FURTHER SPECTROSCOPIC INVESTIGATIONS OF SAMPLES OF THE SHROUD OF TURIN

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Introduction

The June 15, 1980, issue of *Applied Optics* reported a series of Spectroscopic observations carried out by STURP (Shroud of Turin Research Project) directly on the Shroud of Turin at its repository site in Turin:[1-4] Additional studies[5-11] and reviews[12,13] supported the conclusions of these initial reports that the images on this cloth are not paintings. In particular, the body images were identified as an oxidation product of the cellulose of the linen cloth, and the blood images were shown to be consistent with blood-derived material, mainly exudates from clotted wounds. However, an opposing view held that these were painted images.[14-17] The body images were ascribed to iron oxide held to the cloth by a gelatin binder and the blood composed of the same "paint" with the addition of cinnabar (HgS) and traces of calcite ($CaCO_3$) to the paint.

A radiocarbon dating of samples taken from the Shroud reported a mid-14th century date,[18] seemingly settling the authenticity issue.[13] However, it is now argued that since it was not old enough to be authentic, it must be a painting. Unfortunately, a detailed protocol[19] for sampling the cloth to assure both precision and accuracy recommended by a convened meeting of consultants was not followed. Only a single sample was taken from a rewoven edge in a water-stained area a few inches from one of the burn marks incurred in the historically recorded 1532 fire. This location was near the bottom of the frontal body image on the edge where a large section of cloth is missing below the seamed so-called side strip. No historic record exists accounting for this missing material and how or when this damage occurred. The nature and / or extent of the repairs undertaken here are also unknown. Therefore, the possibility exists that this selvage edge might be linen not original to the Shroud.

The selection of this single suspicious sample site is a sufficient reason to doubt the accuracy of the radiodate. This spectroscopic investigation was therefore undertaken to determine whether any evidence can be obtained to support such doubts.

Samples

At the time of the on-site STURP investigation of the Shroud, sticky tape samples were collected from designated areas of interest on the cloth for offsite

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chemical studies.[11] There are problems in utilizing these tapes as sample sources.[11] The cloth has been folded and / or rolled many times. This mechanical action has transported loose materials from one area of the cloth to another. In particular, the blood images, being composed of material that is clearly attached to the cloth, have begun to fracture with time and have migrated everywhere.[11] Further, many artist's copies of the Shroud have been "sanctified" by being pressed to the original thereby transferring artistic materials to the Shroud surface by contact.[20] These and much other confusing adventitious material have been observed by both sets of opposing investigators, though differing interpretations have been attached to their presence.[11-13, 14-17] Dealing with this problem, including extracting samples from these tapes and distinguishing between different sample types by their typical characteristics under reflection, fluorescence, polarization, and phase contrast microscopy has been detailed previously.[11]

Since a preliminary study indicated that reliable spectra could not be directly obtained from specimens on the sticky tapes, fiber samples were removed from the tapes and their identity as to type verified by the methods previously described in the chemical study.[11] Five fibers representing non-image areas in the vicinity of the feet, the waist, and the head of the frontal image were collected from their designated sample tapes. Similarly, four waterstain fibers from the head and knee areas, four scorch fibers from the knee area, two serum coated fibers from the edge of the lance wound, two image fibers from the finger area, two backing cloth fibers from the area adjacent to the radiodate sample area, and two blood globs (particles unattached to fibers) from the lance wound area were also isolated for investigation.

The administrators of the radiodate sampling, L. Gonella and G. Riggi, kindly provided three threads from the radiocarbon sample for our study. Two were warp threads from the outer and inner edges of the trimmed sample and the third was a -weft thread from the middle of this sample. Five fibers were taken from each of these samples for comparison with those collected from the sticky tapes. Interestingly, under microscopic investigation, these samples resembled exaggerated versions of the waterstained specimens. They were non-fluorescent, unevenly colored from dark yellow to splotchy brown, roughly surfaced (even showing patchy encrustations in spots) and showed a very strong and variably multicolored birefringence pattern. Considerable microdebris was also evident.

Two blood simulacra were also prepared as controls. Finely ground iron oxide (Fisher Chemical) and cinnabar with a small amount of calcite (WCSU Geology department collection) were suspended in a 5 percent gelatin solution to provide a sample of "mineral" blood.[17] A traumatic clot exudates simulacrum was approximated[11, 13] by mixing three drops of whole blood (finger stick) with three drops of a bilirubin/ human albumin diagnostic standard (Sigma Chemical). A sample of each of these was applied to a salt plate (for FTIR analysis) and also to the outside face of a 1 cm silica cuvet (for UV-VIS analysis) and allowed to dry as films. Dried whole blood (finger stick), bilirubin (Sigma), and human hemoglobin (Sigma) samples were also employed as controls.

Methods

FTIR: These spectra were acquired on a Bomen MB120 Interferometer equipped with an optical side port option. A global source (operating temp. 1300°K) was employed with the system alignment optimized to give maximum energy in transmission mode. Interferometer modulation is accomplished via the standard Bomen "wishbone" modulator, using a corner cube stray light rejection interferometer and a KBr beam splitter. The side port parallel beam exit sampling option of this instrument was coupled to a Spectratech IR-PLAN microanalysis system equipped with a narrow band liquid nitrogen cooled detector. The interferometer is controlled by an 80386 PC with an 80387 math coprocessor and 220 MB hard drive. A DSP data acquisition card provides real time Fourier Transform data for spectral collection and alignment procedures for monitoring single beam spectra rather than voltage. Galactic Industries Lab Calc version 2.1 software was used for collecting all data, performing alignment procedures, carrying out spectral arithmetic operations, and plotting. Transmission spectra were collected from 4011.6 to 739.8 cm^{-1} at 8 cm^{-1} resolution, 64 scans, and using triangular apodized double-sided interferogram data with zero filling. The redundant aperturing provision of this system was not employed. Control experiments established that keeping the source aperture constant and wider than the objective aperture gave more consistent replicate spectra with less low frequency baseline diffraction distortions from aperture edges.

The IR-Plan is equipped with a Reflacromat 10X condenser, 15X objective Cassegrain optics, and an Olympus DPLAN 10X objective for use only in the visible viewing mode. The Cassegrain optics was adjustable to compensate for the refractive index of the two 2 mm thick NaCl windows used throughout the study. The windows were hand polished to suppress interference fringes in the spectra. Prior to sample analysis a protocol was established to reproducibly align the condenser optics to provide the brightest and most uniform radiation at the plane of the sample location and thereafter all adjustments were made only with the objective optics.

The mounted specimen was first located in the viewing mode and then the objective was adjusted to produce the best optical image of the specimen. This focus was employed in taking the IR spectra as control experiments showed that only this focus could provide reproducible spectra of a sample without distorting the relative intensities of the high vs. low frequency patterns of the spectrum. The objective knife-edge aperture system was then adjusted so that the specimen completely filled the aperture and then the single beam spectrum was taken under a gentle nitrogen purge. Without modifying any adjustments, the stage was then moved to a clear area of the mounting windows and a background spectrum was collected. From these stored single-beam spectra, the absorbance spectrum of the specimen was calculated and plotted on an HP DeskJet 500C plotter.

UV-VIS: A Perkin Elmer Lambda 3B UV / VIS Spectrophotometer coupled to a Perkin Elmer R100A recorder was used to collect the simulated blood control

absorbance spectra from 400 to 650 nm. The tungsten visible source and a scan rate of 60 nm/min were employed.

SEM: An AMRAY 1645 Scanning Electron Microscope equipped with a LaB6 electron source was used for this analysis. This instrument is equipped with a Noran Voyager energy dispersive spectroscopy system utilizing a Norvar window on a SiLi detector, which has 10 mm^2 spatial resolution and 133 eV spectral resolution. Instrument conditions were held constant at 20 KV, spot size 3 or 4, aperture size 200 mm, and a working distance of 24 mm for the fibers. Magnification was mostly between 1000 and 3000X, with a partial field collimation of the beam to restrict it to within the bounds of the fiber samples or the individual particles seen within them. Samples were prepared by applying the specimens onto double sticky tape placed on a sample stub that was then positioned within the instrument sample chamber.

Results

FTIR: Typical spectral absorption patterns for each fiber type and the blood samples are displayed in Figures 1 through 11 and clearly show distinctive differences indicating differences in their chemical makeup. It should be noted that there is more variation in the patterns of the radiocarbon samples representing an area of a few square centimeters than in those of the non-image samples taken from areas a whole body-image length apart. The backing cloth pattern is readily distinguishable from the other patterns. Using the software to identify specific peak frequencies further demonstrates differences in chemical composition.

Comparison to the tabulated data on carbonyl frequencies[21] is most revealing. The position (given in cm^{-1}) and relative intensity of the peaks in the carboxylic acid salt region (1650-1540) and conjugated ketone region (1680-1640) show an apparent progressive oxidation-type pattern with the non-image (1593, 1643) the weakest, then water stained (broad 1697, weak 1640), then image (strong 1694, 1645 shoulder), then scorch (1591, broad 1645), and finally the radiocarbon pattern (1590, 1643, both strong). This can be compared with the progressive thermal oxidation pattern seen in the scorch fibers displayed in Figure 6. Note, there is no evidence of the typical amide pattern (1695-1630) associated with proteins on any of these foregoing fibers; specifically, not on the image fibers, nor on the radiocarbon fibers. However, this amide pattern is clearly seen in the serum fiber samples (complex pattern 1694-1566) and in the blood samples. This is in complete agreement with the previously published chemical investigation" and does not support the painting hypothesis. The peak patterns and relative intensity patterns in other regions of the spectra are also consistent with the conclusion that the spectral patterns of these fibers are all distinguishably different from one another. Note this is specifically true for the radiocarbon fibers and the non-image fibers from the bulk of the cloth, thereby demonstrating that the area selected for the radiocarbon sampling is atypical and is not clearly representative of the rest of the Shroud.

The spectral pattern of the blood globs from the sample tape is in good agreement with the spectral features of the various blood controls. Some of the more

distinctive features of the bilirubin pattern are even weakly evidenced in the scrum fiber spectra (note, these fibers are yellow colored) and was further confirmed by overlaying control spectra. Unfortunately, the only really distinctive features in the mineral simulated blood control, other than the protein peaks, are provided by the calcite present, as the iron oxide and mercuric sulfide spectra are weak and broad featured. However, these distinctive calcite peaks are clearly not evidenced in the blood globs. Therefore, the conclusion that the blood images are derived from blood clot exudates and are not mineral pigments is further confirmed.[5, 11,13]

UV-VIS: The near ultraviolet-visible spectra of the two simulated blood controls are displayed in Figure 12. The peak position pattern and relative overall absorbance ratio of the blue to red region of the spectrum of traumatic clot exudates sample is in excellent agreement with the previously reported spectra of Shroud blood specimens and also the spectra taken from the examination of the whole cloth blood images.[25] The spectrum of the simulated mineral blood showing only two broad weak peaks at 470 and 514 nm is in complete disagreement with these previously reported spectra.

SEM: The typical weight percent elemental composition patterns of the various Shroud fiber types are given in Table 1. Again, it should be noted that a great deal of variability was evidenced in the radiocarbon samples. Some of the patchy encrustations were so thick as to mask the underlying carbon of fibers whose continuity were clearly obvious in the microscope images. As this is a surface-analysis technique, this is not unexpected. Microdebris identifiable as particles of gold, iron oxide, and mercuric sulfide were also seen in these samples. The trend in weight %C compared to the opposite trend in "mineral" content of the radiocarbon samples (even compared to the waterstain fibers) clearly indicates that the radiocarbon sampling area is a strongly contaminated "waterstain" area.

Table 1

TYPICAL WEIGHT % ELEMENT COMPOSITION PATTERN
OF SHROUD FIBER TYPES

Sample	C	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe	Cu	Au	Hg	Ti	Mn
Warp	21	49	8.3	0.9	2.0	1.6	0.4	0.6	3.1	4.3	8.5	0.6	0.1	0.0	0.0	0.0	0.3
Warp	33	43	6.7	0.1	1.1	1.4	0.0	0.4	2.5	3.4	6.1	1.4	0.0	0.5	0.4	0.0	0.0
Weft	22	48	6.6	1.0	0.2	1.6	0.2	0.6	1.9	4.3	12	0.5	0.3	0.9	0.3	0.1	0.0
Waterstain	66	27	0.6	0.0	0.0	0.1	0.0	0.0	0.5	0.1	0.1	5.5	0.1	0.0	0.0	0.0	0.1
Non-image	93	3.2	1.7	0.0	0.1	0.1	0.0	0.0	1.5	0.1	0.4	0.4	0.1	0.0	0.0	0.0	0.0

Discussion

There is insufficient evidence to conclusively demonstrate the presence of any adventitious linen in the radiocarbon sample area. However, there is a clearly evident chemical compositional difference between this sample area and the non-image areas of the cloth. In fact, the FTIR data for the radiocarbon sample, in a sense confirming its inappropriate physical location, shows physical characteristics of both the waterstain and scorch regions of the cloth. To what extent this affects the observed date is not at all obvious. Nevertheless, the accuracy of the reported date is justifiably suspect. Further, comparison of the dorsal head wounds on the Shroud with a similar pattern of wounds on the 7th century Cloth of Oviedo confirms the inaccuracy of the reported radiocarbon date.[22]

These new findings support previous conclusions that the body image chromophore is an oxidation product of the cellulose itself and that the blood images are derived from clotted blood wounds.[1-13] They do not support the painting hypothesis.[14-12] The microdetection of artist's materials in the debris might seem to support the painting hypothesis. However, as neither of the X-ray examinations of the whole cloth produced any evidence for the presence of mercury in the blood images at the macroscopic level,[8, 9] it seems more reasonable to attribute the presence of artist's materials to the historically recorded practice of sanctifying copies of this image by pressing them to the original.[20]

The Shroud of Turin is a complex object, defying oversimplified explanations of the mechanism by which it was produced. As no acceptable laboratory test exists that can give us the identity of the man whose image is portrayed, science can never authenticate the Shroud. However, future research could reveal to us the mechanism of image productions, providing a basis for a properly planned conservation program.

Acknowledgements

We wish to express our indebtedness to Melanie Behrens for technical assistance and to Lucas Adler of LA Engineering Computer Services for aid in preparing the figures.

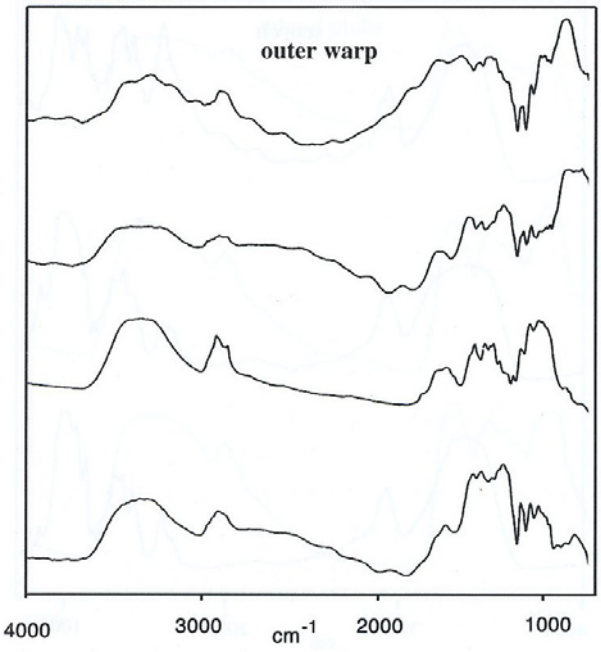

Fig. 1. Typical FTIR absorbance patterns of radiocarbon sample outer warp fibers.

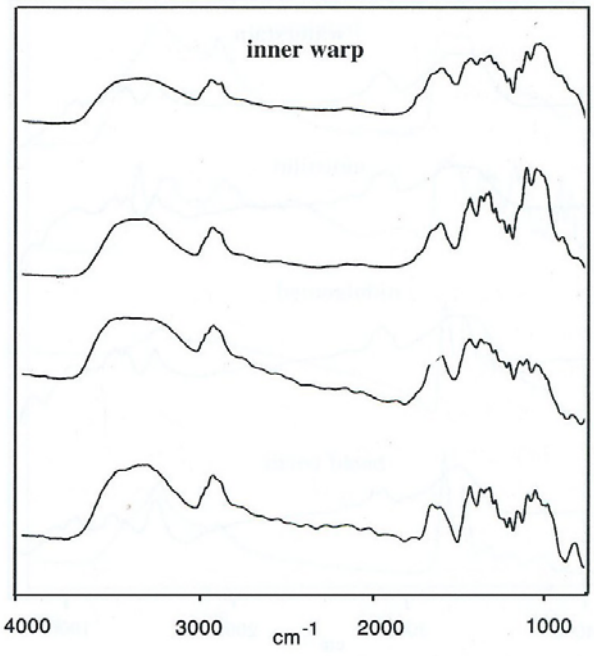

Fig. 2. Typical FTIR absorbance patterns of radiocarbon sample inner warp fibers

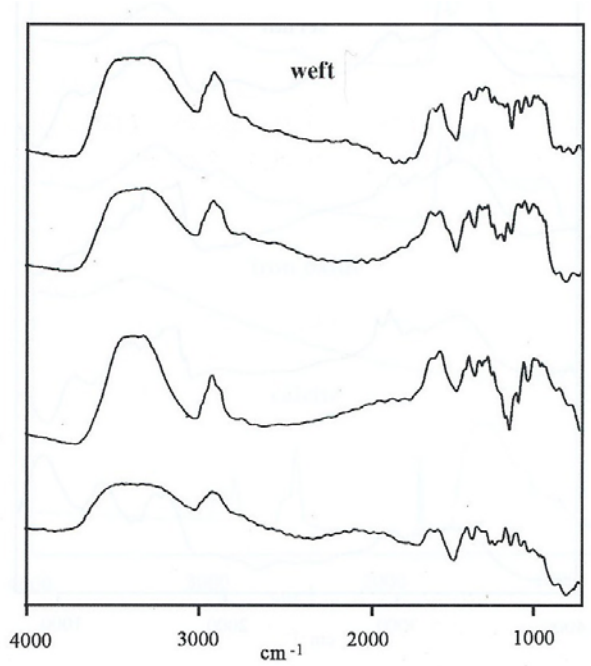

Fig. 3. Typical FTIR absorbance patterns of radiocarbon sample weft fibers.

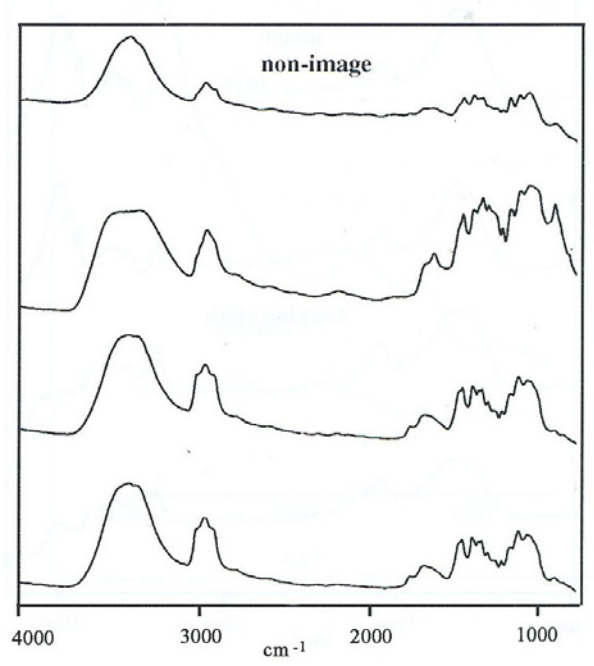

Fig. 4. Typical FTIR absorbance patterns of non-image fibers

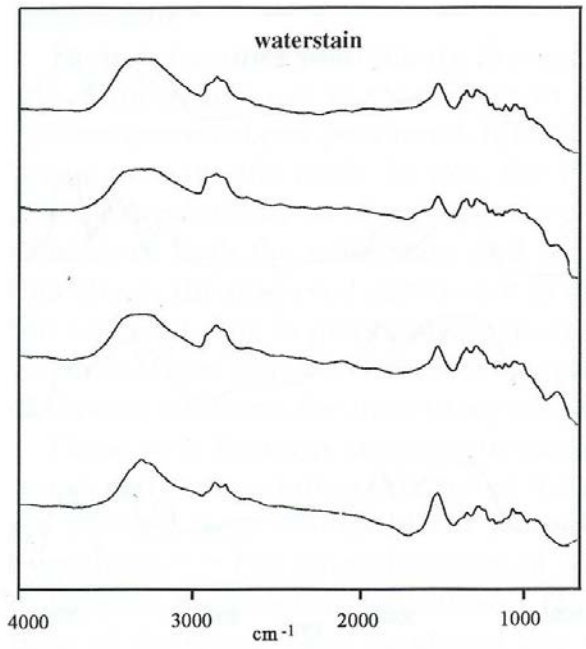

Fig. 5. Typical FTIR absorbance patterns of water stain fibers.

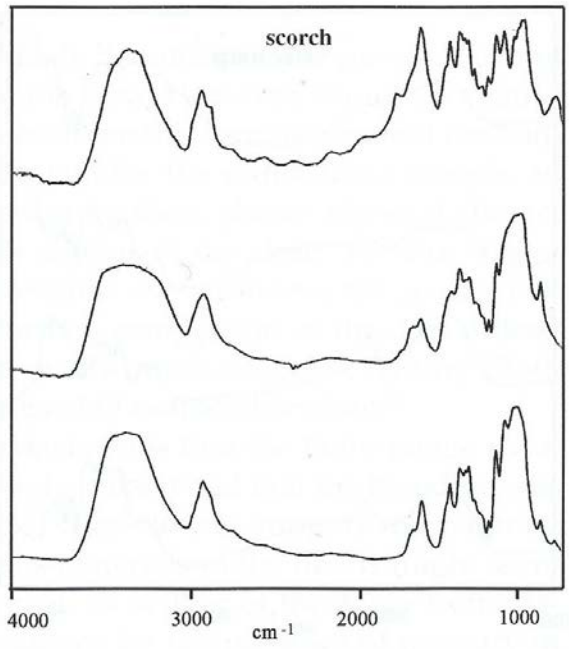

Fig. 6. Typical FTIR absorbance patterns of scorch fibers

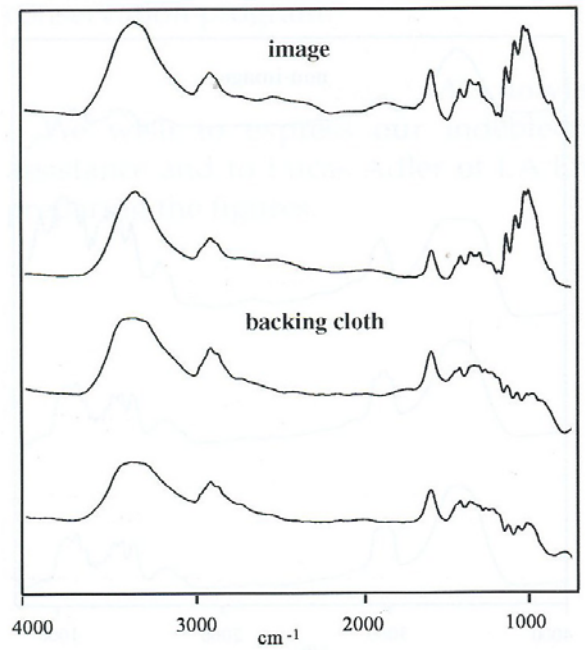

Fig. 7. Typical FTIR absorbance patterns of image and backing cloth .

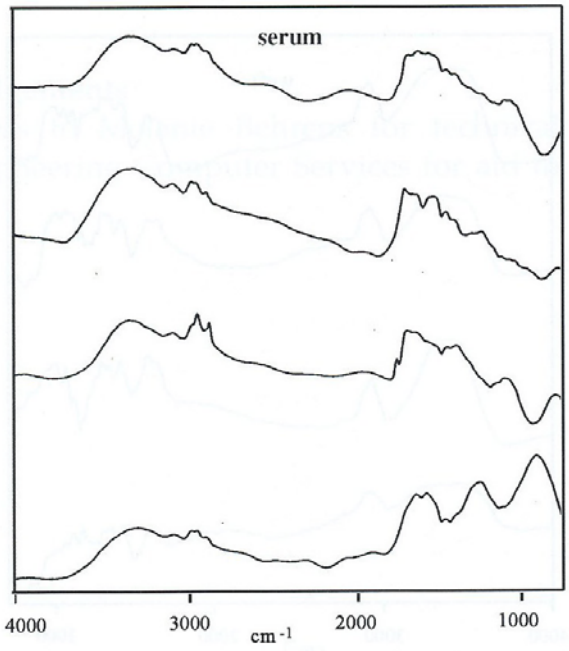

Fig. 8. Typical FTIR absorbance patterns of serum fibers

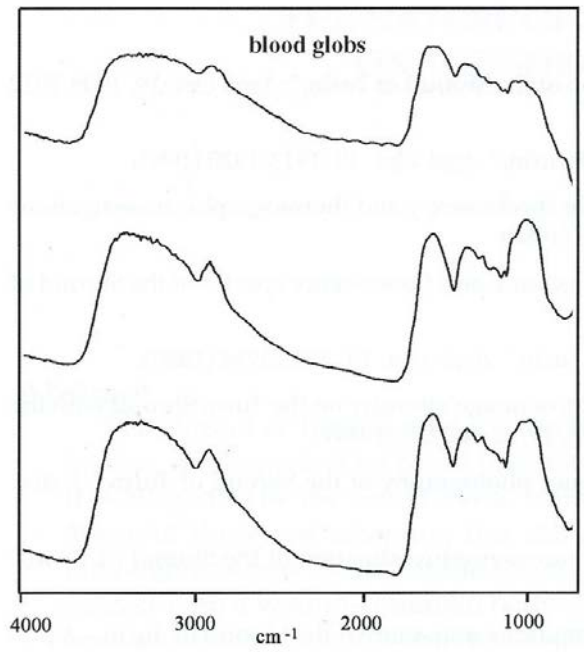

Fig. 9. Typical FTIR absorbance patterns of blood globs.

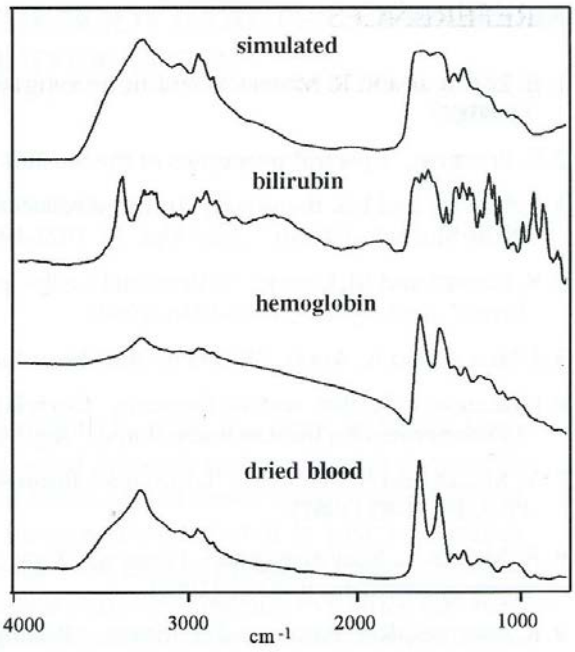

Fig. 10. Typical FTIR absorbance patterns of simulated exudate blood clot controls.

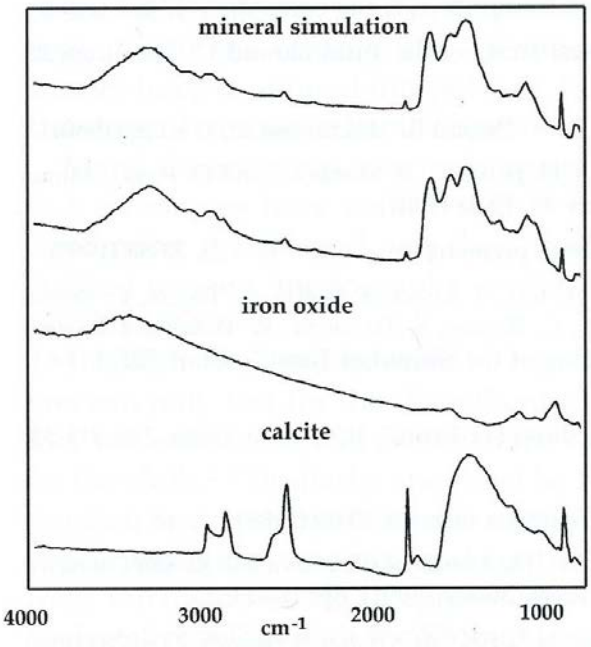

Fig. 11. Typical FTIR absorbance patterns of simulated mineral blood controls.

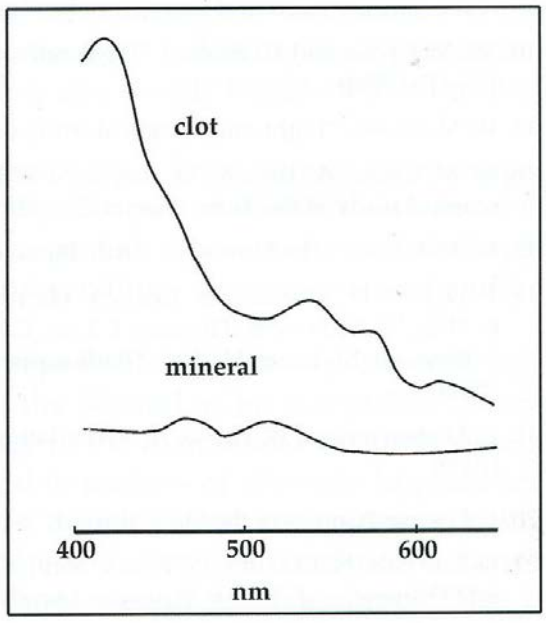

Fig. 12. Comparison of UV-VIS absorbance spectra of simulated exudate blood clot and mineral blood controls

REFERENCES

1. E. JUMPER and R. MOTTERN, "Scientific investigation of the Shroud of Turin," *Appl. Opt.* 19, 1909-1912 (1980).
2. S. PELLICORI, "Spectral properties of the Shroud of Turin," *Appl. Opt.* 19, 1913-1920 (1980).
3. J. ACCETTA and J. S. BAUMGART, "Infrared reflectance spectroscopy and thermographic investigations of the Shroud of Turin," *Appl. Opt.* 19, 1921-1929 (1980).
4. R. GILBERT and M. GILBERT, "Ultraviolet-visible reflectance and fluorescence spectra of the Shroud of Turin," *Appl. Opt.* 19, 1930-1936 (1980).
5. J. HELLER and A. ADLER, "Blood on the Shroud of Turin," *Appl. Opt.* 19, 2742-2744 (1980).
6. J. JACKSON, E. JUMPER, and W. ERCOLINE, "Correlation of image intensity on the Turin Shroud with the 3-D structure of a human body shape," *Appl. Opt.* 19, 2244-2270 (1984).
7. V. MILLER and S. PELLICORI, "Ultraviolet fluorescence photography of the Shroud of Turin," *J. Biol. Phot.* 49, 71-85 (1981).
8. R. MORRIS, L. SCHWALBE, and J. LONDON, "X-ray fluorescence investigation of the Shroud of Turin," *X-ray Spectrometry* 9, 40-47 (1980).
9. R. MOTTERN, R. LONDON, and R. MORRIS, "Radiographic examination of the Shroud of Turin — a preliminary report," *Materials Eval.* 38, 39-44 (1980).
10. S. PELLICORI and M. EVANS, "The Shroud of Turin through the microscope," *Archaeology* 34, 34-43 (1981).
11. J. HELLER and A. ADLER, "A chemical investigation of the Shroud of Turin," *Can. Soc. Forens. Sci. J.* 14, 81-103 (1981).
12. L. SCHWALBE and R. ROGERS, "Physics and chemistry of the Shroud of Turin," *Anal. Chim. Acta* 135, 3-49 (1982).
13. E. JUMPER, A. ADLER, J. JACKSON, S. PELLICORI, J. HELLER, and J. DRUZIC, "A comprehensive examination of the various stains and images on the Shroud of Turin," *ACS Adv. in Chem.* 205, 447-476 (1984).
14. W. McCRONE and C. SKIRIUS, "Light microscopical study of the Turin Shroud I," *Microscope* 28, 105-113 (1980)
15. W. McCRONE, "Light microscopical study of the Turin Shroud II," *Microscope* 28, 115-128 (1980).
16. W. McCRONE, A. TEETSOV, M. ANDERSEN, R. HINCH, H. HUMECKI, B. MAJEWSKI, and D. PIPER, "Microscopical study of the Turin Shroud III," *Microscope* 29, 19-38 (1981).
17. W. McCRONE, "The Shroud of Turin: Blood or artist's pigment," *Acc. Chem. Res.* 23, 77-83 (1990).
18. P. DAMON, D. DONAHUE, B. GORE, A, HATHEWAY, A. JULL, T. LINICK, P. SERCEL, L. TOOLIN, C. BRONK, E. HALL, R. HEDGES, R. HOUSLEY, I. LAW, C. PERRY, G. BONANI, S. TRUMBORE, W. WOELFLI, J. AMBERS, S. BOWMAN, M. LEESE, M. TITE, "Radiocarbon dating of the Shroud of Turin," *Nature* 337, 611-615 (1989).
19. G. HARBOTTLE and W. HEINO, "Carbon dating the Shroud of Turin," *ACS Adv. in Chem.* 220, 313-320 (1989).
20. L. FOSSATI, "Copies of the Holy Shroud," *Shroud Spectrum Inter*. 13, 23-39 (1984).
21. D. LIN-VIEN, N. COLTHUP, W. FATELY, and J. GRASSELLI, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, (Academic Press, Boston, 1991), pp. 117-146.
22. A. ADLER, "Updating recent studies on the Shroud of Turin," *ACS Symp. Series* 625, 223-228 (1996).