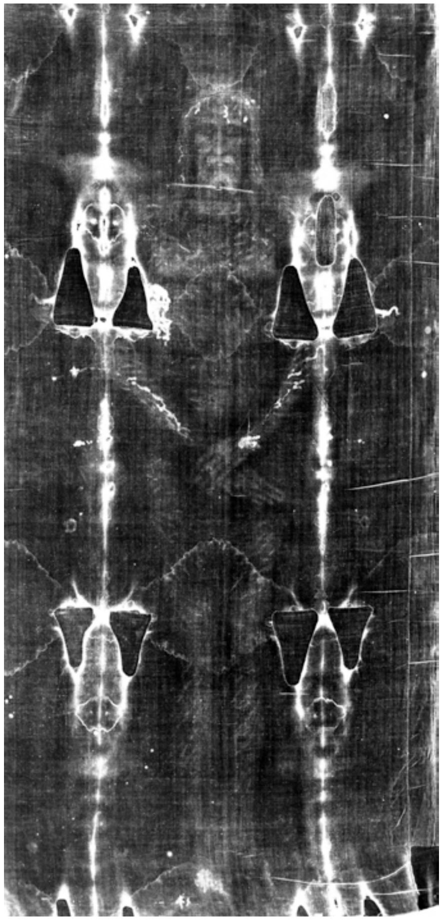
Spectroscopic Analyses of Fibers from the Shroud of Turin - What Do They Mean? Jon R. Schoonover



The Shroud of Turin is a centuries old linen cloth that appears to show the image of a crucified man, which many believe to be Jesus of Nazareth. For years the debate has raged as to whether this is the cloth that wrapped Jesus' crucified body or a clever medieval forgery. In 1988 carbon dating studies demonstrated the Shroud to be medieval (1260-1390). However, a theory suggesting that samples were taken from an area of the Shroud that was damaged then repaired and rewoven in medieval times was forwarded. A chemist from Los Alamos, Ray Rogers, verified the carbon dating was valid, but that the sample appeared to not be representative of the entire Shroud. Bob Villarreal, another Los Alamos chemist, was asked to carry on Ray Rogers' work upon his death in 2005. We have studied fibers from the Shroud with several analysis techniques and will discuss our findings and interpretations of the data.

Outline

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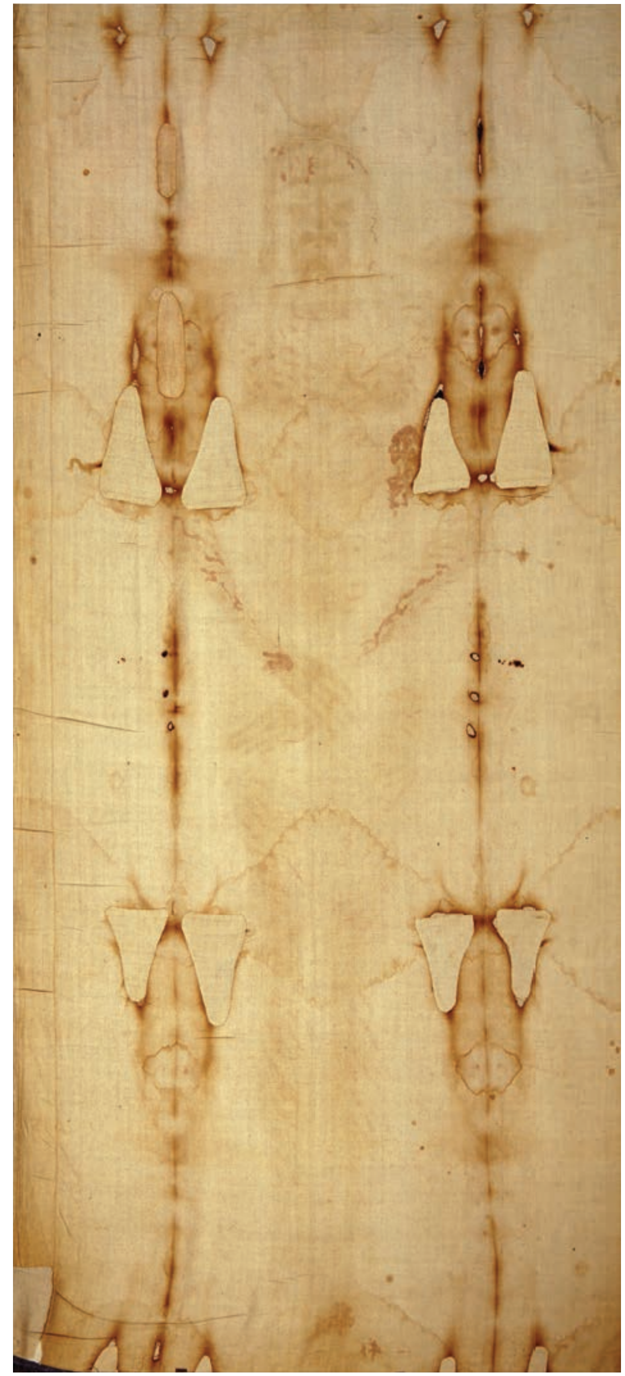
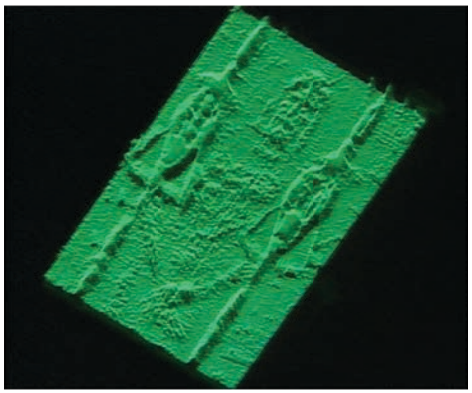
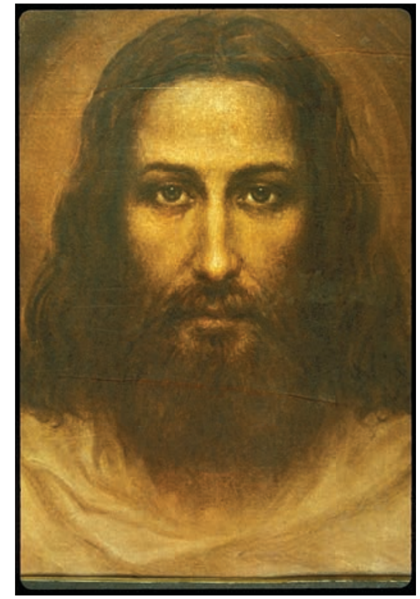
VI. Conclusions



History





I. The Shroud of Turin is a linen cloth bearing the image of a man who appears to have been physically traumatized in a manner consistent with crucifixion.

II. Negative image first observed on May 28, 1891 by Secondo Pia, while it was being exhibited in the Turin Cathedral.

III. The shroud is a subject of intense debate for some scientist, historians, and people of faith.

IV. Various test have been performed on the shroud and the debates continue. Radiocarbon dating in 1988 and published in *Nature* indicated that the shroud dated in the Middle Ages, about 1300 years after Jesus lived.

V. December 14, 2008, the Discovery Channel provides and updated version of the shroud controversy titled "*Unwrapping the Shroud: New Evidence*."

Shroud Description

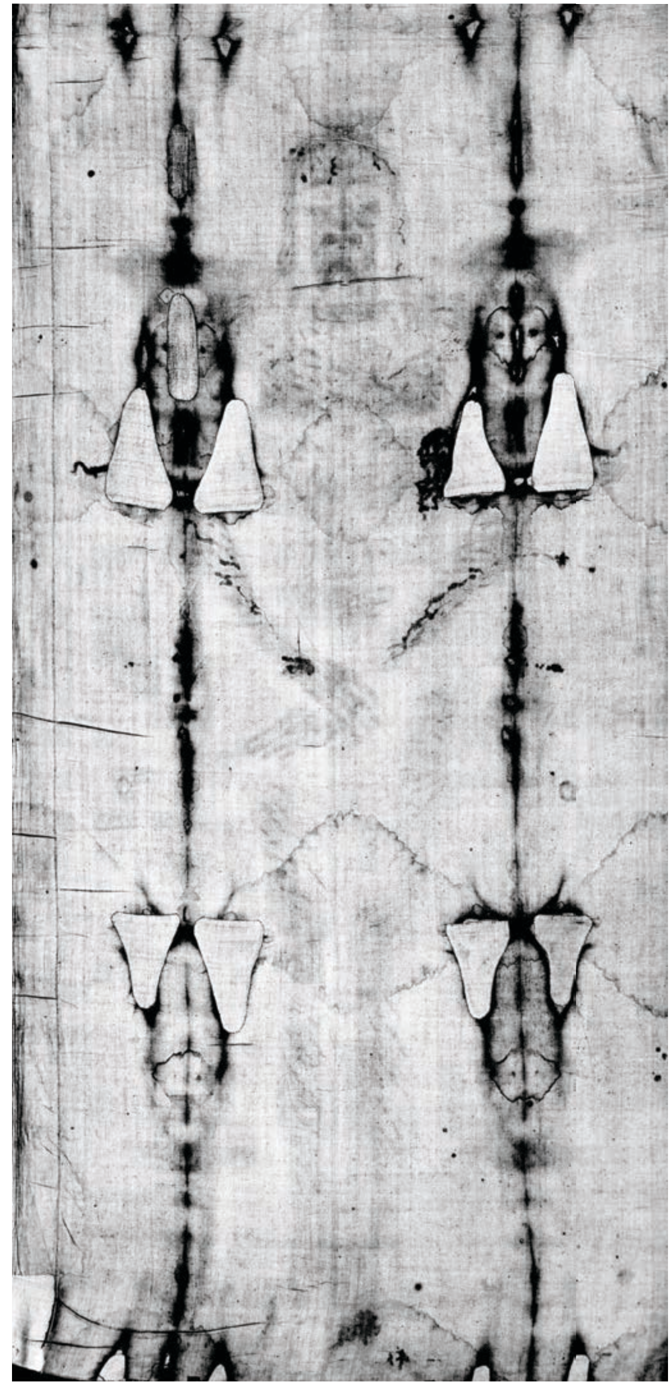
I. The shroud is rectangular , 14.3’ x 3.7’, made of woven cloth with flax fibrils.

II. Yellowish image of a front and back view of a naked man with his hands folded over his groin.

III. The man has a beard, moustache, and shoulder-length hair parted in the middle. He is muscular and tall, 5’9” to 6’2”.

IV. One wrist bears a large, round wound, maybe from a piercing. There is an upward gouge in the side penetrating the thoracic cavity. Small punctures are around the forehead and scalp with facial swelling. Wound indicative of a Roman flagrum on the legs. Streams of blood down both arms consistent with a crucifixion.

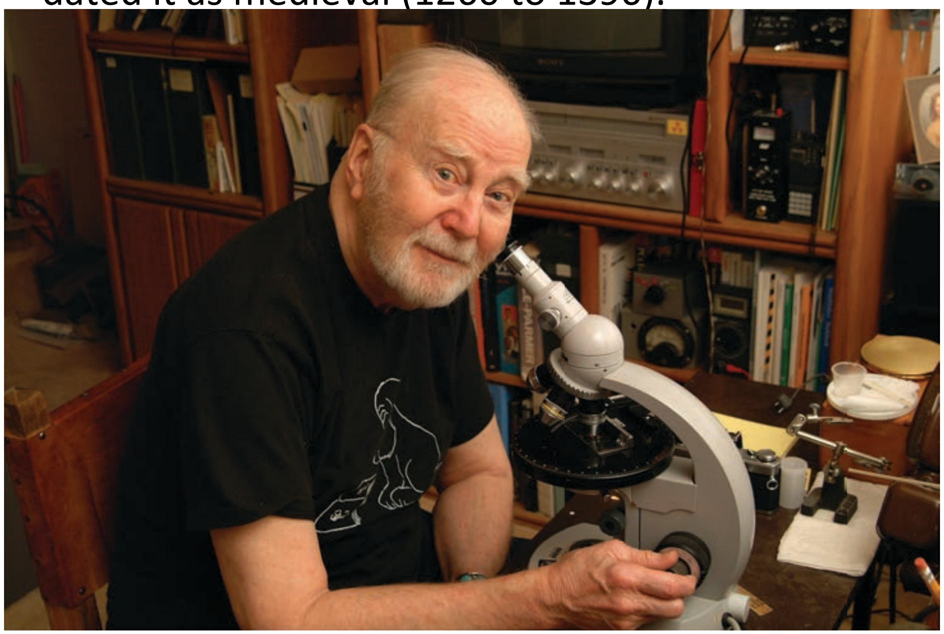
V. Other physical characteristics include water stains and burn holes and scorched areas from molten silver (1532). Small burn holes and creases.

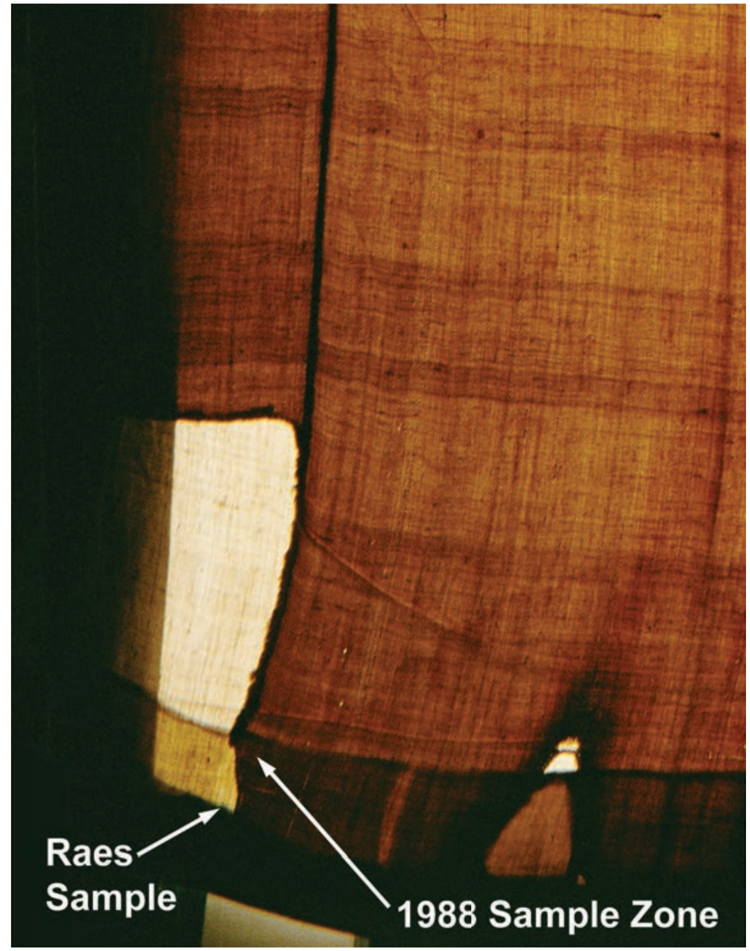


Carbon 14 Dating

I. In 1978, the Shroud of Turin Research Project (STURP), which consisted of 24 scientist, had five days to study the shroud. The team included Ray Rogers (LANL) and Barrie Schwortz.

II. In 1988, teams from Arizona, Oxford, and Zurich analyzed portions from a single strip of cloth taken from one corner of the shroud. They dated it as medieval (1260 to 1390).





Our Involvement

I. Two nonscientists called into question the 14C dating, claiming samples came from part of the shroud that was repaired in the 16^{th} century.

II. This got Ray Rogers really upset. He set out to prove this theory wrong, but found evidence that this area was cotton. He published his data in Thermochimica Acta. Ray Rogers died five weeks after his paper was published.

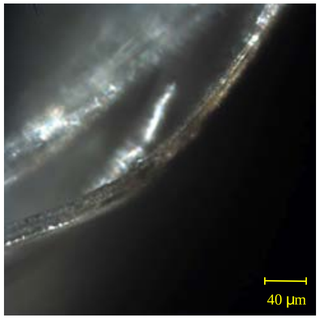
III. Bob Villarreal, another Los Alamos chemist, has carried on Ray's work.

IV. The ongoing question is 'were the dating samples taken from a repaired portion of the shroud.'

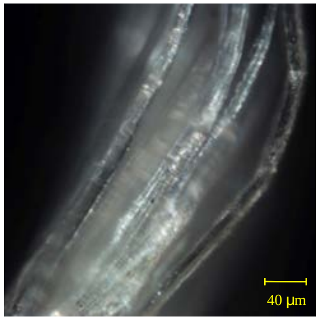
500x

long piece
white light

fuzzy
end



middle
of
fiber



Spectroscopic Methods

I. High Resolution Photo-microscopy (Olympus BX 51 optical microscope with and Optronics digital CCD camera) – Warren Steckle, LANL

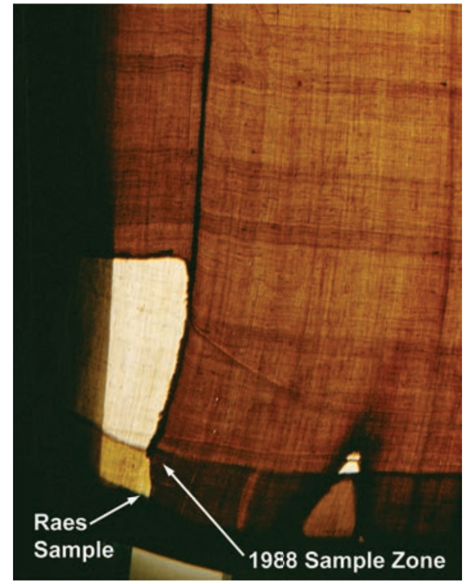
II. Radioisotope and Tube Excited Micro-spot Energy Dispersive X-ray Fluorescence Spectrometry (EDAX Eagle II micro x-ray fluorescence spectrometer, 20 kV, 400 mA, vacuum) – Brian Patterson and George Havrilla, LANL

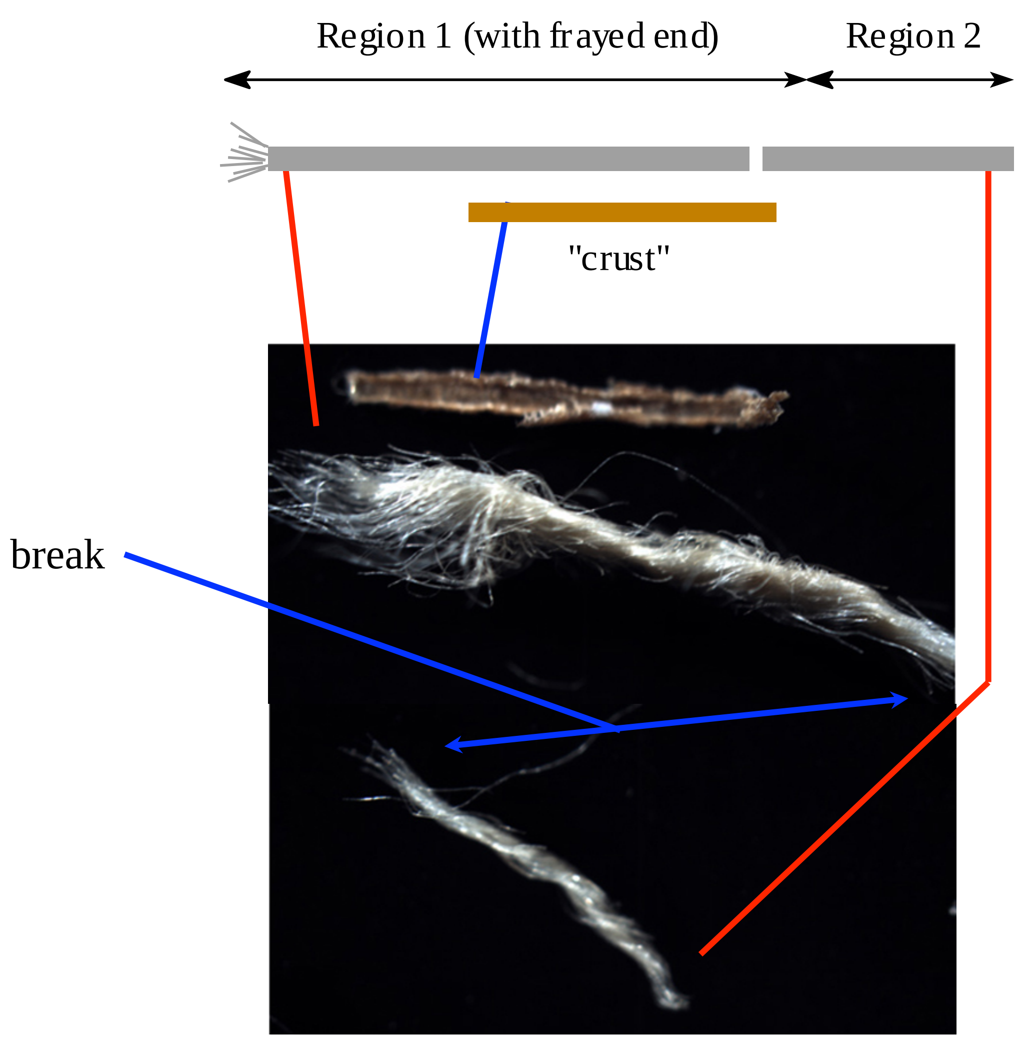
III. X-ray Photoelectron Spectroscopy (XPS) aka Electron Spectroscopy for Chemical Analyses (ESCA) – Roland Schulze, LANL

IV. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) with R-500 Reflecton by Kore Technology, LLC – Doug Farr, LANL

V. Fourier Transform Infrared Spectroscopy (FTIR) with reflectance/transmittance capability – Kevin Hubbard and Jon Schoonover, LANL

VI. Confocal Raman Spectroscopy – Jon Schoonover and Steve Doorn, LANL





XPS Analysis of Thread R1

I. X-ray Photoelectron Spectroscopy (XPS) also know as Electron Spectroscopy for Chemical Analysis (ESCA)

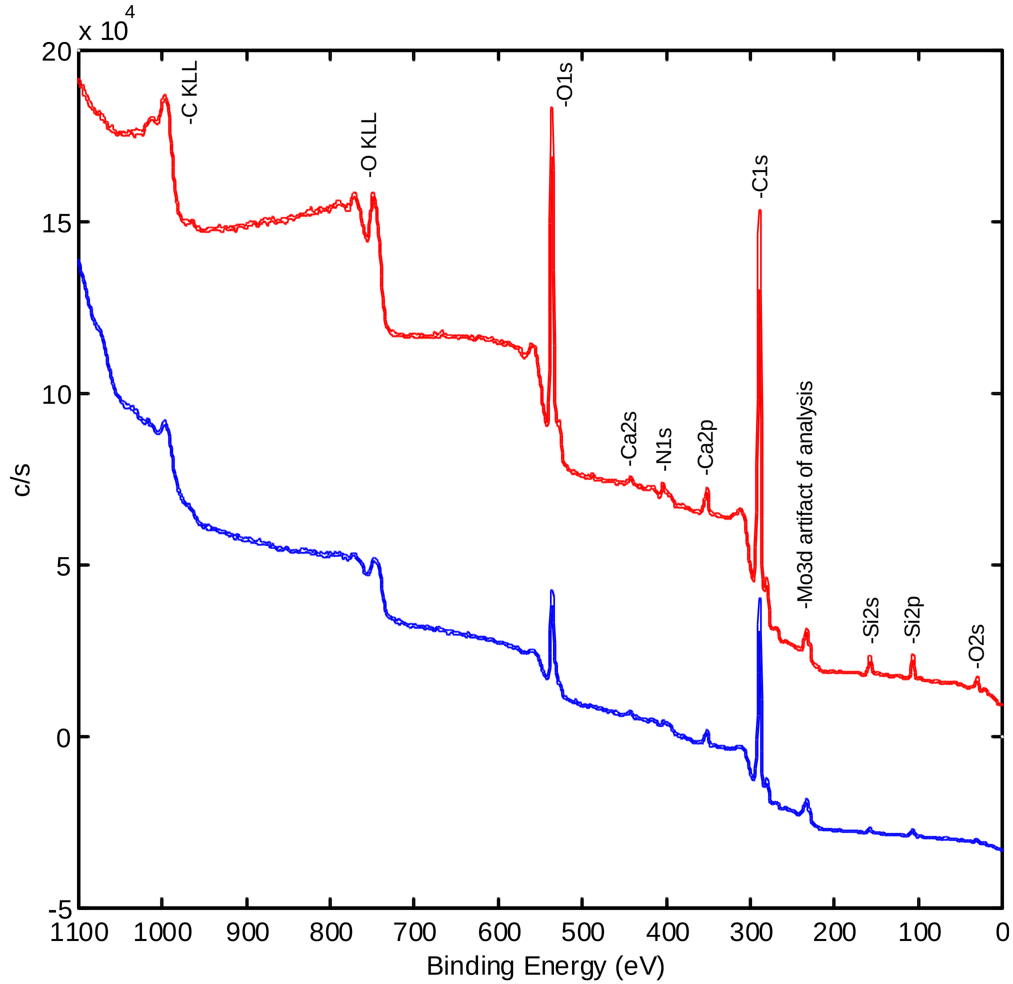
II. Excitation / process: soft x-ray photon (1253.6 eV), which is absorbed by an atom in the sample and results in an ejected photoelectron of characteristic elemental and chemical energies.

III. Analysis: the photoelectrons emitted from the sample are collected and energy analyzed. The intensities of various photoemission peaks from different elements are proportional to the concentration of that element in the sample surface.

IV. Chemical information: The measured binding energies (chemical shift) of photoemitted electrons yields information on chemical environment of the atom in the sample surface.

V. Thread is suspected to be from region of Shroud repair (cloth material transition) - examination of both ends of thread for chemical differences.

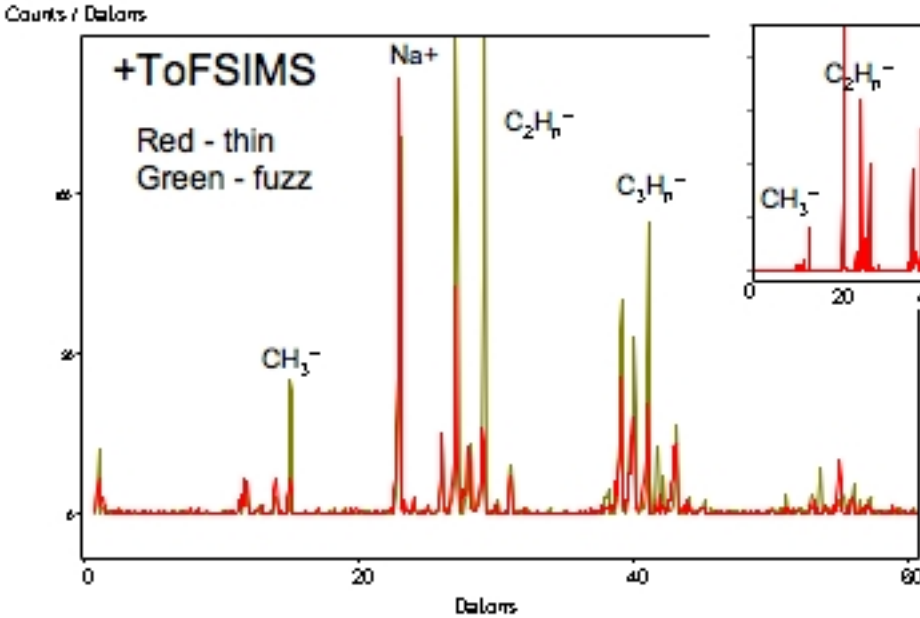
XPS Analysis of Thread R1

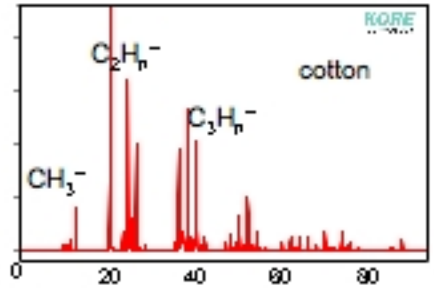


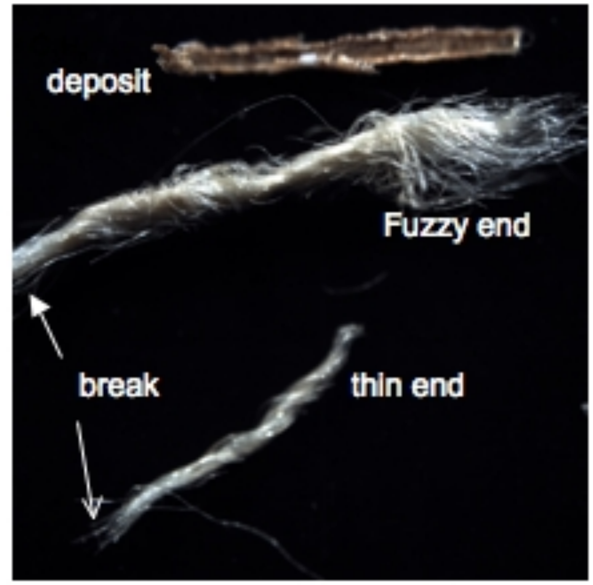
Atomic Concentration (atom%)

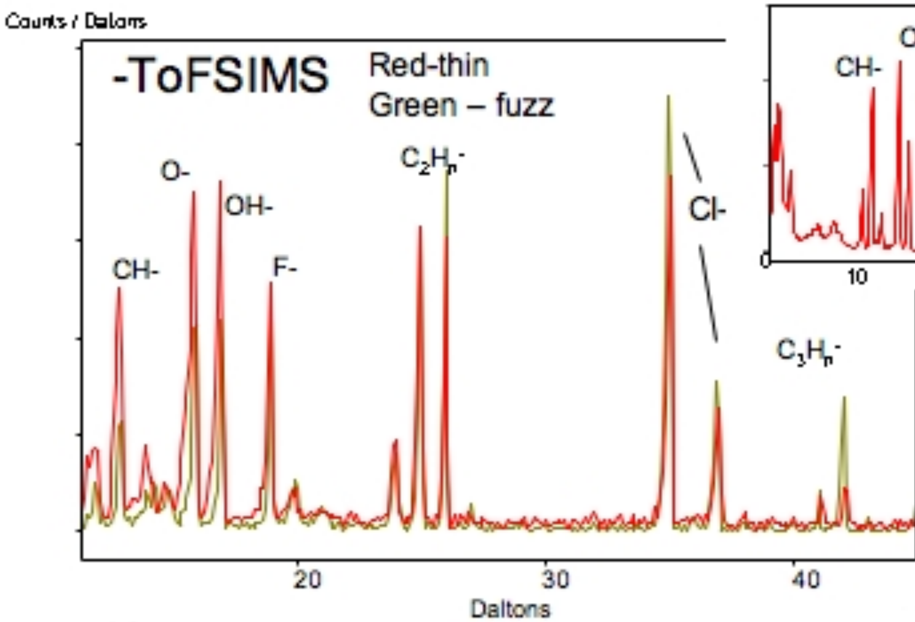
	C 1s	N 1s	O 1s	Si 2p	Ca 2p
Fuzzy End	**70.66**	**1.04**	**24.37**	**3.14**	**0.79**
Twist End	**79.68**	**1.14**	**16.12**	**2.07**	**0.99**

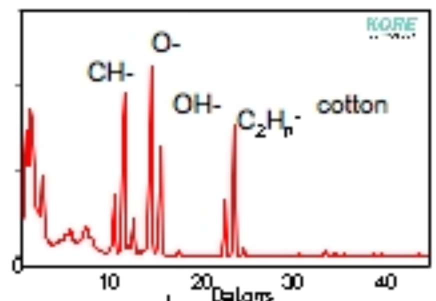
ToFSIMS on a Thread from the Shroud of Turin











Unknown material was observed
In the middle of the thread, deposited
on the surface, encasing it like a sheath.
This material separated from the thread
during handling. A piece of this coating
is shown in the above photomicrograph.
Warren Steckle, MST-7

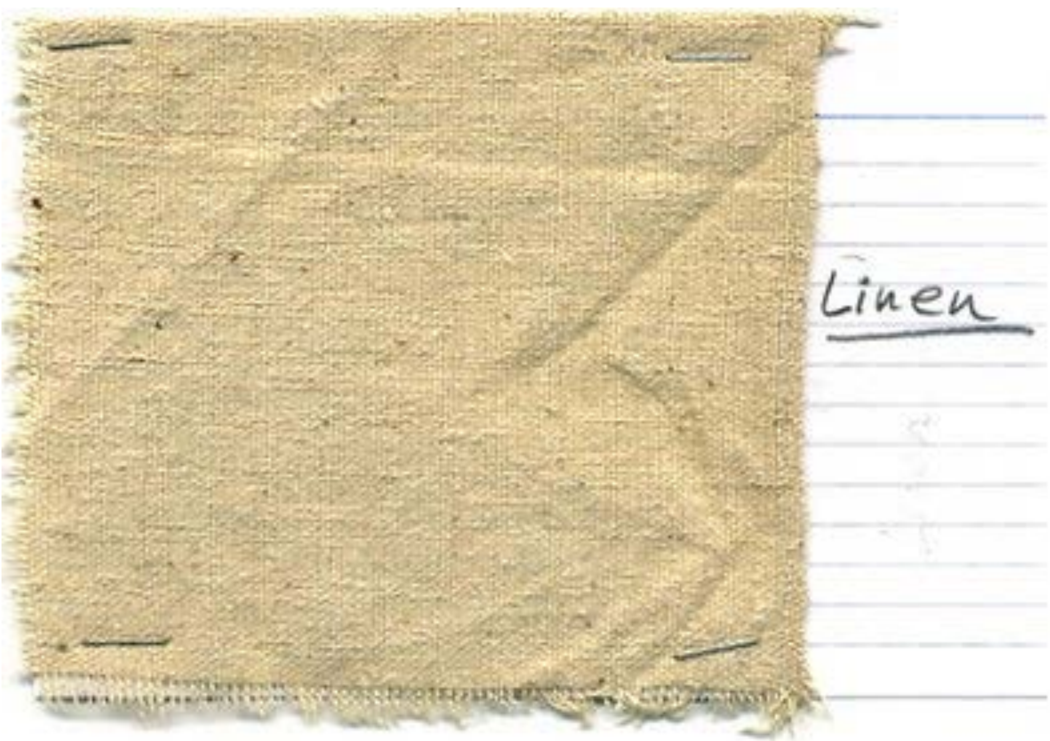
Both positive and negative SIMS spectra show simple, Low mass species expected for cellulose and other organic fibers like cotton.
Impurities detected were Na, F and Cl.
No consistent significant differences were observed in the surface chemistry between the thin and fuzzy ends of the fiber.

Doug Farr, MST-16

Linen Versus Cotton

I. Linen is a textile material made from the fibers of the flax plant. Linen is one of the earliest products known to civilization. Linen cloth was used to wrap mummies in early Egyptian tombs.

II. Cotton is nearly as old as linen and became popular in the 200 to 1200 AD period.



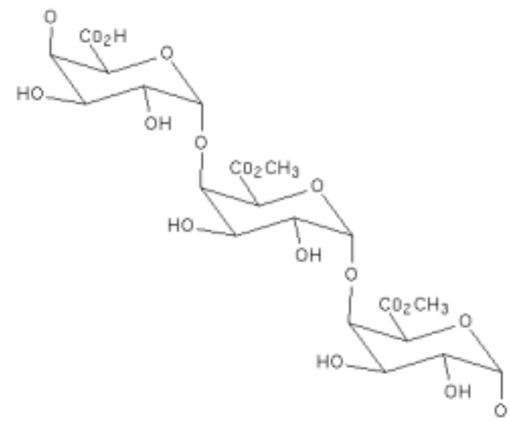
Components of Linen and Cotton

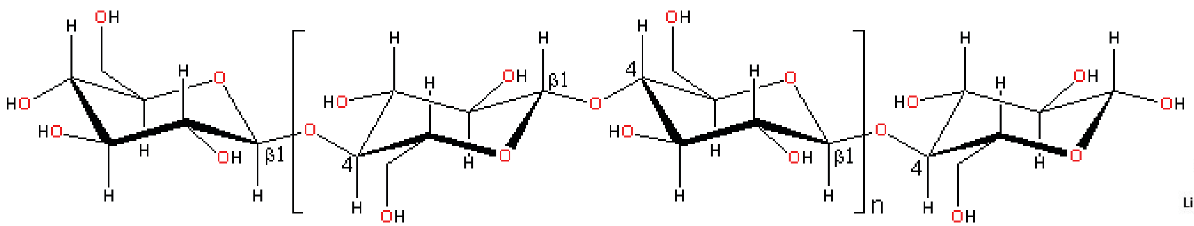
I. All plant fibers have a cellular structure and are largely made up of cellulose along with hemicelluloses, pectins, lignin, and water.

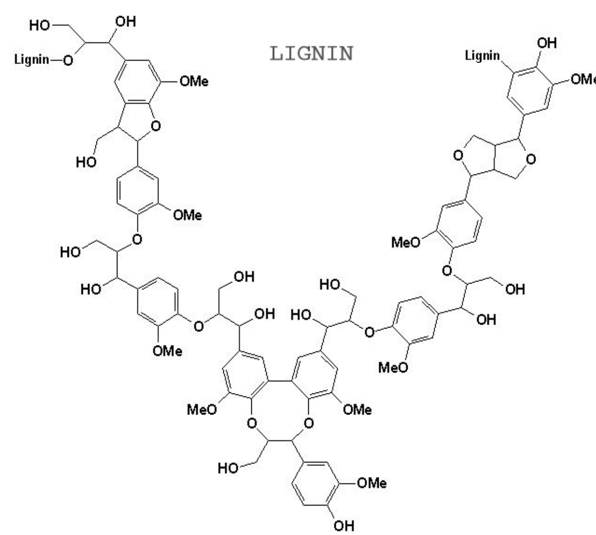
II. Pectins are jelly-like acidic polymers of galacturaonic acid incorporating other units

III. Lignin is an amorphous phenolic polymer with a poorly characterized structure.

IV. Potential infrared signatures for these components include C=O ester band near 1735 cm^{-1} from pectin and from lignin the C=C aromatic vibration near 1600 cm^{-1}.

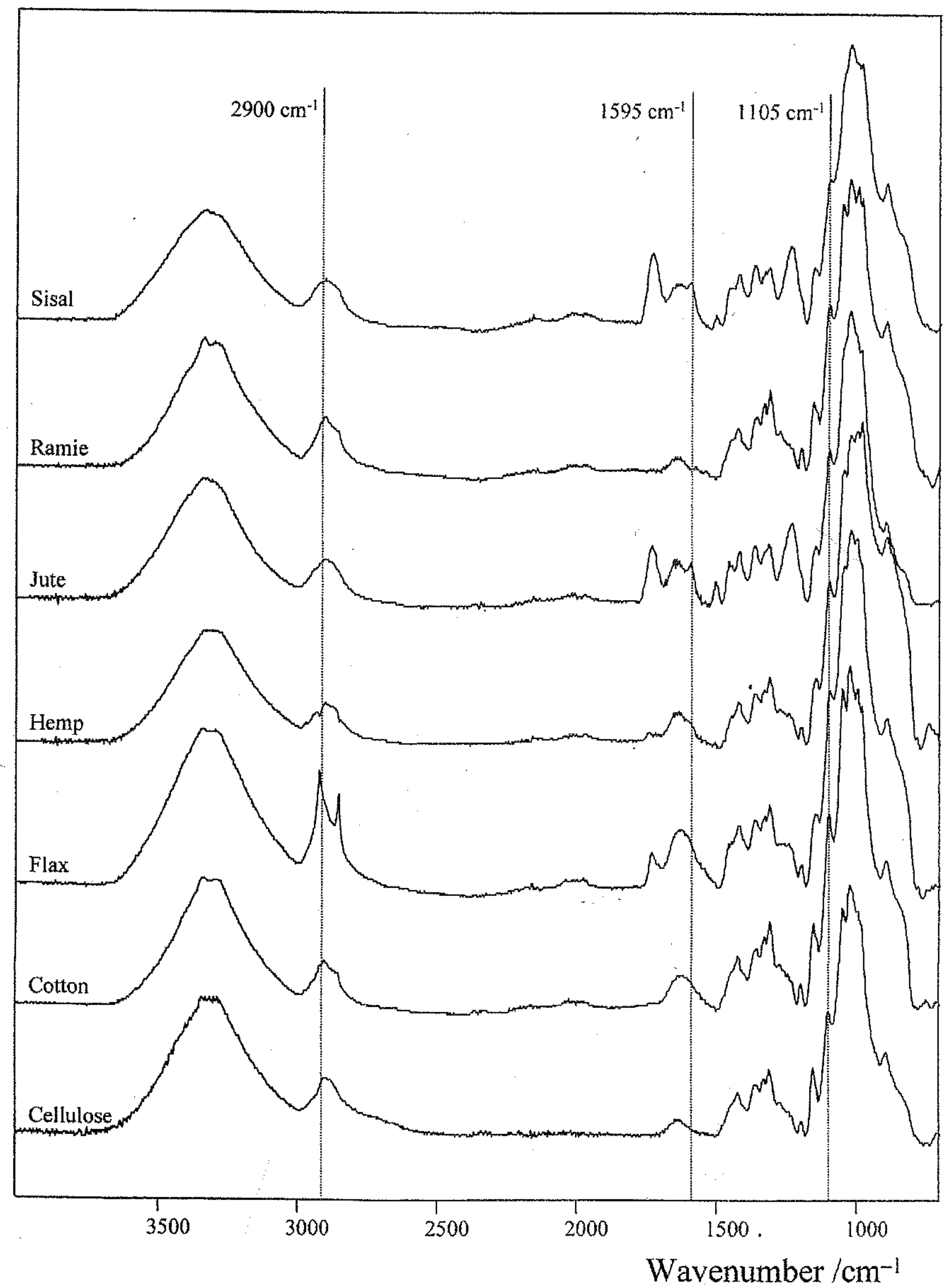






Transmission	Reflectance	Assignment
3650-3100	3550-3100	O-H stretch
2980-2800	2980-2800	C-H stretch
1730	1750	C=O of ester, pectin
1640	1644	Absorbed water
1595	1600	C=C aromatic, lignin
1433	1429	C-H wagging
1372	1368	C-H bending
1320	1316	O-H in-plane bending
1281	1281	C-H deformation
1238	1247	O-H in-plane bend
1203	1203	O-H in-plane bend
1169	1160	Asym. C-O-C (bridge)
1113	1108	Asym. C-O-C (bridge)
1061	1057	In-plane ring stretch
1031	1030	C-O stretch
992	1000	C-O stretch
898	900	Asym. C-O-C

Figure 2: Infrared ATR spectra of the plant fibres recorded over the range 4000 – 750 cm−1.



Effects of Aging

I. 1532 fire damage and heating effects

II. Polymer decomposition by slow oxidation

III. Photo-oxidation creates increased carboxylic acid absorptions.

IV. Cellulose oxidation results in increased absorption in the 1750-1600 cm^{-1} regions.