measuring the peak area of the endotherm.

Cellulose samples with different Cr.I. were analyzed by using a DuPont Thermal Analyzer equipped with a differential scanning calorimeter (DSC) cell and a data analyzer. The calibration coefficient  $E$  for the DSC cell was determined using weighed samples of indium. For each cellulose material, duplicate pellets of about 15 mg were placed in tared DSC pans, weighed to an accuracy of 0.01 mg, and scanned at a heating rate of 40°C/min. In separate experiments, it was determined that neither peak area nor peak maximum temperature was affected by the heating rate. Heats of dehydration were estimated by using the Interactive DSC Data Analysis Program which integrates the peak areas between specified temperatures and calculates the corresponding energy changes. For each DSC curve the peak maximum temperature ( $T_{\max}$ ) was first determined, and the integration was then performed between the temperature  $T_1 = T_{\max} - 60^\circ\text{C}$  and  $T_2 = T_{\max} + 60^\circ\text{C}$ .

#### *Cellulose Crystallinity Estimation*

The endothermic dehydration peak appearing between 110 and 160°C in a typical DSC curve of cellulose increases when the degree of crystallinity of cellulose sample decreases. Since crystalline areas of cellulose only absorb a very small amount of water, water sorption in cellulose occurs almost entirely in the amorphous regions. This is particularly true for the generally amorphous samples which we used. Therefore, assuming that cellulose moisture content (accessibility to water) is directly proportional to the amorphous fraction of cellulose, the amount of heat required to dehydrate a cellulose sample can be taken as a direct measure of its amorphous fraction.

Since the area of the endothermic dehydration peak decreases when cellulose crystallinity increases, the area for a completely amorphous cellulose sample (0% crystalline) must be a maximum. At the same time, although there is no 100% crystalline cellulose in nature, the area for an ideal 100% crystalline cellulose would be a minimum. Therefore, we define cellulose crystallinity (CC) (or accessibility to water) as

$$\text{CC (\%)} = \frac{\Delta H_0 - \Delta H_s}{\Delta H_0} \times 100 \quad (2)$$

where  $\Delta H_0$  = heat required to dehydrate the standard cellulose, a completely amorphous cellulose, previously exposed at a certain constant relative hu-

midity until constant weight is obtained (cal/g), and  $\Delta H_s$  = heat required to dehydrate the cellulose sample, previously exposed at the same conditions as the standard (cal/g). In this way, when  $\Delta H_s$  tends to  $\Delta H_0$ , cellulose crystallinity (CC%) approaches zero; and when  $\Delta H_s$  tends to zero, cellulose crystallinity (CC%) goes to 100.

It is known that cellulose moisture regain depends largely on relative humidity and temperature. Therefore, before applying the DSC technique to determine cellulose heats of dehydration, the sample and the standard celluloses were conditioned at the same constant relative humidity and temperature until constant weights were obtained. Completely amorphous cellulose obtained by anhydrous deacetylation of cellulose triacetate was taken as the standard amorphous cellulose. For this amorphous standard, DSC scans were taken on five pellet samples, about 15 mg each, and the corresponding energy changes were calculated. The estimated value of the standard heat of dehydration ( $\Delta H_0$ ) was the average value of the five independent measures of energy change obtained. Then, for each cellulose sample, duplicate pellets of about 15 mg each were weighed to within  $\pm 0.01$  mg and DSC scans were taken. The average value of the two measures of energy change was taken as  $\Delta H_s$ , and cellulose crystallinity was estimated by applying eq. (2).

## RESULTS AND DISCUSSION

### Amorphous Cellulose Sample Obtained by a Chemical Procedure

The Cumberbirch and Harland method,<sup>14</sup> which consists of anhydrous deacetylation of cellulose triacetate, is commonly used to provide a completely amorphous cellulose. The highly amorphous cellulose obtained by this chemical method is probably due to using an anhydrous medium for the saponification, which prevents possible recrystallization of the regenerated cellulose. The initial crystalline structure of cellulose is lost during the esterification process in which cellulose triacetate is formed.

As expected, the X-ray diffractograms of amorphous cellulose prepared from cellulose triacetate presented only a diffuse background without any intensity peak from Bragg angles of  $10^\circ$  and  $30^\circ$  as shown in Figure 1. For comparison, Figure 1 also shows the diffractogram of a highly crystalline sample of cellulose I. Since no diffraction intensities were apparent, this deacetylated sample was considered to be completely amorphous.

### AMORPHOUS CELLULOSE SAMPLE OBTAINED BY A MECHANICAL PROCEDURE

The Wiley mill treatment not only provided particle size uniformity, but also increased the decrystallization-effectiveness of ball milling. The finer the particle was ground, the lower the crystallinity achieved. The effects of the grinding treatment on the crystallinity of cotton linter cellulose are shown in Table I. The data given are average (from duplicate samples) percent crystallinity indices estimated by the X-ray procedure of Segal et al.<sup>15</sup>

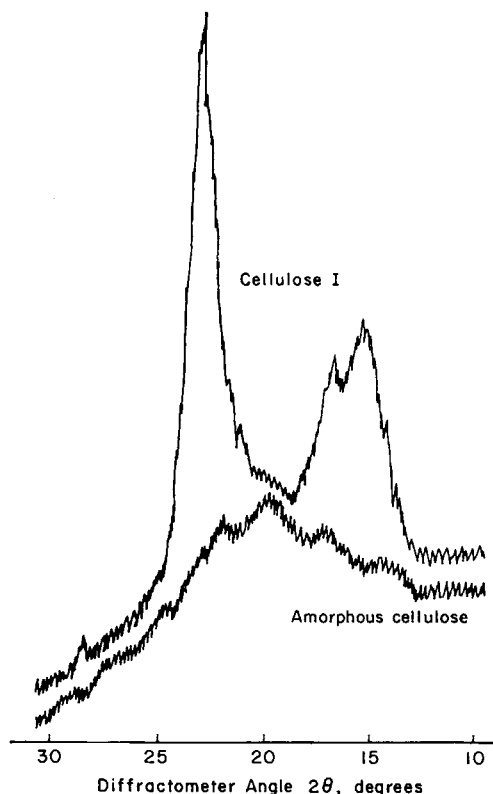


Fig. 1. Diffractometer traces of cellulose I and completely amorphous cellulose.

TABLE I  
Effect of Ball Milling Time on Cotton Linter Cellulose

Percent Cr.I.	74	67	63	49	41	32	a	a
Ball milling time (h)	0	1	4	6	8	10	24	48

<sup>a</sup> Not determined; no diffraction intensities detected or too small to be measured.

A crystallinity of about 30% was obtained with only 10 h of ball milling. Longer ball milling times produced further decreases in crystallinity of the cellulose samples, although these very low degrees of crystallinity could not be accurately measured by the X-ray technique.

### THERMAL BEHAVIOR OF CELLULOSE

A typical differential scanning calorimeter curve for our cellulose samples shows an endotherm at 110–160°C, which is assumed due to dehydration, that is, loss of absorbed water. If a sample was cooled to room temperature after a DSC scan over the range 50–250°C and immediately rescanned over the same range, the endothermic peak almost disappeared as shown in

Figure 2. Heating during the first DSC scan drove off essentially all of the moisture in the cellulose sample.

### EXPERIMENTAL EVIDENCE FOR DEHYDRATION

In order to demonstrate that the endothermic peak which has a maximum at about 145°C is due to dehydration, an amorphous sample of cellulose from ball-milled cotton linter was subjected to DSC analysis. This amorphous material was stored in a desiccator containing anhydrous CaSO<sub>4</sub> (drierite) at ambient temperature and then scanned in the DSC from 50 to 250°C. The calculated heat of dehydration was 14.1 cal/g sample. This sample was then scanned twice more, giving greatly reduced peaks with heats of dehydration of 3.83 and 1.15 cal/g sample. The results on the second and third scans of the same sample are probably due to loss of the small amount of remaining adsorbed water. In addition, due to the strongly hygroscopic nature of cellulose, it is also likely that some absorption of ambient moisture occurred during the time between two consecutive runs on this sample. Finally, the same sample was exposed to a saturated aqueous solution of ammonium chloride which gives a constant relative humidity of 79% over a wide range of temperatures. After 5 h of exposure, the peaks at 110–160°C became over twice as large as they had been for the initial amorphous sample, and had a heat of dehydration of 30.1 cal/g sample. These data demonstrate the reversibility (at least under these conditions) of the water sorption process and the strong dependence of the heat of dehydration on the conditions under which the sample is prepared.

To further quantify these observations, the following experiments were performed: Two samples from the amorphous ball-milled cotton linters, about 0.5 g each, were exposed to 79% relative humidity. In order to monitor the weight gain with time, one of the samples was accurately weighed after different exposure times. Triplicate determinations of heat of dehydration were performed by the DSC technique on the other exposed sample at the same exposure times. The results of weight gain and the average values of heat of dehydration with their standard errors at different times of exposure are shown in TABLE II.

It is obvious from Table II that only about 24 h of exposure are necessary to obtain constant sample weight and that the average values of heat of dehydration become constant at the same exposure time. The results also show a direct relationship between the increase in weight due to absorption of water and the increase in heat of dehydration.

TABLE II  
Weight and Heat of Dehydration Changes in Cellulose Exposed to 79% Relative Humidity

Exposure time	0 h	1 h	17 h	1 day	2 days	10 days
Weight gain (g/g sample)	0.0000	0.0244	0.0494	0.0500	0.0500	0.0500
Average $\Delta H$ (cal/g sample)	15.9 ±0.9	25.4 ±0.8	43.0 ±0.8	46.9 ±0.6	46.6 ±1.5	46.6 ±0.8

Since the heat of vaporization of water at its normal boiling point is 9729 cal/mol, or 540.5 cal/g, and the weight gain by the exposed cellulose sample due to absorption of water was 0.05 g/g sample, the value 27 cal/g sample ( $= 540.5 \text{ cal/g} \times 0.05 \text{ g/g sample}$ ) is an estimate of the heat required to evaporate the observed amount of absorbed water. This estimated value of 27 cal/g sample is close to 30.7 cal/g sample, which is obtained from Table II as the difference between the heat of dehydration before water adsorption began and the heat of dehydration after constant sample weight was achieved (46.6–15.9). Furthermore, we would expect the heat of dehydration of the cellulose sample measured by DSC to be somewhat higher than the heat of vaporization of pure water, as our results show, since the bonds between water and cellulose must first be broken before vaporization could occur and this would require additional heat input. Therefore, we conclude that the energy change measured by the DSC technique, which is called heat of dehydration, is indeed due to loss of absorbed water, as previously assumed.

### RELATIONSHIP BETWEEN HEAT OF DEHYDRATION AND CELLULOSE CRYSTALLINITY

The endothermic peak for cellulose as detected in these DSC curves becomes larger when the crystallinity of the sample decreases. Figure 3 shows the DSC curves of various celluloses with different crystallinity indices. The average values of heat of dehydration determined by the DSC technique for all these cellulose samples, previously conditioned at ambient temperature in a desiccator containing anhydrous  $\text{CaSO}_4$ , are shown in Table III, where they can be compared with the corresponding crystallinity indices. These heat of dehydration values are plotted against the crystallinity index in Figure 4.

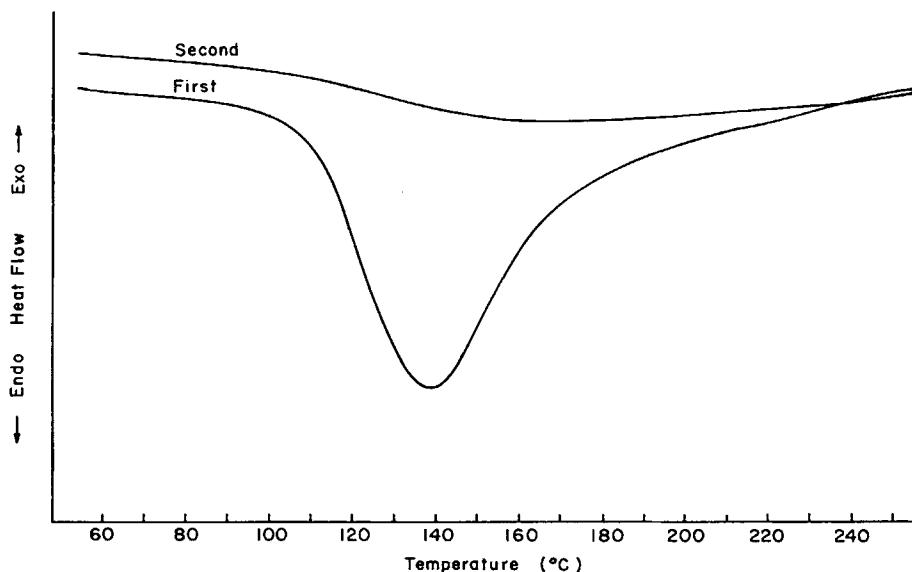


Fig. 2. Two consecutive DSC curves for amorphous cellulose.



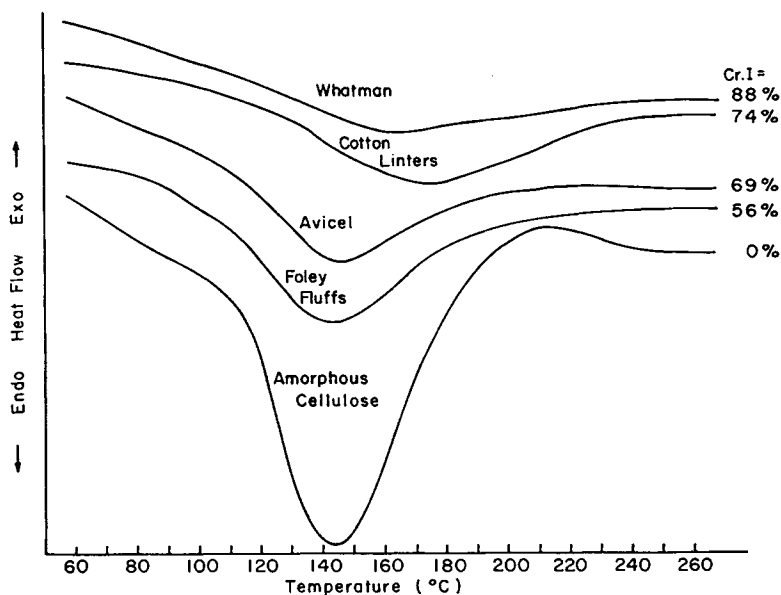


Fig. 3. DSC curves for cellulose samples with different crystallinity indices. All samples were preconditioned at room temperature in a desiccator containing anhydrous  $\text{CaSO}_4$ .

TABLE III  
Heat of Dehydration for Various Celluloses, Previously Conditioned at Ambient Temperature in a Desiccator Containing Anhydrous  $\text{CaSO}_4$

Cellulose source	Cr.I. (%)	Average $\Delta H$ (cal/g)
Whatman CF-11	88	9.7
Cotton linter	74	13.5
Avicel	69	15.9
Foley fluffs wood pulp	56	23.2
Amorphous cellulose (from cellulose triacetate)	0	51.6

To determine the dependence of heat of dehydration on cellulose crystallinity, cellulose samples with different crystallinity indices but from the same source, cotton linter, were selected and their heats of dehydration were determined by the DSC technique after conditioning at ambient temperature over anhydrous  $\text{CaSO}_4$ . The results are shown in Table IV. These heat of dehydration values vs. Crystallinity indices are also plotted in Figure 4.

From the data shown in Tables III and IV, which are plotted in Figure 4, we conclude that there is a linear relationship between the heat of dehydration of cellulose samples and their crystallinity indices. This is to be expected. The accessibility of the samples to water (the quantity measured by the DSC technique) is closely related to the amorphous fraction of the sample upon which the bulk of the water is adsorbed. We feel justified, therefore, in using the DSC technique as an alternate means of estimating

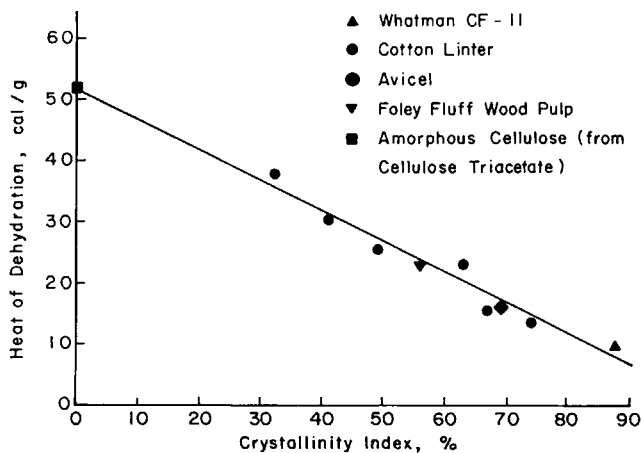


Fig. 4. Heat of dehydration for cellulose samples preconditioned at ambient temperature in a desiccator containing anhydrous  $\text{CaSO}_4$  vs. crystallinity index: ( $\blacktriangle$ ) Whatman CF-II; ( $\bullet$ ) cotton linter; ( $\blacklozenge$ ) Avicel; ( $\blacktriangledown$ ) Foley fluff wood pulp; ( $\blacksquare$ ) amorphous cellulose (from cellulose triacetate).

TABLE IV  
Average Values of Heat of Dehydration for Cotton Linter Cellulose Samples, Previously Conditioned at Ambient Temperature in a Desiccator Containing Anhydrous  $\text{CaSO}_4$

Ball milling time (h)	0	1	4	6	8	10
Cr.I. (%)	74	67	63	49	41	32
Average $\Delta H$ (cal/g)	13.5	15.6	23.0	25.4	30.5	37.6

cellulose crystallinity (accessibility) particularly for more amorphous cellulose samples.

To determine whether the same relationship exists between heat of dehydration and crystallinity for samples preconditioned at different relative humidities, three cotton linter samples with different crystallinity indices were conditioned at 79% relative humidity over saturated ammonium chloride. After these samples reached constant weight, quadruplicate DSC curves were taken from each sample and their heats of dehydration were estimated. The average values of heats of dehydration and their standard errors were calculated and are shown in Table V.

TABLE V  
Heat of Dehydration for Cotton Linter Cellulose Samples, Previously Exposed to 79% Relative Humidity

Ball milling time (h)	0	6	10
Cr.I. (%)	74	49	32
Average $\Delta H$ (cal/g)	$19.4 \pm 1.5$	$32.3 \pm 1.1$	$46.9 \pm 1.0$

Comparing the results from Table V with those from Table IV, it is obvious that, for each cellulose sample, the heat of dehydration increases considerably when the sample is previously conditioned at higher relative humidities. However, the relationship between heat of dehydration and crystallinity of the sample is again linear, as shown in Figure 5 where these values are plotted.

### CELLULOSE CRYSTALLINITY ESTIMATION BY THE DSC METHOD

Cellulose crystallinity measurements were made by applying eq. (2) according to the DSC method described here. Using the average heats of dehydration presented in Table II, percent cellulose crystallinity (CC%) values were estimated by the DSC method for different celluloses. The standard heat of dehydration used was  $\Delta H_0 = 51.6$  cal/g, which is the value for the amorphous cellulose sample obtained from cellulose triacetate after conditioning at ambient temperature in a desiccator containing anhydrous  $\text{CaSO}_4$ . In Table VI, the results obtained by the DSC technique can be compared with those obtained by the X-ray technique: crystallinity indices (Cr.I. %).

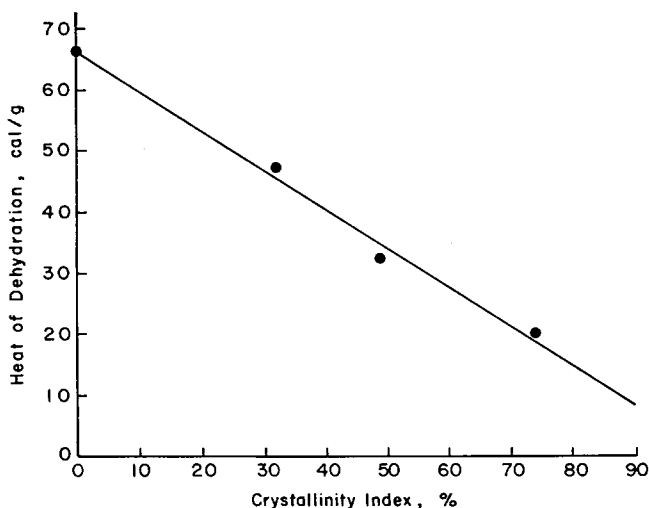


Fig. 5. Heat of dehydration for cellulose samples preconditioned at 79% relative humidity vs. crystallinity index.

TABLE VI  
Percent Crystallinity Indices Estimated by the X-Ray Technique and Percent Cellulose Crystallinity Estimated by the DSC Method for Different Celluloses

Cellulose source	Cr.I. (%) (X-ray)	CC (%) (DSC)
Whatman CF-11	88	81.2
Cotton linter	74	73.8
Avicel	69	69.2
Foley fluffs wood pulp	56	55.0

TABLE VII  
Percent Crystallinity Index and Percent Cellulose Crystallinity Estimated by the DSC Method at Two Different Relative Humidities for Cotton Linter Cellulose Samples

Ball milling time (h)	Cr.I. (%)	CC (%)	
		Ambient RH	79% RH
0	74	73.8	70.7
6	49	50.8	51.1
10	32	27.1	29.0

Using the average heats of dehydration presented in Tables IV and V, percent cellulose crystallinity (CC%) values were estimated by the DSC method for the three cotton linter cellulose samples with different degrees of crystallinity. For the samples exposed to 79% relative humidity, the standard heat of dehydration used was 66.1 cal/g, the average value found for the amorphous cellulose sample obtained from cellulose triacetate and exposed to 79% RH until constant weight was obtained. Both sets of results can be compared with the crystallinity index values estimated by the X-ray technique for the same samples. This information is presented in Table VII.

From the results presented in Tables VI and VII, very good agreement prevails between the crystallinity indices estimated by the X-ray technique and the cellulose crystallinities determined by the DSC method. Also, cellulose crystallinities by the DSC method are very similar for the same samples previously conditioned at two different relative humidities, as shown in Table VII. Therefore, it appears that percent cellulose crystallinity (CC%) estimated by this DSC procedure is independent of the relative humidity at which the samples are preconditioned.

## CONCLUSIONS

The endotherm appearing between about 110 and 160°C as detected in a typical DSC curve of our pure cellulose samples is due to loss of absorbed water. Therefore, the energy change calculated by measuring the area of this endothermic peak may be termed the heat of dehydration. A linear relationship exists between heat of dehydration and the X-ray crystallinity of the cellulose samples. By preconditioning a sample at a constant relative humidity, it is possible to estimate the degree of crystallinity of the sample by measuring its heat of dehydration with the DSC procedure and then relating this value to that obtained with a completely amorphous cellulose preconditioned in the same manner. The cellulose crystallinity values obtained by the new DSC method compare very well with those obtained by the traditional X-ray technique for the same samples and seem independent of the relative humidity at which the samples are preconditioned. The new DSC technique should be particularly useful with less crystalline samples for which the X-ray method has diminished accuracy. In fact, the accuracy of the DSC technique is greatest for the less crystalline samples.

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