# Deuteration of Cotton Fibers.  II.  A Novel Method of Deuteration-Infrared Study of Cellulose in Fiber Form

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## Synopsis

A new technique enabling the use of cellulosic material in the fiber form during deuteration-infrared studies is reported.  A minipress, modified to suit the new technique, is described.  Since the material was studied in the fiber form, danger of fiber modification during film formation was avoided.  Although the usual KBr pellet technique was utilized for scanning the spectra of the deuterated fibers, preparation of pellet as well as scanning were carried out under fully dry conditions, thus completely avoiding the rehydrogenation of deuterated fibers.  The modified minipress containing the pellet forms an airtight assembly allowing repeat scans after any length of time without affecting the quality of the spectra of the deuterated sample.

## INTRODUCTION

Elis and Bath[1] were perhaps the first to show the presence of hydrogen bonds in cellulose by infrared spectroscopy using a semitransparent ramie specimen in a mixture of carbon disulfide and carbon tetrachloride.  Holliday[2] developed an elaborate process of filament winding in order to overcome some of the serious drawbacks in infrared study of fibrous materials such as scattering, specimen mount, etc.  Very little success, however, seems to have been achieved in this direction.  Rowen, Hunt, and Plyler[3] used thin films of regenerated cellulose fibers in their infrared studies. Subsequently, a number of workers used this technique to study the cellulose structure by infrared technique or during deuteration-infrared studies.[4-8]  However, additional changes in the internal structure of fibers are introduced as a result of solvent action during film formation.  Secondly, no commonly available and suitable solvents are to be found for cotton fibers.

There are many solvents that can be used to dissolve cotton fiber to form films.  In forming a film, it is obvious that there would be a rearrangement of the H-bonds for such reasons as that the crystal form would be transformed from cellulose I to II. The solvents are difficult to remove, and the cellulose film has a tendency to retain residual solvent.  Although the Nujol technique reduces light scattering at adjacent surfaces, it involves considerable grinding of the sample, which is accompanied by serious degradation and structural changes.  Apart from this, strong Nujol bands in the region of $-CH_3$ and $>CH_2$ stretching and
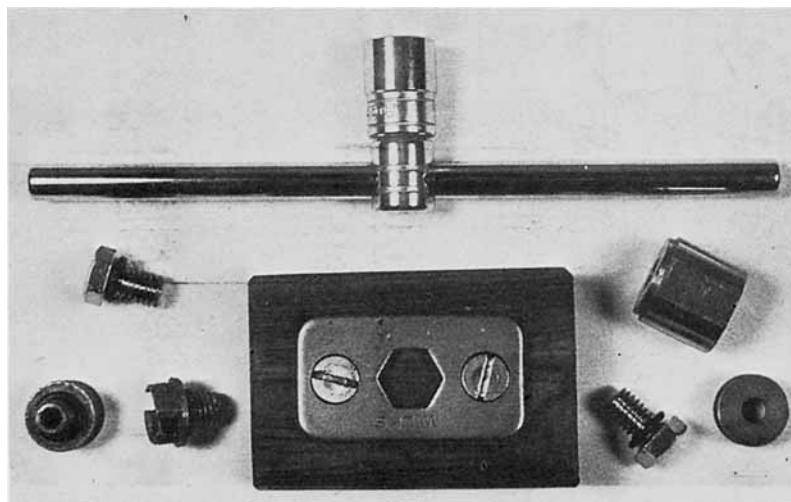
Fig. 1. Details of minipress.

deformation[9] vibrations affect the accuracy of measurement in the OH region. The novel direct pressing technique of Zhbankov et al.[10–12] eliminates all the above-mentioned drawbacks, since a mechanically stable semitransparent disk of fibers with flat lustrous surface is used in scanning the spectra. O'Connor, Du'Pre, and McCall[13] successfully employed the KBr disk technique originally reported by Anderson and Woodall[14] for rapid, simple, and reproducible recording of infrared spectra of cotton fibers.

The credit of combining deuteration technique with infrared spectroscopy to characterize the structure of cellulose would have gone to Rowen and Plyler[15] but for the fact that the reported results were not correct, possibly due to defective deuteration technique. Almin,[16] however, successfully combined the two techniques where films of cellulose acetate were employed. Cumberbirch and Spedding[17] extended Zhbankov's direct pressing technique to the deuteration infrared dichroism studies of cellulose fibers in the 3-$\mu$ region. Deuteration was carried out after the pressing when splits appeared in the mounted layers during the drying, redeuteration, and redrying stages. Although Fortisan filaments could be studied with certain success, cotton fibers, which were of the order of 15 $\mu$ in diameter, however, were found to be too thick to allow accurate measurements of OH stretching bands. Knight et al.[18,19] improved upon Zhbankov's technique by first deuterating a three- to six-fiber-thick layer followed by application of pressure comparable to that used in KBr disk technique. It is reported that the authors encountered the serious error of rehydrogenation of deuterated samples by atmospheric moisture, and every operation carried out under open atmosphere on the deuterated sample was made "as quickly as possible" in order to minimize the sources of error.

The aim of the present investigation was to attempt to overcome some of these difficulties and to develop a method so that the deuteration-infrared technique could be carried out without danger of rehydrogenation of the deuterated cellulose in the fiber form. It was possible to gather more reliable and extended data by using the new technique. Some of the results obtained with the new technique have already been reported.[20]
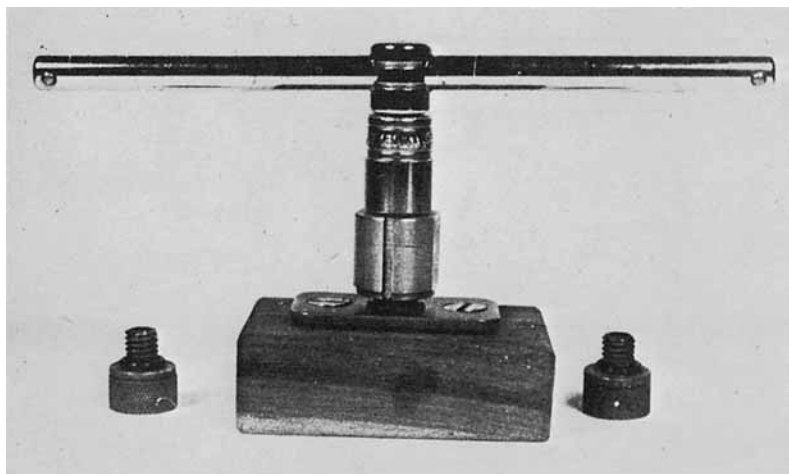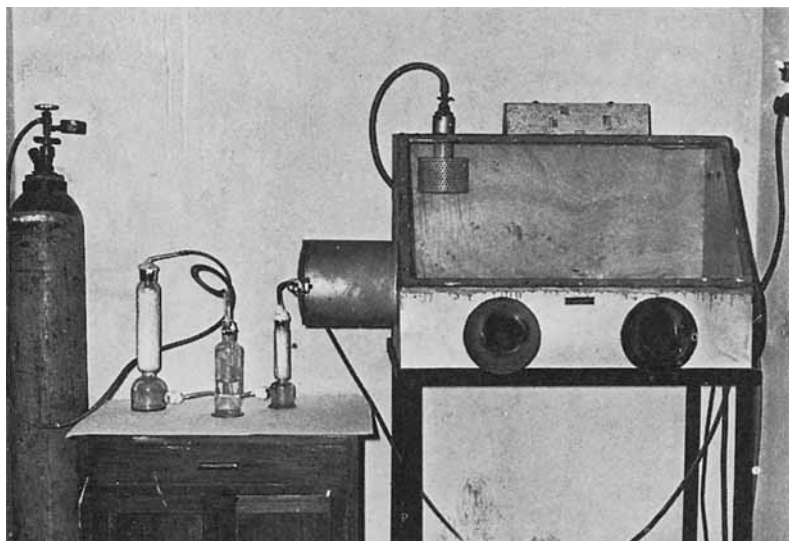
Fig. 2. Minipress and two modified screws.



Fig. 3. Deuteration assembly.

## EXPERIMENTAL

### Materials

**Fibers.** Good-quality Sudanese cotton, ramie, wood pulp in fiber form, and viscose filaments were used in the present work.

**Chemicals.** Deuterium oxide, 99.5% pure, supplied by Bhabha Atomic Research Centre, Bombay, and spectroscopic-grade KBr supplied by SPEX Industries, Inc., U.S.A., were used in the present work.

**Minipress.** The Minipress manufactued by Wilks Scientific Corporation, U.S.A., was used (Figs. 1 and 2). Essentially, the minipress is a hollow, stainless steel cylinder with two screws to be screwed up inside the cylinder from both ends. Further modification of the minipress was effected by fabricating a set of brass
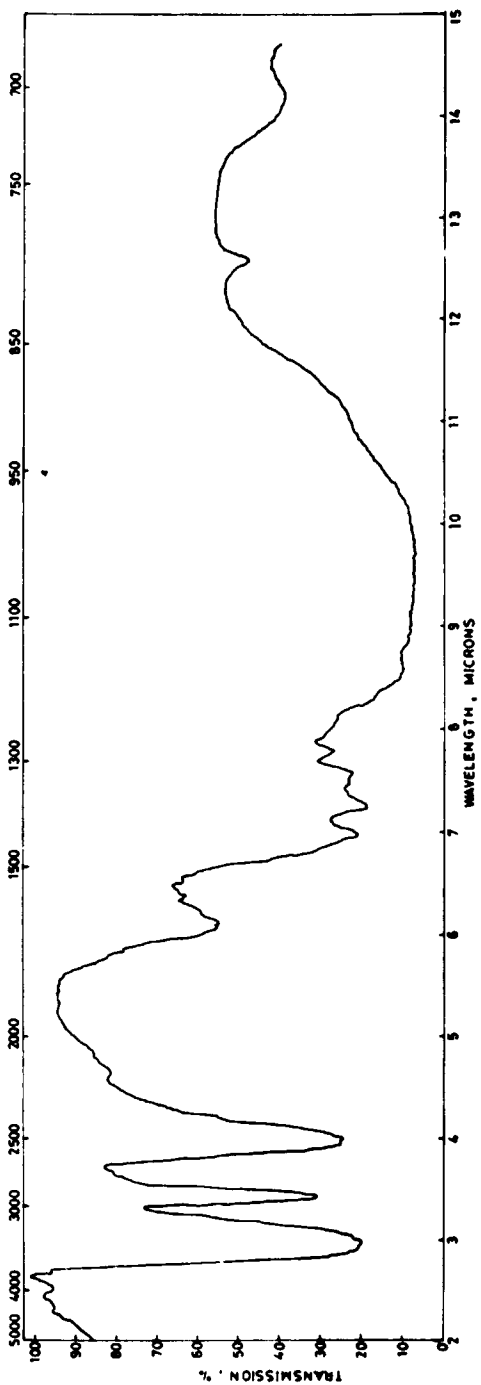
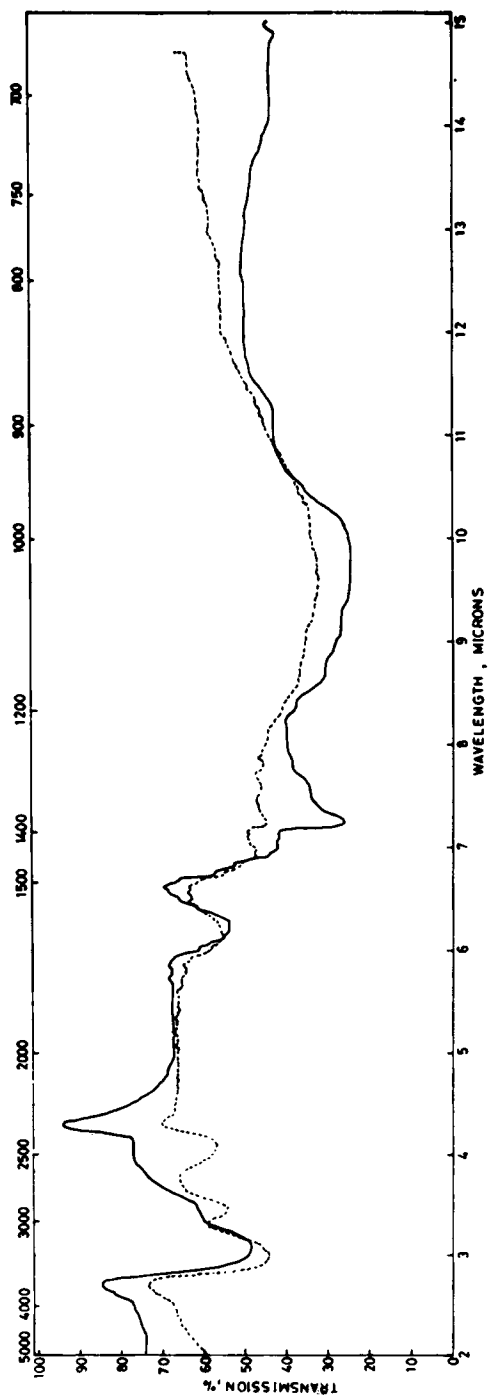Fig. 4. Infrared spectrum of deuterated cotton fibers.

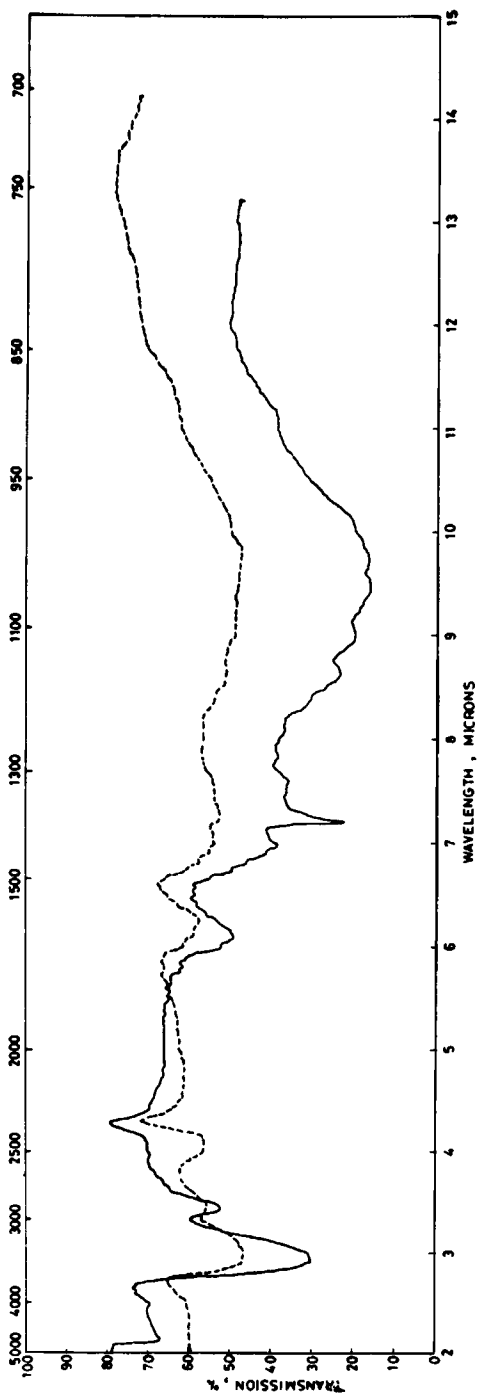Fig. 5. Infrared spectra of ramie fibers: (—) control; (- -) deuterated.

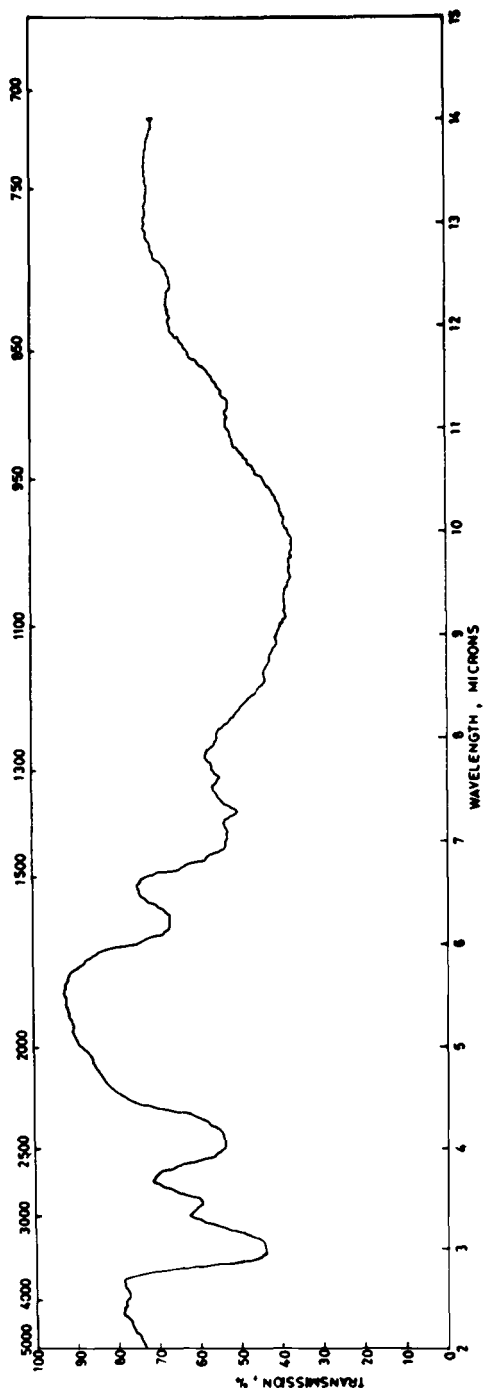Fig. 6. Infrared spectra of pulp fibers: (——) control; (- - -) deuterated.
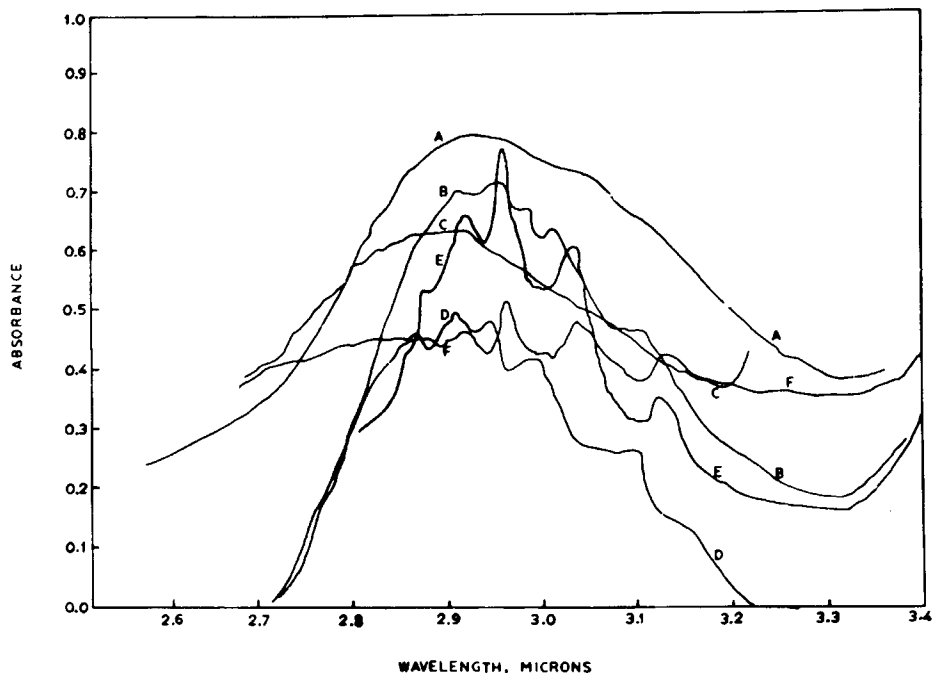
Fig. 7. Infrared spectra of deuterated viscose filaments.

Fig. 8. Infrared spectra in the 3-$\mu$ region: (a) Cotton fibers, undeuterated; (b) cotton fibers, deuterated; (c) viscose filaments, undeuterated; (d) viscose filaments, deuterated; (e) ramie fibers, deuterated; (f) pulp fibers, deuterated.

screws exactly similar to the original ones except that they were hollow throughout, with a groove on the top to hold the NaCl plate. The arm of the modified screw was shorter than the original solid screw. The whole assembly was made airtight by using rubber washers at appropriate places.

**Dry Box.** The dry box was of usual design and was made of cast iron, with a trap door on one side to insert or remove the samples and chemicals, a gas inlet valve, and an arrangement for the application of vacuum on the other side. It was possible to carry out operations inside the dry box in a dry atmosphere created and maintained over sufficiently long periods by the flow of nitrogen gas passing through a drying trap assembly consisting of a sulfuric acid column followed by two towers containing fused calcium chloride (Fig. 3).

**Spectrophotometers.** A Perkin–Elmer 21 double-beam spectrophotometer was used for recording infrared spectra in the region of 2–12$\mu$. With a view to increasing the dispersion and resolution of the peaks, spectra were recorded on a Beckman DK-2 spectrophotometer in the 3-$\mu$ region using appropriate stray light filters.

## Methods

Cellulosic fibers were cut to a very fine state of division avoiding any serious changes in the supermolecular structure of the fibers, and were dried over $P_2O_5$ for 24 hr. Exactly 3 mg of the dried fibers was taken in a clean minibeaker. Exactly 297 mg dry KBr was thoroughly ground in a mortar which was then inserted in the dry box. A bottle containing heavy water ($D_2O$) and all the com-

ponents of the modified minipress were also placed inside the dry box. The trapdoor was shut and a flow of dried nitrogen gas started. After ensuring the creation of moisture-free atmosphere inside the dry box, liquid $D_2O$ was added to the cellulosic fibers and allowed to dry. About five to six deuteration-drying cycles followed. Finally, the dried deuterated fibers were added to the previously weighed KBr powder, mixed well, and ground thoroughly.

One of the two stainless steel screws of the minipress was fitted in position, and a small portion of the above mixture was poured into it. The remaining screw was then screwed up and a pellet pressed by adjusting the pressure on the screws at both ends. They were then unscrewed, removed, and the modified set of hollow screws fitted with an airtight assembly containing NaCl plates was introduced into the minipress. This assembly was then removed from the dry box and mounted directly on the infrared spectrophotometer or Beckman DK-2 spectrophotometer for scanning the spectra.

## RESULTS AND DISCUSSION

Infared spectra of deuterated cotton, ramie, pulp, and viscose in fiber form obtained by the technique described in this paper are shown in Figures 4–7. A prominent OD peak is seen at 4.1 $\mu$, and the general quality of the spectra is quite good.

To obtain a better resolution of the OH peak in the 3-$\mu$ region, spectra of the deuterated cellulosic fiber were recorded on the Beckman DK-2 spectrophotometer from 2.6 to 3.4 $\mu$. The four spectra are given in Figure 8. It may be seen from these results that four well-resolved peaks are obtained for the H-bonded regions in cotton, ramie, pulp fibers, and viscose filaments. The resolution of the four peaks in the 3-$\mu$ region for any deuterated cellulosic fibers is better than that obtained previously,[21–23] possibly because of the new infrared-deuteration technique employed in the present investigation which allowed us to study the fibers directly in a moisture-free atmosphere.

The frequencies of the four main bands in case of cotton, ramie, and wood pulp (cellulose I structure) are 3230, 3298, 3350, and 3400 $cm^{-1}$. For viscose filaments (cellulose II structure), frequencies of the four absorption bands observed are 3230, 3350, 3445, and 3493 $cm^{-1}$, which correspond well to those observed by Mann and Marrinan[21] using regenerated cellulose in film form.

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