

Digital Comparison of X-Ray Diffraction Data from Cotton Textiles

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Synopsis

It is proposed that step-scanned digital x-ray diffraction data from closely similar samples be compared only after averaging several scans. The comparison of averaged data for two samples is shown directly by a running difference curve; more subtle differences are indicated by a running sum of difference curve. In order to compensate for inequalities arising from experimental difficulties, scaling of the two data sets may be optionally accomplished by either equating the total intensity sums or performing a least-squares fitting. Comparison of the two scale factors and consideration of the intercept (background) and resulting standard deviation provide a quantitative estimate of the difference between samples. The proposed techniques are illustrated for hydrocellulose II, cotton treated with acid, flame retardant, and permanent-press agent, and for the experimental differences of intact cloth versus pressed pellet and different beam-current settings on the diffractometer.

INTRODUCTION

In studies of chemically or physically modified cotton, it is often difficult to ascertain whether small differences in x-ray diffraction patterns have arisen from structural differences within or between crystalline microstructural units or from uncontrolled variation in the method of measurement. The physical performance properties of cotton fibers are often changed substantially, without adequate appreciation for the small changes that may have occurred in the microstructure of the cotton fiber to account for the change in performance. There is a need, therefore, for methodology (x-ray diffraction and otherwise) that detects and defines small changes in the microstructure.

Chromatographic, infrared, and other types of spectral data have been processed via computers to identify small differences, and much valuable information has resulted. However, to our knowledge, no such application has been reported for powder diffractometry. We report herein a preliminary assessment of a computer technique for processing and comparing data from samples that may have small differences in their microstructures.

Several aspects of powder diffractometry make digital treatment attractive. Counting statistics, current fluctuation, and placement of sample in the x-ray beam yield random variations in peak height. If samples that differ only slightly are being compared, the effects resulting from structural features may be eliminated or lost in the random variation. If the data require scaling before comparison, digital data are easily scaled. Finally, the subtraction of the data for

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the original, unmodified (control) sample from the data for the experimental variation yields an array of differences that can be plotted adjacent to the original diffraction curves to show exactly the magnitude and position of the differences. In this article, we describe the digital technique that we have employed and discuss our findings in connection with several modified cotton celluloses.

MATERIALS

Samples of unmodified or modified cotton cellulose that were examined in this study were materials that were available from other research. Preparation of these samples is described and cited as each is mentioned in the text or legends. Thin platelets, 0.5 by 1.0 in., were prepared from the particulate samples by compressing 100-mg quantities of cotton under 25,000 psi in an aluminum mold that served as the specimen holder. Samples of intact fabric were placed over an aluminum block and held in place with an aluminum frame. The warp direction of the fabric was located parallel to the long axis of the sample holder.

APPARATUS

A General Electric XRD-5 diffractometer* was equipped with Cu tube, Ni filter, proportional counter, Leeds and Northrup direct recorder, Slo-Syn indexer, Harshaw amplifier, analyzer scaler, and Teletype interface. A teletype printer was fitted with punched paper tape output. The punched paper tapes were processed on a CDC 1700 computer with a locally written FORTRAN IV program.

PROCEDURE

Diffraction counts were accumulated for 10 sec at each interval of $0.2^\circ 2\theta$, scanning from 30° to 6° with the tube voltage at 40 kV and a tube current of 15 mA. The general procedure was to scan each sample three times. However, a single sample of hydrocellulose II was scanned ten times to determine the effect of averaging and to ascertain the resolving capabilities of powder diffractometry for polysaccharides. In addition, fabric samples chemically modified with *N*-methylolacrylamide were given special treatment, as they exhibited only small differences; three specimens of each of these samples were selected and each of the specimens was scanned three times, resulting in nine measurements per composition. These results were averaged prior to comparative analysis.

Instead of counting for longer times on a single scan, repeated, short scans were selected for two reasons. First, the effect of gradual fluctuations in line voltage would be minimized, and second, deterioration in the sample because of exposure to the x-ray beam would produce less change in the reflections that were scanned early versus those scanned later.

* Names of companies or commercial products are given solely for the purpose of providing specific information; their mention does not imply recommendation or endorsement by the U.S. Department of Agriculture over others not mentioned.

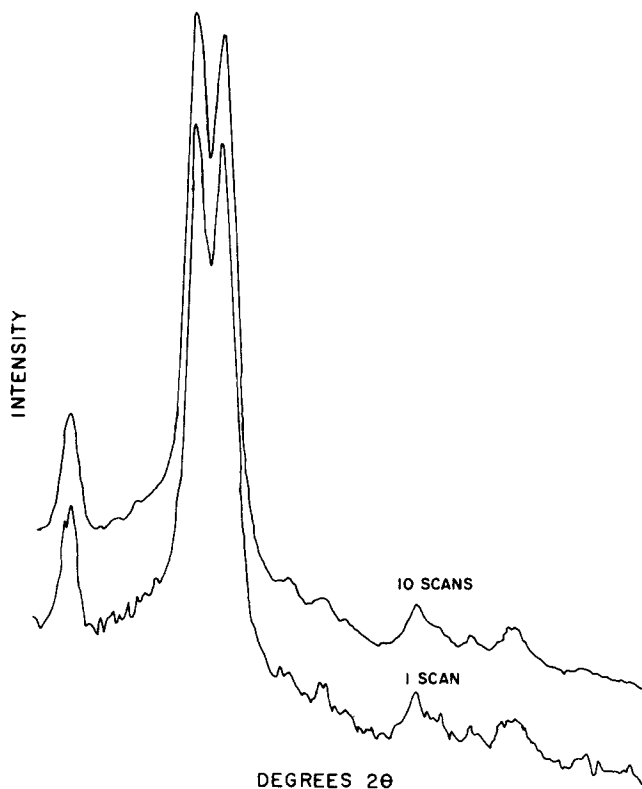


Fig. 1. Comparison of diffraction curves from single scan (lower) and average of ten scans (upper) of hydrocellulose II.

COMPUTER PROGRAM

The program incorporates four options. Option 1 reproduces and graphs the input digital data or the average of the data if there is more than one run. Option 2 plots the intensity curves of two data sets for which comparison is desired. The program chooses a scale factor F so that the maximum intensity of the sample considered to be the control equals 100. This ensures that the curve of the control sample will be contained appropriately on the paper and allows differences between the experimental and the control to be expressed as percent of the maximum height. After both the control and experimental samples are scaled by F , the point-by-point difference is calculated. The scaled intensity curves are drawn, with that from the control placed ten units above that from the experimental sample. Beneath these curves, the difference (Δ) curve is drawn. Additionally, the sum of the incremental differences ($\Sigma\Delta$) is computed and drawn, starting from the difference at $2\theta = 30^\circ$. In the present work, it was convenient to have the y-axis scale four times as large for the $\Sigma\Delta$ curve as for the other three curves.

Options 3 and 4 produce output similar to option 2 except that the intensities of the experimental curves are modified to yield closer agreement with the intensities of the control sample. Option 3 sums all of the incremental intensities for each data set. The ratio $\Sigma I_{\text{control}}/\Sigma I_{\text{experimental}}$ of these sums becomes a scaling factor that automatically forces the final value of the Σ curve back to zero.

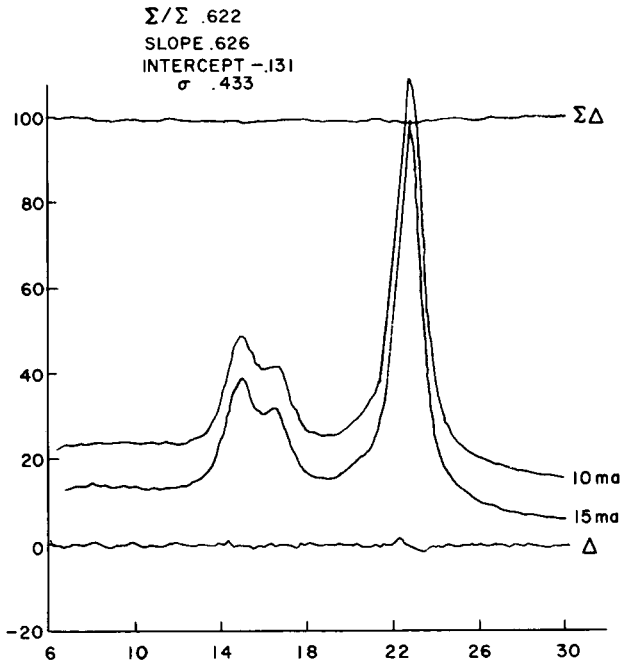


Fig. 2. Comparison of diffraction curves from pressed pellet of cotton at 10- and 15-mA tube current.

Option 4 uses the slope (scale factor) and intercept (background correction) from a least-squares regression analysis of the two intensity sets. The regression equation fitted was

$$I_{\text{control}} = I_{\text{experimental}} \times \text{slope} + \text{background}$$

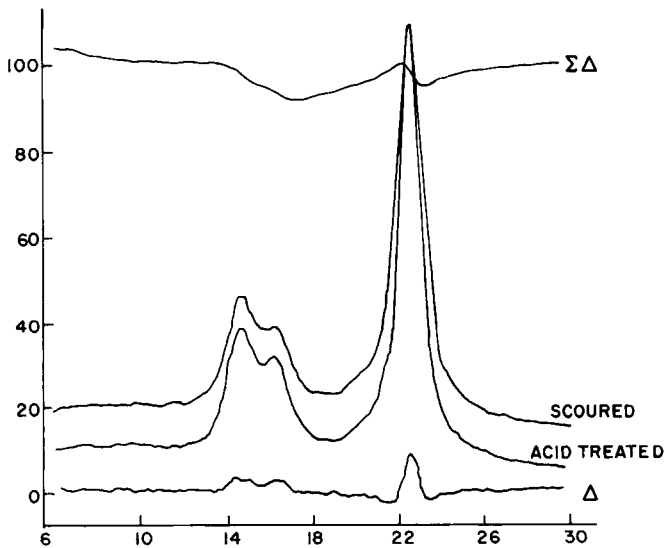


Fig. 3. Comparison of diffraction curves of acid-treated scoured yarn (87% CrI) and scoured-only yarn (85.3% CrI).

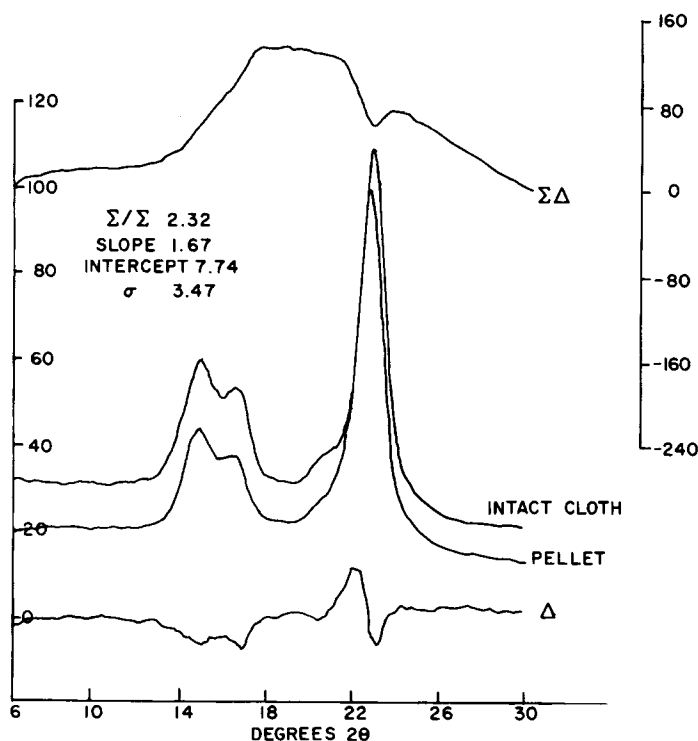


Fig. 4. Comparison of diffraction curves of cotton in form of pressed pellet and in form of original cotton printcloth.

with the data being the observed intensities at each 0.2° increment. Option 4 also reports the standard deviation of the regression, a numerical estimate of the fit of the two curves.

RESULTS AND DISCUSSION

Shown in Figure 1 are the curve from a single scan of hydrocellulose II (from the hydrolysis of thrice mercerized cotton yarn with $2.5N$ HCl at reflux¹) and the curve derived from averaged intensities of ten such runs. Many irregularities in the curve from the single scan can be attributed to noise that is smoothed out by the averaging process. This smoothing alters peak shape slightly, with the more correct shape found in the averaged curve.

Figure 2 shows a comparison of curves from averaged scans of a pressed pellet of Wiley-milled cotton (desized, scoured, bleached printcloth, chopped to pass a 20-mesh screen) measured at 10- and 15-mA tube currents. The maximum counts recorded were 10,331 and 16,640, respectively. Option 4 treatment was applied to these data, and the regression analysis yielded a slope of 0.626 and an intercept of -0.131 . After correction by these terms, the two data sets are virtually identical. Because the intercept value is so small, the difference in background level at the two currents must be inconsequential. The $\Sigma I_{10 \text{ mA}} / \Sigma I_{15 \text{ mA}}$ scale factor of 0.622 agrees closely with the slope, again indicating close agreement between the two curves.

In Figure 3, the reality of an effect from $0.5N$ HCl at 80°C for 90 min on scoured

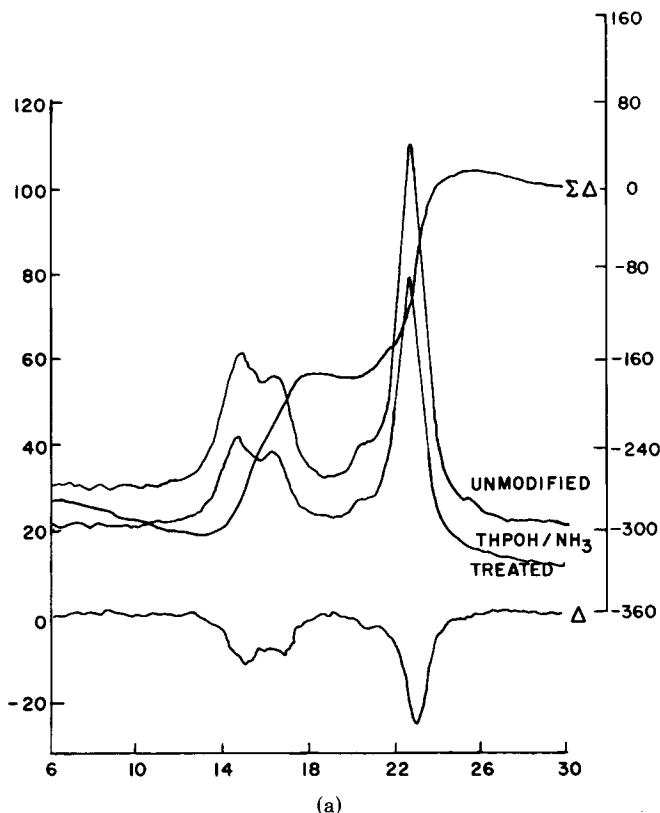
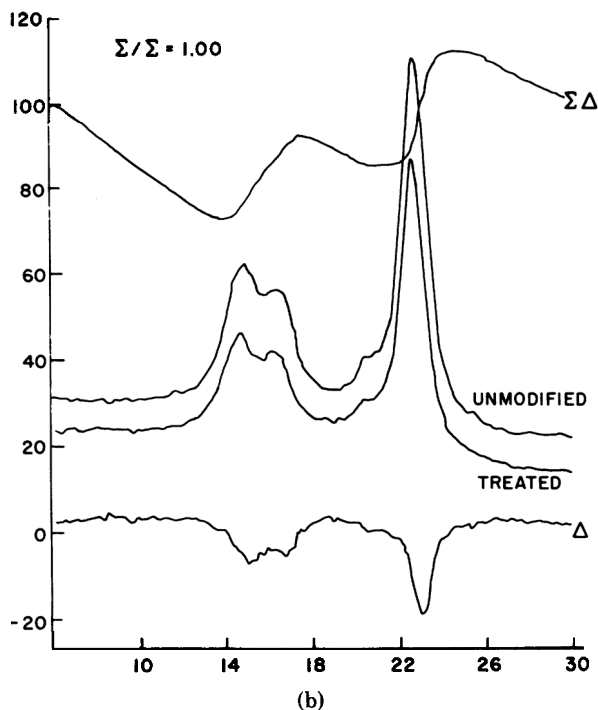


Fig. 5. (a) Diffraction curves of THPOH/NH₃-cotton and the original cotton, no scaling of data. (b) Diffraction curves for THPOH/NH₃-cotton and the original cotton, data scaled by Σ/Σ factor. (c) Diffraction curves for THPOH/NH₃-cotton and original cotton, scaled by least-squares regression.

cotton yarns is examined. Both the acid-treated and the original cotton yarns were ground for preparation of pressed pellets. Figure 3 shows an option 2 (uncorrected) comparison of the two diffraction curves. The "W" shape in the Δ curve is indicative of a difference in crystallinity. The lower diffraction curve, from the acid-treated cotton, has the higher, narrower main peak, giving an intensity surplus at the center and an intensity deficit on each side of the center, relative to the control curve. Only the increased central intensities are apparent in the Δ curve for the two overlapped smaller peaks. By a frequently used formula for crystallinity index,² $CrI = 100 (I_{22.6^\circ} - I_{18.0^\circ}) / I_{22.6^\circ}$, crystallinity indices were found to be 85.3 and 87.0% for the scoured cotton and for the acid-treated scoured yarn, respectively. This difference would not usually be considered highly significant. Option 4 treatment of the data for these two samples of cotton (not shown) resulted in a slightly smaller positive peak in the center of the "W" in the Δ curve because of the intercept correction; but the effect of a real increase in crystallinity because of the acid treatment is still clear.

Figure 4 provides a comparison of the diffraction curves of an intact piece of cotton printcloth and a pressed pellet of the same cotton after being ground in a Wiley mill to pass a 20-mesh screen. Although the printcloth nominally has



uniplanar molecular orientation, the "randomly packed" compressed chopped cotton exhibits greater orientation. Because of the greater orientation, the second layer peak (0 1 2) at $20.5^\circ 2\theta$ does not appear in the pattern from the pressed pellet. Also, the heights of the equatorial $(-1\ 1\ 0)$ and $(1\ 1\ 0)$ peaks are lower, relative to the major peak (0 2 0), for the pressed pellet and the peak positions are shifted downscale $0.1^\circ 2\theta$.

The large deviation from zero for the $\Sigma\Delta$ curve, the difference between the $\Sigma I_{\text{intact fabric}}/\Sigma I_{\text{pressed pellet}}$ scaling factor and the slope, the standard deviation, and the intercept all indicate a difference between samples. In this case, however, the difference arises from the overall physical nature of the sample, not from its internal structure. The 0.1° shift in peak position is caused by the difference in thickness of the two samples. This demonstration of changes in peak intensity and position underscores the necessity of careful preparation of analogous samples.

Samples with crosslinks are not so susceptible to orientation caused by pressure used to prepare pellets as the samples without crosslinks are. For this reason, intact fabric samples were selected when comparisons between treated and untreated fabrics were desired. Changes in fabric dimensions during crosslinking treatments are inconsequential in comparison to the orientation during pellet formation.

In Figure 5, the experimental sample under examination was prepared by treatment of cotton sheeting with neutralized tetrakis(hydroxymethyl)phosphonium chloride followed by ammonia vapors (designated THPOH/NH₃-

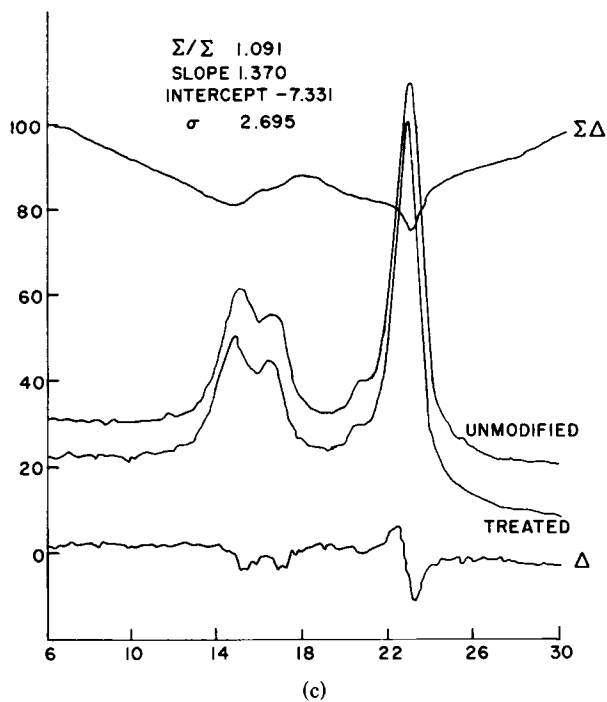


Fig. 5 (Continued from previous page.)

cotton).^{3,4} The add-on was 33%, essentially the limit of material that may be expected to penetrate into the pores of the cotton fiber. The diffraction curve for this THPOH/ NH_3 -cotton is compared to the curve for the original sheeting in the three parts of Figure 5. Options 2, 3, and 4 are applied in Figures 5(a),

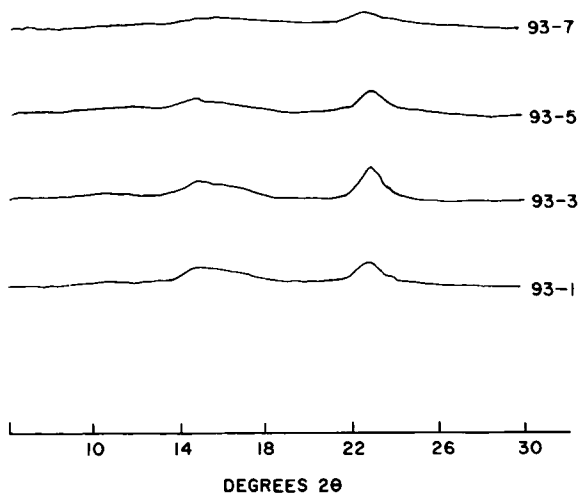


Fig. 6. Running sum of difference ($\Sigma\Delta$) curves between each of four *N*-methylolacrylamide-treated cottons and the original cotton. The treated cottons differ only in the amount of phosphate salt present during the finishing reaction: 93-1, none; increasing amounts from 93-3 through 93-7.

5(b), and 5(c), respectively. In Figure 5(a), the peak heights in the diffraction curve of the THPOH/NH₃-cotton are substantially reduced relative to the background. The difference curve (Δ) is an inverted cellulose I diffraction curve without background. The areas of major differences between the curves are also indicated by the steep slopes of the incremental difference ($\Sigma\Delta$) curve in the regions of the diffraction peaks and by the near-zero slope in the background areas.

Option 3 [Fig. 5(b)] reduces the difference between curves for THPOH/NH₃-cotton and the unmodified cotton, but the $\Sigma\Delta$ curve still indicates that the two diffraction curves are substantially different from each other. Note that the $\Sigma\Delta$ curve has been rotated by the $\Sigma I_{\text{unmodified cotton}}/\Sigma I_{\text{THPOH/NH}_3\text{-cotton}}$ fitting, a procedure that forces the final value of the $\Sigma\Delta$ array to zero.

The least-squares fitting of option 4 [Fig. 5(c)] intensified the peaks relative to the background by multiplying all values by the slope, in this case 1.37, and then adding a negative value of the intercept -7.3 . The value of the standard deviation of the regression, 2.7, may be compared with 0.4 resulting from the test with two beam currents (Fig. 2). Despite the improved fit of the curves for THPOH/NH₃-cotton and unmodified cotton, there is very substantial evidence that these curves are different. Once this real difference is ascertained, analysis should be performed on the original diffraction curves to determine the reasons for the differences in the diffraction patterns. The utility of option 4 is that the curves may be shown to be dissimilar despite large possible corrections for background and scaling. The standard deviation, slope, and intercept that accompany the regression provide indication of the minimum real difference. Another THPOH/NH₃-cotton at slightly lower add-on (29%) and other selected flame-retardant cottons at 29–33% add-ons did not show such strong differences with the unmodified cotton. The THPOH/NH₃-cotton that is the basis for differences shown in Figure 5 is different from the others in having a measurably nonuniform distribution of reagent residues, as detected via electron microscopic examination.⁵

Figure 6 relates to a series of chemically modified cotton fabrics that have comparable add-ons (7%) of *N*-methylolacrylamide, equivalent and attractive durable press ratings, and increasing levels of retention of strength and abrasion resistance in progression from sample 93-1 to 93-7. The durable-press treatments of cotton printcloth were carried out with zero (93-1) and increasing concentrations (93-3 through 93-7) of phosphate salts in the reaction mixtures. However, measurable phosphate is not incorporated into the chemically modified cotton,⁶ indicating that the phosphate functions as a buffer or a catalyst. In Figure 6 are shown the $\Sigma\Delta$ curves for the experimental samples; these curves are shown without the diffraction curves because the latter exhibited no obvious differences among themselves or between each experimental sample and the control sample (unmodified printcloth). As evident in the $\Sigma\Delta$ curves, the diffraction patterns of 93-7 showed the least difference from that of the control. This difference decreases from sample 93-3 to 93-7. The indication is that the conditions involved in the chemical reaction to prepare sample 93-7 altered or disrupted the microstructure of the cotton to a lesser degree than did the other treatments. This finding parallels observations from other tests on these samples of chemically modified cotton; e.g., scanning electron microscopy shows that sample 93-7 fails abrasion tests with fibrillation generally similar to that of un-

treated cotton fabric. The progression from blunt, brittle breaks to fibrillar breaks increases from sample 93-1 to 93-7.

In summary, the averaging of several diffractometer runs, together with scaling corrections, gives a diffraction pattern that may be compared with other patterns from similar materials. With the present technique, differences are indicated directly by the difference curve plotted with the two diffraction curves under comparison. If there are only slight differences, indications of difference in either peak or background are still found in the running sum of difference curve.

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