

# Characterization of Cellulose Aldehyde Using Fourier Transform Infrared Spectroscopy

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**ABSTRACT:** Fourier transform infrared spectroscopy has been used to study cellulose aldehyde groups in bleached cotton, unbleached cotton, and in periodate oxidized cotton. Second derivative spectroscopy could reproducibly identify aldehyde bonds in oxidized cotton only if the samples were predried at 110°C for 24 h; the aldehyde band appeared at 1732–1734  $\text{cm}^{-1}$ . Diffuse reflectance spectroscopy in the Environmental Chamber readily detected the above aldehyde absorbances at temperatures above 100°C. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1195–1202, 2001

## INTRODUCTION

Oxidation of cotton cellulose may occur in textile wet processes, such as bleaching, and the extent of oxidation is limited by controlling temperature, pH, and the concentrations of oxidizing agents and metal ions. Although practically all the oxidizing agents used attack cellulose heterogeneously, some agents tend to produce more aldehyde groups than carboxyl groups, whereas others may act in the opposite way, depending on the oxidation conditions. However, many oxidation processes bring about a decrease in fiber tensile strength because of cellulose depolymerization. In addition the oxidized cellulose is more susceptible to degradation in subsequent reactions.

Periodate oxidation of cellulose, initially studied by Jackson and Hudson<sup>1</sup> and further examined by others,<sup>2–10</sup> is a selective oxidation process that converts the 1,2-glycol groups of the glucose residues into two aldehyde groups. The resulting cellulose aldehyde derivatives can be used as intermediates to produce a variety of products, including oxidized and reduced species, diamines,

dioximes, and Schiff's bases.<sup>11</sup> Earlier infrared (IR) studies by Higgins and McKenzie<sup>7</sup> and Spedding<sup>8</sup> of the free aldehyde group absorbance at  $\sim 1740 \text{ cm}^{-1}$  indicated that the moisture content of the sample made such analyses difficult. However, even after thorough drying, the aforementioned researchers failed to produce samples that gave spectra showing a strong free aldehyde group band. Spedding concluded from his research on drying dialdehydocellulose samples that several forms of combined aldehyde groupings existed; namely, hydrated aldehyde, hemiacetal, and hemialdol. In particular, his work suggested that these samples existed mainly in the hemialdol form.

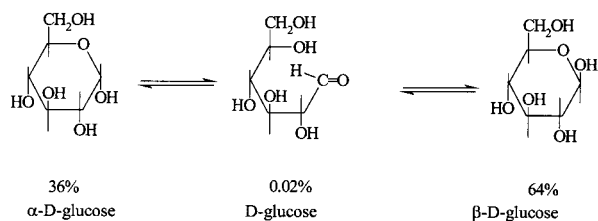
Generally, the equilibrium between an aldehyde and a hemiacetal favors the aldehyde. One important exception to this occurs when a molecule has a hydroxyl group  $\gamma$  or  $\delta$  (1,4 or 1,5) to an aldehyde carbonyl group so that an intramolecular reaction to form a five- or six-membered hemiacetal ring is possible. This phenomenon is clearly demonstrated using glucose as an example (see Figure 1).

When either anomer of pure glucose is dissolved in water, a slow equilibration with the free aldehyde (open chain form) and with the other anomer occurs. Regardless of which anomer is employed, the resulting equilibrium mixtures will

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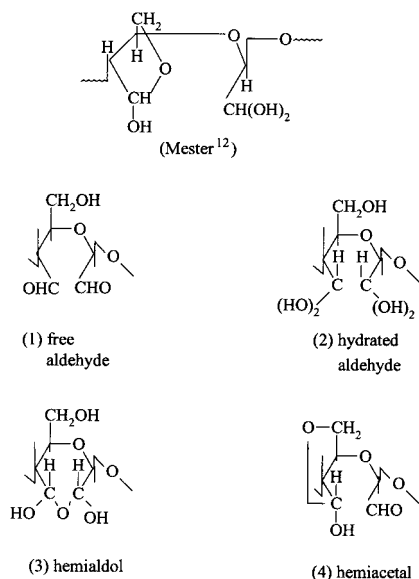


**Figure 1** Equilibria between different glucose forms in water.

contain just 0.02% of the free aldehyde form of D-glucose. Other aldoses, if they have a 4-hydroxyl or 5-hydroxyl group, will also exist in water primarily in the furanose or pyranose hemiacetal ring forms, having just a trace of the free aldehyde (open chain) form.

Many chemical derivatives of cellulose aldehyde were made, but in no case did the IR spectrum of cellulose aldehyde show specific absorption near  $1740\text{ cm}^{-1}$ , which is characteristic of aldehydic carbonyl groups. This result is probably explained by the formation of a cyclic hemiacetal through the reaction of one of the aldehyde groups with the primary C6 hydroxyl group accompanied by hydration of the second aldehyde group. This structure was confirmed by Mester,<sup>12</sup> and this and other possible reaction products are depicted in Figure 2.

From a chemical point of view, numerous structures for periodate-oxidized cellulose can be drawn, involving linkages between different an-



**Figure 2** Possible structures of periodate-oxidized cellulose.

**Table I** Treatments of Cotton with 0.1M NaIO<sub>4</sub> Aqueous Solution

Parameter	Sample			
	A01-1	A02-1	A03-1	A04-1
Time (min)	15	30	60	90

hydro-glucose units either in the same chain or between different chains.

A recent paper<sup>13</sup> highlighted the potential of Fourier transform IR (FTIR) for studying cellulose aldehyde, and this potential has been investigated in this paper.

## EXPERIMENTAL

### Materials

Loomstate cotton plain weave fabric ( $58\text{ g/m}^2$ ) and bleached and unmercerized cotton plain weave fabric ( $140\text{ g/m}^2$ ) were used in this study. All chemicals used were of laboratory grade.

### Oxidation

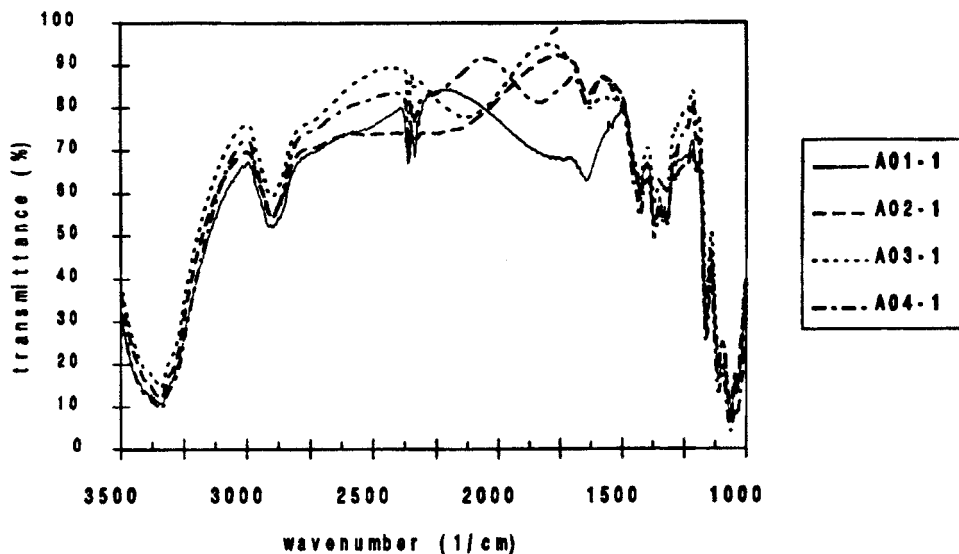
Cotton samples (2.00 g) were immersed in NaIO<sub>4</sub> aqueous solutions of various concentrations at 25 °C. The ratio of cotton to solution was 1:50. The oxidation was carried out in a sealed tube housed in a Rotadyer (J Jeffreys) dyeing machine. When the required reaction time had elapsed, the samples were rinsed three times with tap water and two times with distilled water. The samples were then dried overnight in air or in a vacuum desiccator and were ready for FTIR analysis.

### Fourier Transform Infrared Spectroscopy (FTIR)

Several sampling methods, including conventional potassium bromide (KBr) disc transmittance, attenuated total internal reflectance (ATR), and diffuse reflectance, were applied in this research

**Table II** Treatment of Cotton with Distilled Water

Parameter	Sample			
	B01-1	B02-1	B03-1	B04-1
Time (min)	15	30	60	90



**Figure 3** FTIR microscope transmission spectra of bleached cotton treated with periodate.

using the Perkin-Elmer 1740 FTIR spectrometer equipped with the respective reflectance attachments. Fiber transmittance spectra were also obtained using the IR-Plan microscope (Spectra-Tech). The second derivative data were obtained by using the PE IR Data Manager version 3.5 software (in all cases, the software converts transmittance values to absorbance values prior to differentiation).

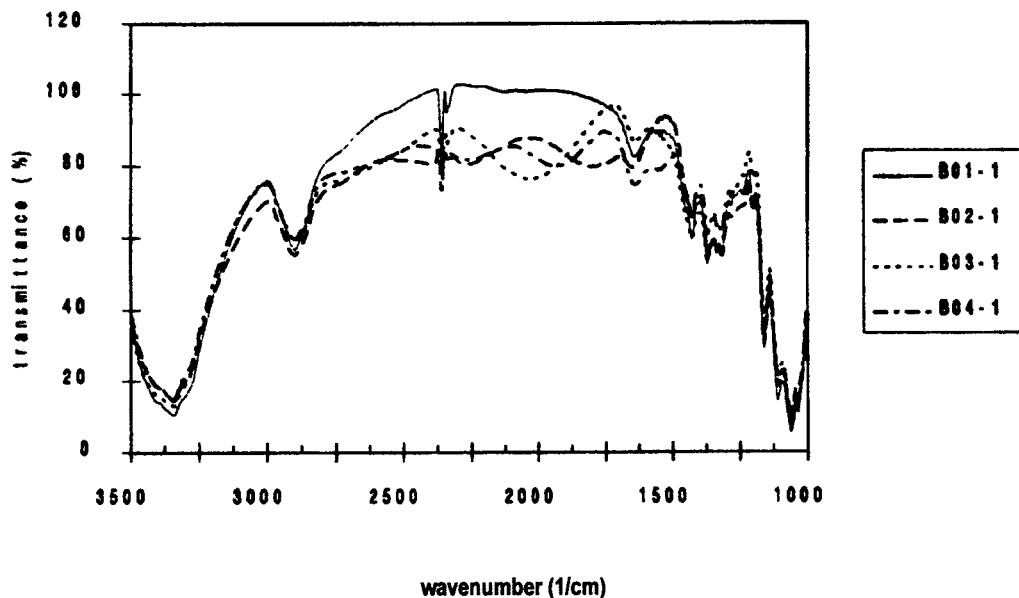
The general measurement conditions were as follows: scan speed, 0.4 cm/s; 100 scans; resolution, 4 cm<sup>-1</sup>; and ambient temperature.

## RESULTS AND DISCUSSION

### Low Periodate Concentration and Short Treatment Times

These initial experiments were carried out on commercially bleached cotton fabric. The treatment conditions used in this section to produce samples for FTIR microscopy analysis are shown in Tables I and II.

The transmission spectra were obtained using the IR-Plan<sup>®</sup> microscope (Spectra-Tech). From the



**Figure 4** FTIR microscope transmission spectra of bleached cotton treated with distilled water.

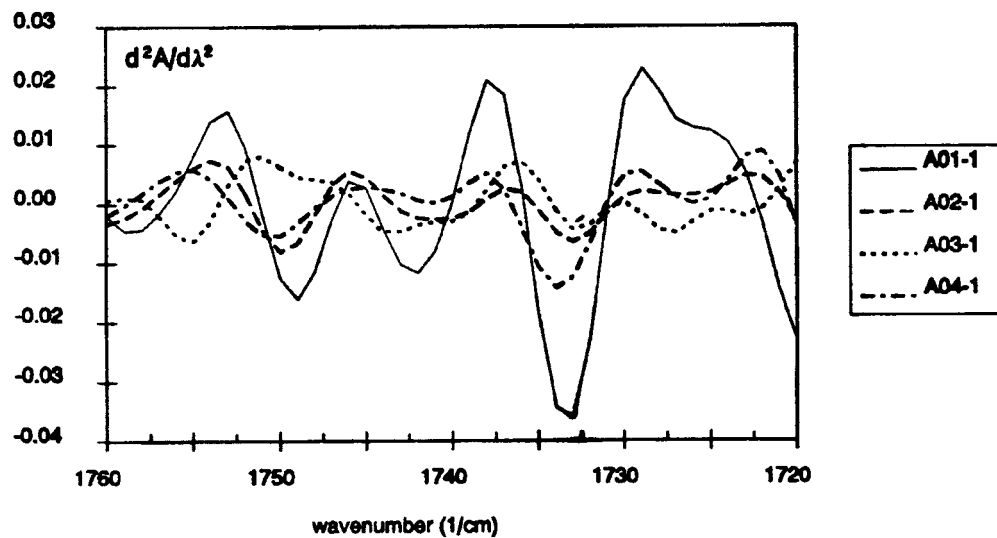


Figure 5 FTIR microscope second-derivative absorbance spectra of bleached cotton treated with periodate.

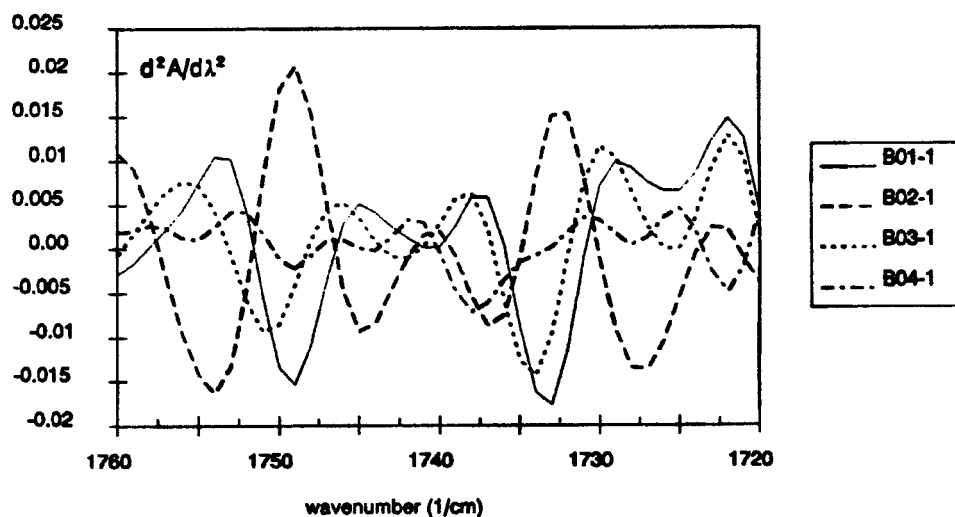
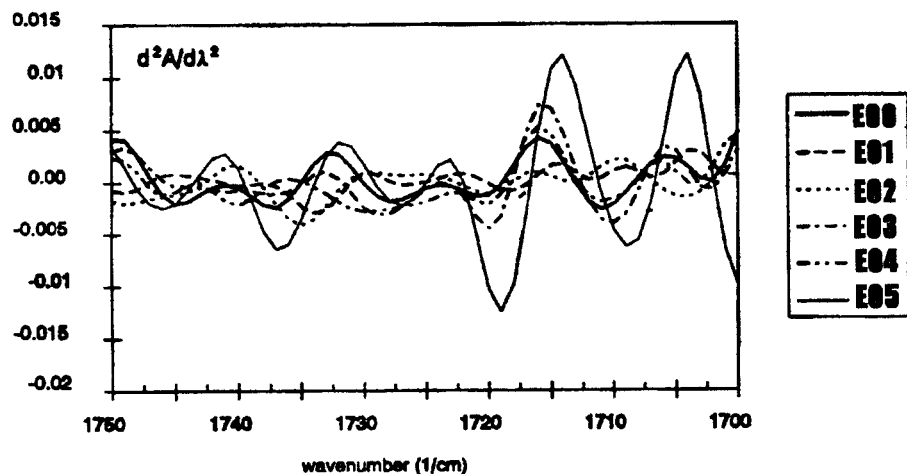


Figure 6 FTIR microscope second-derivative absorbance spectra of bleached cotton treated with distilled water.

Table III Treatment of Bleached Cotton with Distilled Water or Periodate

Parameter	Sample					
	E00	E01	E02	E03	E04	E05
Chemical	Water	NaIO <sub>4</sub>	NaIO <sub>4</sub>	NaIO <sub>4</sub>	NaIO <sub>4</sub>	NaIO <sub>4</sub>
Time (h)	96	5	10	24	48	96



**Figure 7** FTIR microscope second-derivative absorbance spectra of bleached cotton treated with distilled water or periodate. (Higher periodate concentration and longer treatment time than Figure 5).

underivatized regular spectra (Figures 3 and 4), it can be seen that there is little difference in the region  $1720\text{--}1760\text{ cm}^{-1}$ , where it was expected to find bands attributed to the aldehyde groups generated by the periodate oxidation. The second derivative spectra of the above, in the region  $1720\text{--}1760\text{ cm}^{-1}$ , are shown in Figures 5 and 6. There is no clear evidence for aldehyde bands at this stage.

#### Effect of Higher Periodate Concentration and Longer Time Treatments

Because no distinct absorbance peaks for the aldehyde group in either regular or second-derivative spectra were seen in the previous experiments, stronger oxidation conditions were employed, as shown in Table III. The amount of periodate used was the theoretical amount (mole ratio of cotton to  $\text{NaIO}_4 = 1:1$  or 2 g cotton to 2.64 g of  $\text{NaIO}_4$  in 100 mL of water), assuming each anhydroglucose unit (AGU; MW = 162) on cotton fibers can react with one molecule of periodate (MW = 213.89).

Because second-derivative spectra can resolve more detail than the regular spectra, only the second-derivative spectra of the treated bleached cotton are shown. From the second-derivative spectra shown in Figure 7, the absorbance in the region  $1720\text{--}1760\text{ cm}^{-1}$  has no specific location for the expected aldehyde groups. It was postulated that the concentration of periodate in this case may be too high, leading to side reactions that increase the complexity of the resultant spectra.

#### Extended Treatments with Different Periodate Concentration

The previous experiments were carried out on industrially bleached cotton that may contain aldehydes. Subsequent treatments were similar to those already described except that loomstate cotton was used and a stainless steel dyeing tube was used to ensure a dark reaction. These changes were made to eliminate the variable effect of cotton pre-bleaching on the reducing end groups of cellulose and to avoid any photooxidation effects. The experimental conditions are shown in Table IV.

All samples were treated at  $25\text{ }^\circ\text{C}$  for 24 h, and the ratio of cotton to solution was 1:50. Samples were washed in distilled water and air dried prior to FTIR measurement using an ATR system.

From the spectra (Figure 8), it can be seen that there is a new peak in the region  $1730\text{--}1736\text{ cm}^{-1}$  for the oxidized cotton. It is obvious that unoxidized cotton did not produce such a peak in this region. From these results, it was postulated that the IR absorbance peak of the aldehyde group in the periodate oxidized cotton may be located in the region  $1730\text{--}1736\text{ cm}^{-1}$ .

**Table IV** Treatment of Loomstate Cotton with Distilled Water or Periodate

Parameter	Sample				
	D00	D01	D02	D03	D04
$\text{NaIO}_4$ (% omf)	Water only	1	2	5	10

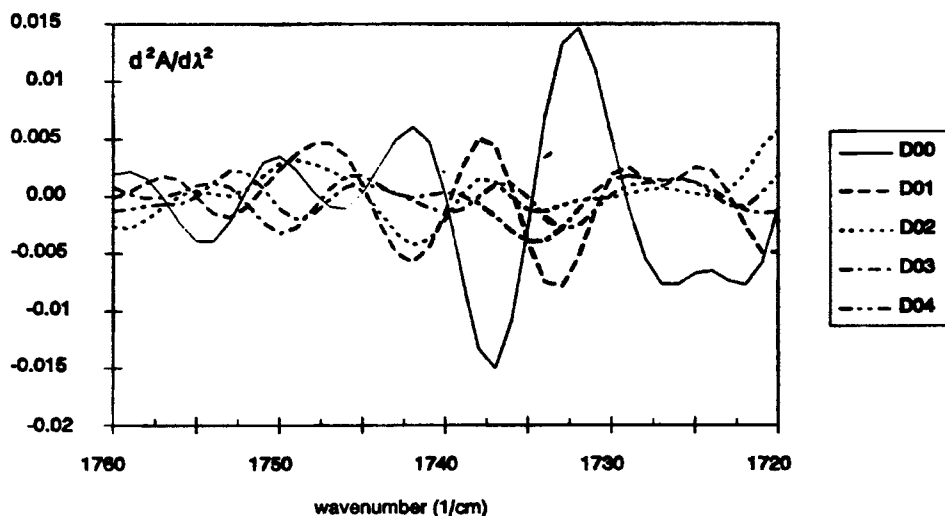


Figure 8 FTIR-ATR second-derivative absorbance spectra of loomstate cotton, both oxidized and unoxidized (vertical ATR attachment).

Because aldehydes tend to react with hydroxy groups in the presence of water to form acetals and hemiacetals, it was decided to remove regain water from the fabrics prior to IR measurements to push the aforementioned equilibrium reaction to the free aldehyde side. This water removal was done by Spedding's method;<sup>8</sup> the samples were placed in an oven at 110 °C for 24 h to remove the absorbed water and then put in a vacuum desiccator to cool. Before the FTIR measurement, the maximum air exposure of the samples was 1 min. The resultant second-derivative spectra are shown in Figure 9, and comparative second-deriv-

ative spectra of samples exposed to air for >48 h after heating are shown in Figure 10. Comparing Figures 9 and 10, a distinct new peak appeared in the region 1732–1734  $\text{cm}^{-1}$  for the 110 °C dried periodate oxidized samples, but no such peak was present for the subsequently air exposed (48-h) samples. Thus, the conclusion can be reached that the aldehyde IR absorbance peak in periodate oxidized cotton is sited in the region 1732–1734  $\text{cm}^{-1}$  and may be attributed to the C=O stretching vibration in the free aldehyde.

In periodate oxidized cotton exposed to normal moist atmospheres there will always be a mixture

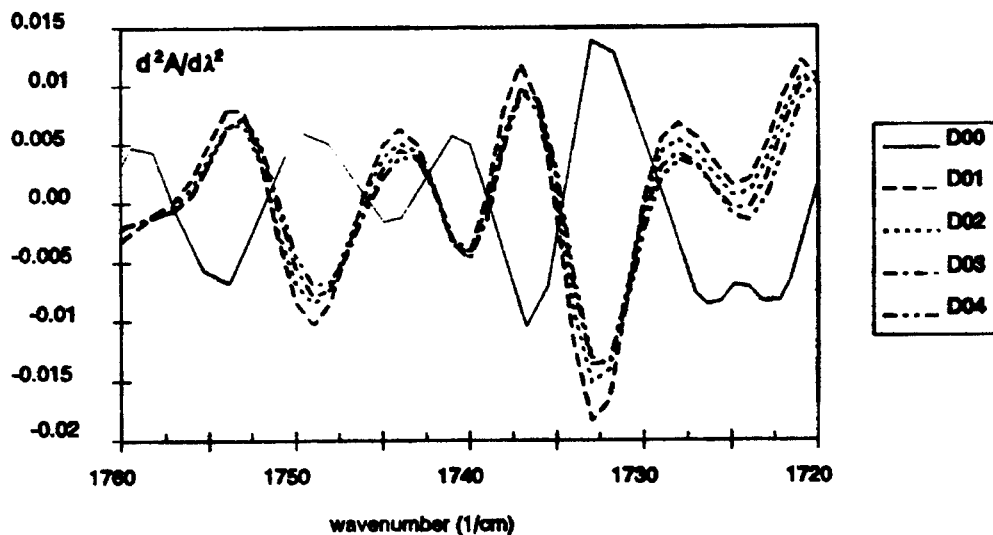


Figure 9 FTIR second-derivative absorbance spectra of oxidized-dried loomstate cotton (vertical ATR attachment).

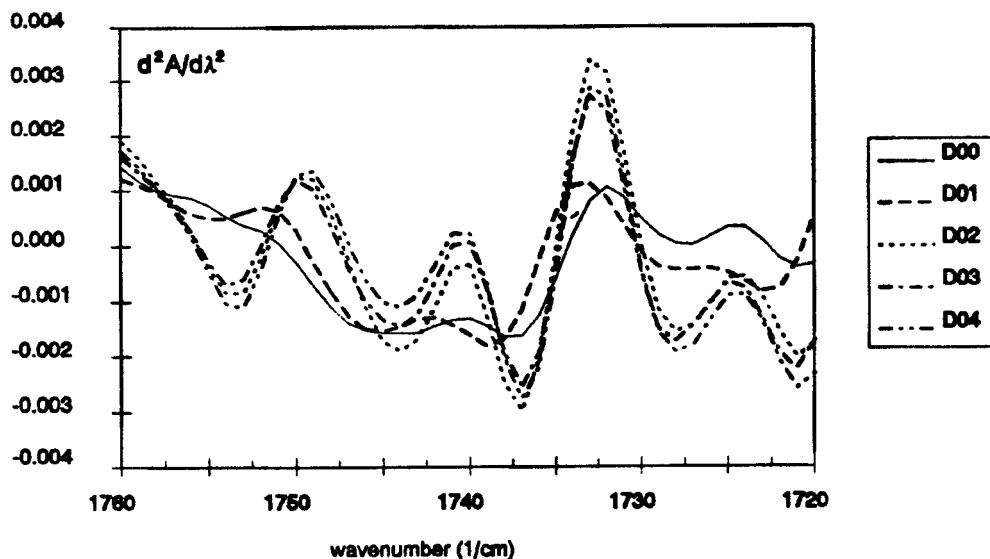


Figure 10 FTIR second-derivative absorbance spectra of oxidized, 110 °C, dried, air-exposed loomstate cotton (vertical ATR attachment).

of hydrated aldehyde groups, hemiacetal groups, and hemialdol groups, which explains the spectra shown in Figure 8. For dried  $\text{NaIO}_4$  oxidized cotton, the free aldehyde groups were produced and gave reproducible  $\text{CH}=\text{O}$  IR bands, as shown in Figure 9. For the samples of dried  $\text{NaIO}_4$  oxidized cotton, re-exposed to air, both hemialdol and hydrated aldehyde groups may be present, accounting for the IR spectra shown in Figure 10.

The concentration of free aldehyde groups in periodate-oxidized cotton is thus greatly affected by water, and these groups can form some of the derivatives shown in Figure 2. Because of this effect of water, it is difficult to detect the existence of cellulose aldehyde by the usual IR spectroscopy methods; careful drying and then using FTIR in the derivative mode or other special techniques are therefore essential.

#### Diffuse Reflectance Thermal FTIR Characterization of Cellulose Aldehyde

As the previous sections have pointed out, cellulose aldehyde obtained from the periodate oxidation of cotton is difficult to detect using regular FTIR spectroscopy at normal room temperature and room humidities; therefore an alternative way was explored, using an Environmental Chamber incorporating the COLLECTOR™ (Spectra-Tech) for diffuse reflectance spectroscopy at elevated temperatures.

Periodate oxidation (typically 10% omf) of loomstate cotton was conducted at 25 °C for 24 h

at a liquor-to-material ratio of 50:1. The chopped periodate-oxidized cotton sample was placed in the Environmental Chamber. The temperature of the sample chamber was raised by an electronic heating control unit instantly to values between 25 and 350 °C. FTIR measurement of every sample was made at 25, 50, 100, 150, 200, 250, 300 and 350 °C; in all cases, a 10-min dwell time was necessary to allow the sample to reach thermal equilibrium at each measurement temperature prior to analysis.

From the resulting underivatized diffuse reflectance FTIR spectra (Figures 11 and 12), it can be seen clearly that the peak at  $1646\text{ cm}^{-1}$  in all

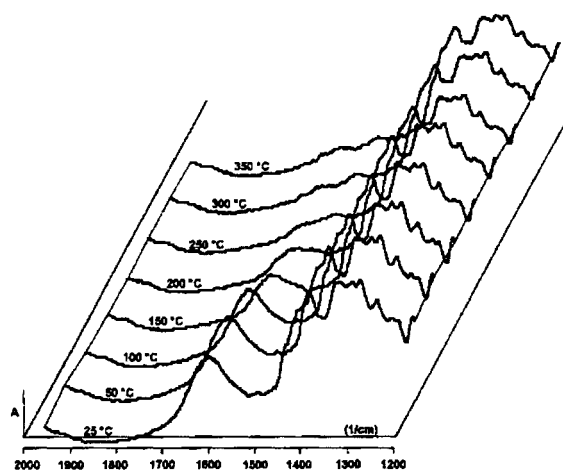
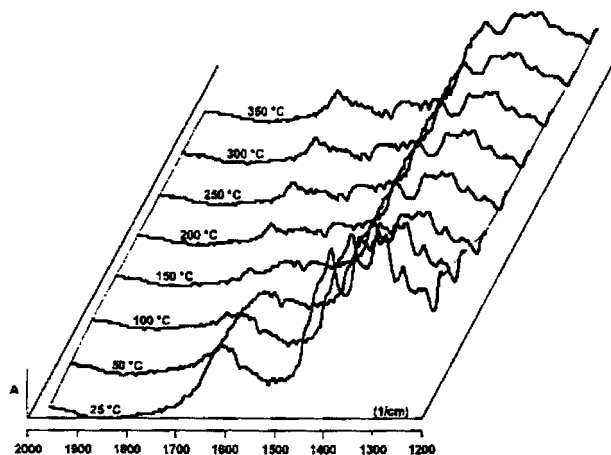


Figure 11 FTIR spectra of unoxidized loomstate cotton.



**Figure 12** FTIR spectra of oxidized loomstate cotton using 10% omf periodate.

the samples, whether oxidized or unoxidized, decreased with increasing temperature and time and can thus be attributed to the symmetric deformation vibration of absorbed water molecules.<sup>14</sup>

Figure 12 shows that for the 10% omf periodate-oxidized samples, the aldehyde carbonyl absorbance at  $1734\text{ cm}^{-1}$  only appeared as a distinct peak after heating the samples at  $100\text{ }^{\circ}\text{C}$  and above. In all the oxidized samples, the intensity of the aldehyde absorbance increased when the samples were heated, whereas the absorbed water IR band decreased.

## CONCLUSIONS

Cellulose aldehyde can be obtained by selective periodate oxidation of the secondary hydroxyl groups at the C2 and C3 positions of the anhydroglucose units in cellulose. It is not easy to detect the existence of aldehyde groups because they

readily combine with water or neighboring groups to produce hydroxyl group absorbance in the IR spectrum. On drying the  $\text{NaIO}_4$ -oxidized cotton, the cellulose aldehyde group can be easily characterized in the region  $1732\text{--}1734\text{ cm}^{-1}$  by both second-derivative FTIR spectra and high-temperature diffuse reflectance FTIR spectra with the help of accessories such as the Environmental Chamber (Spectra-Tech).

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