Special presentation:

Analytical Results on Threads Taken from the Raes Sampling Area (Corner) of the Shroud

Robert Villarreal

Barrie Schwortz

M. Sue Benford

Getting Started on Shroud Studies

- **Ray Rogers request for help**
  - Alpha-particle source needed
  - Alpha-particle penetration depth calculation (in linen/flax)
  - Ray Rogers assertions
    - Spliced thread sample
    - XPS and Roland Schulze and Cyril O'Piel
    - What other instruments do you have access to?
  - Ray Rogers passed away
    - Spliced fiber status by Joan Rogers
- **After 18 months**
  - Enter Barrie Schwortz
  - Continue Analyses
  - Enter Sue Benford

Getting Started on Shroud Studies

- **Analytical Situation and Capabilities**
  - What did I have to offer?
  - Available instrumentation
    - High Resolution Photo-microscopy (Olympus BX 51 optical microscope with and Optronics digital CCD camera) – Warren Steckle, LANL
    - Fourier Transform Infrared Spectroscopy (FTIR) with reflectance/transmittance capability – Kevin Hubbard, LANL
    - X-ray Photoelectron Spectroscopy (XPS) aka Electron Spectroscopy for Chemical Analyses (ESCA) – Roland Schulze, LANL
    - 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
    - Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) with R-500 Reflecton by Kore Technology, LLC – Doug Farr, LANL
    - Auger Electron Spectroscopy System – Doug Farr, LANL
    - Confocal Raman Spectroscopy – Jon Schoonover and Steve Doom, LANL
  - Available expertise per instrument
  - Hot and cold labs and equipement
  - Equipment status—In preparation or operation
  - Sequence of analyses
  - Recognition of expertise and type of sample to be analyzed
  - Thread samples are religious symbols

Analytical Results in Order of Analyses

- **XPS**
- **Micro-photography**
- **ToFSIMS**
- **FTIR**
- **Assessment of results**
- **Re-analysis by FTIR**
- **Micro-spot Energy Dispersive X-Ray Fluorescence**

XPS Analysis of Twisted Overlap (R1 Thread)

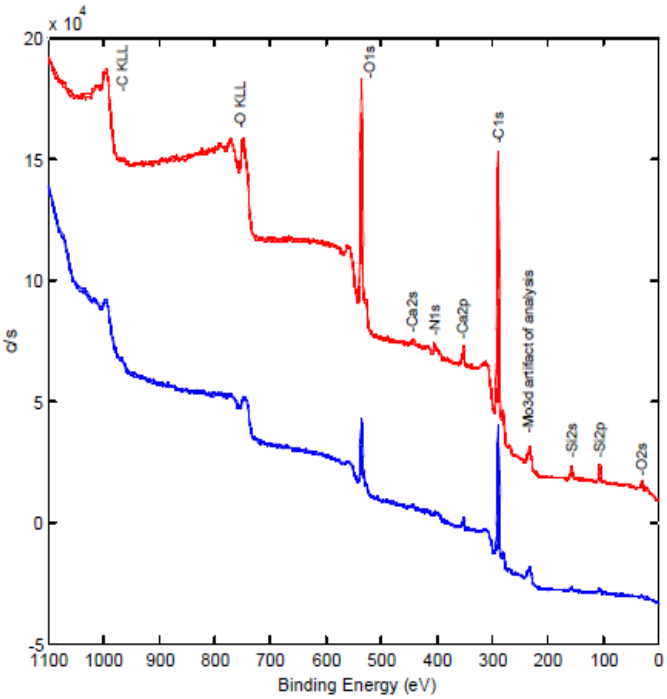
- X-ray Photoelectron Spectroscopy (XPS) also know as Electron Spectroscopy for Chemical Analysis (ESCA)
- Excitation / process: soft x-ray photon (1253.6 eV), which is absorbed by an atom in the sample and results in an ejected photoelectron of characteristic elemental and chemical energies.
- Analysis: 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.
- Chemical information: The measured binding energies (chemical shift) of photoemitted electrons yields information on chemical environment of the atom in the sample surface.
- Thread is suspected to be from region of Shroud repair (cloth material transition) - examination of both ends of thread for chemical differences.

XPS Survey Spectra for Twisted Overlap (R1 Thread)

twisted overlap thread - fuzzy end

twisted overlap thread - tight twist end

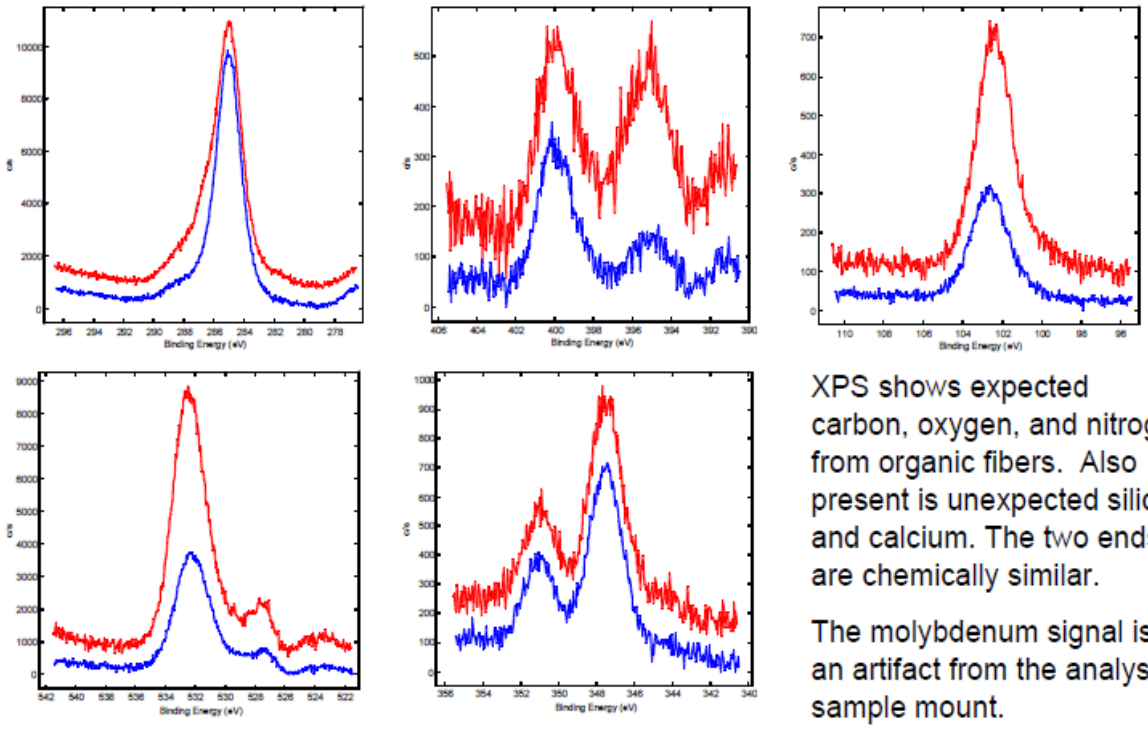
- XPS shows expected carbon, oxygen, and nitrogen from organic fibers. Also present is unexpected silicon and calcium.
- The molybdenum signal is an artifact from the analysis sample mount.



XPS High Resolution Spectra for Twisted Overlap (R1 Thread)

twisted overlap thread - fuzzy end

twisted overlap thread - tight twist end



XPS shows expected carbon, oxygen, and nitrogen from organic fibers. Also present is unexpected silicon and calcium. The two ends are chemically similar.

The molybdenum signal is an artifact from the analysis sample mount.

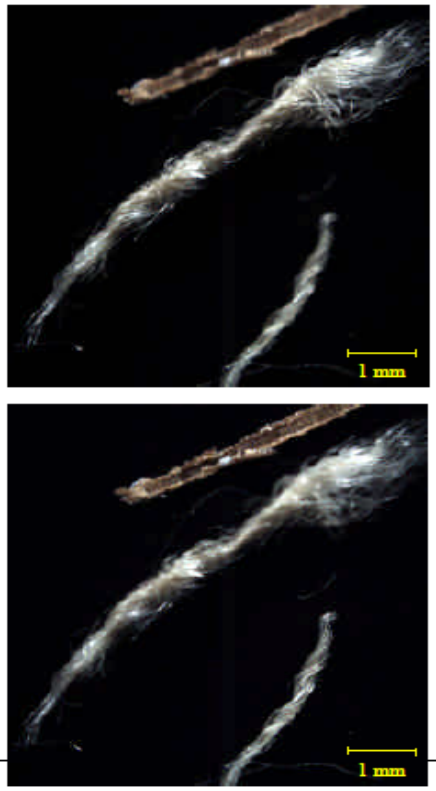
XPS Atomic Concentration Table

Atomic Concentration (atom%)

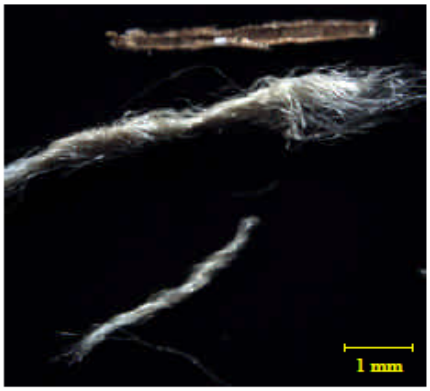
	C 1s	N 1s	O 1s	Si 2p	Ca 2p
Fuzzy End	70.66	1.04	24.37	3.14	0.79
Twist End	79.68	1.14	16.12	2.07	0.99

Note that there are some moderate differences between one end of thread and the other. The tight twist end has a higher concentration of carbon, a lower amount of oxygen, and a lower amount of silicon.

Splice Fiber with Brown Crust



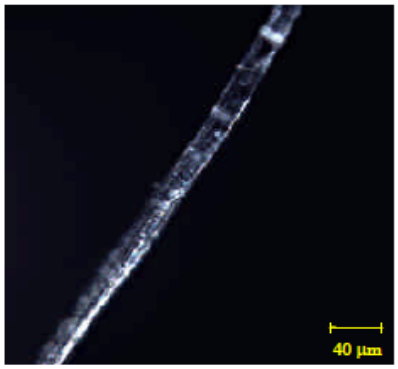
25x
white light



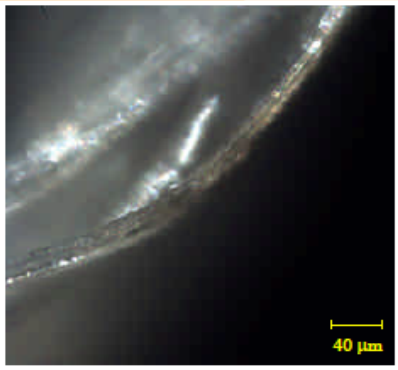
Splice Fiber with Individual Strand and Strand Bundle

500x

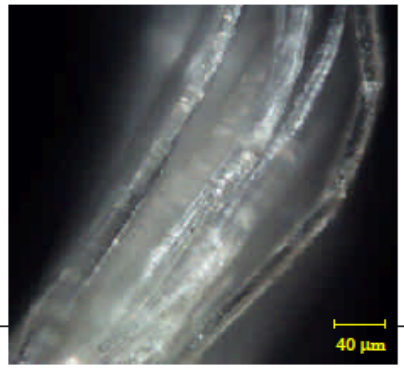
long piece
white light



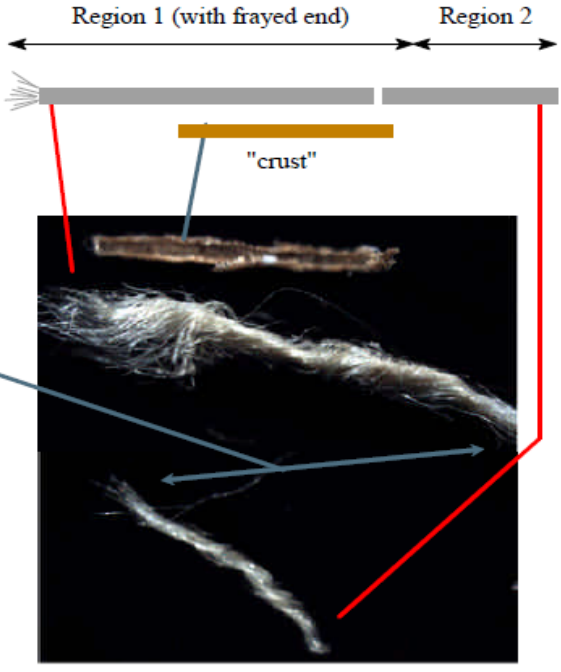
fuzzy
end



middle
of
fiber

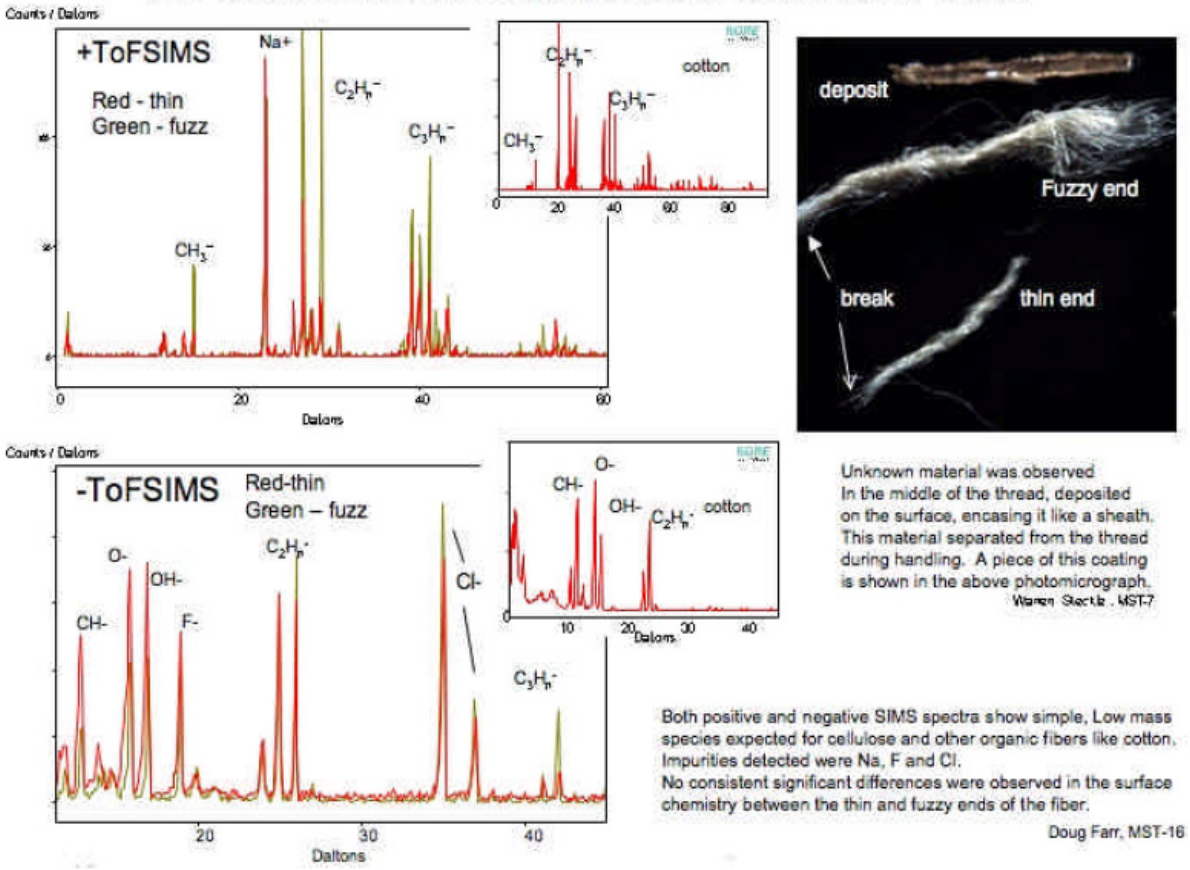


The Splice Fiber Sample



Boundary between Regions 1
and 2 is approximate

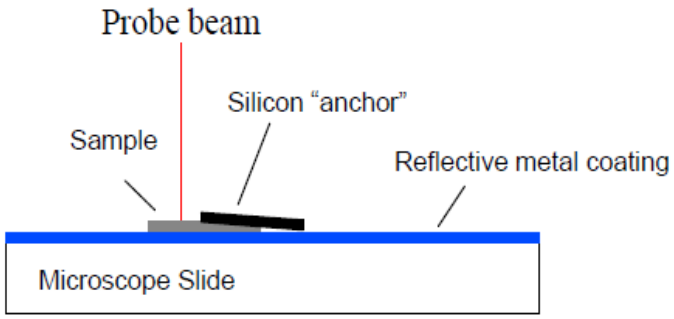
ToFSIMS on a Thread from the Shroud of Turin



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

Data Collection – Infrared Spectroscopy

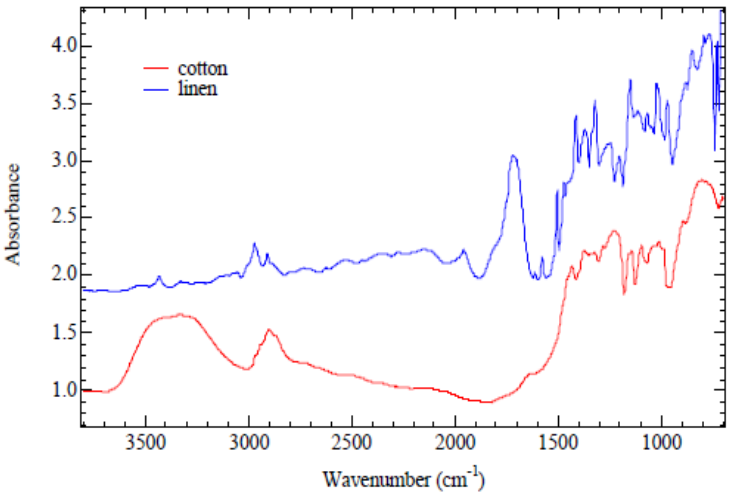


Analysis was performed using an FTIR microscope in reflectance mode, sampling at most a few fibers per spectrum

Several (4-6) spectra were obtained at each chosen position along the length of the thread

Issue: Some spectral characteristics depend on the vertical position of the fibers relative to the focal plane (fibers must lie flat for reliable data)

Linen and Cotton Standards



Spectra are dominated by:

Linen

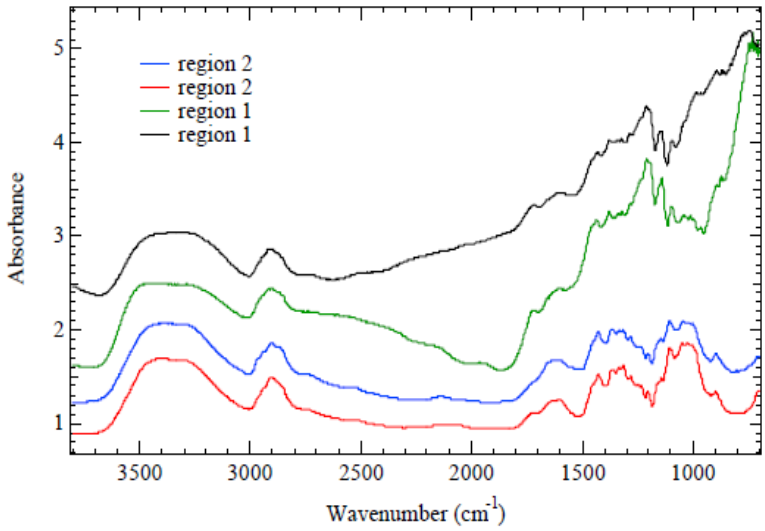
- Sharp CH_n stretch bands
  - sp^3 $-CH_3$ and >CH-
- C=O

Cotton (cheesecloth)

- Broader distribution of sp^3 CH_n
- -O-CH<
- $-CH_2$-OH
- -OH

Very different…

FTIR Data – Region 1 vs. Region 2



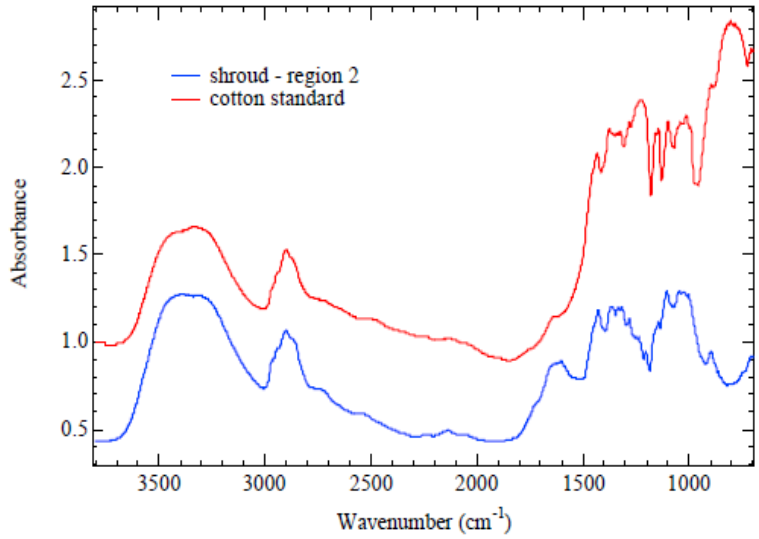
Region 1 is the fuzzy end

Region 2 is the thin end

Spectra obtained from regions 1 and 2 appear to exhibit some differences, especially for -OH absorption features

This may result from differences in microstructure and/or composition caused by different environmental exposure, treatment, or handling (related to brown crust???)

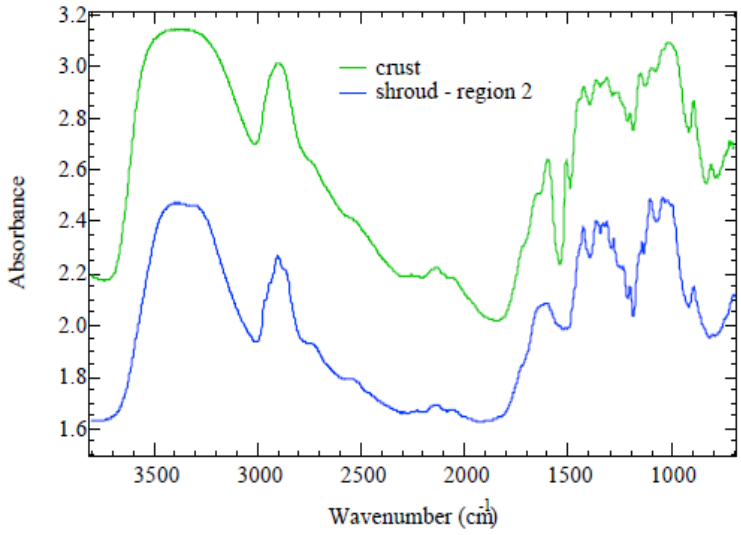
Thread Identification by FTIR



Data obtained from the Shroud thread, especially from Region 2 (thin end), are a good match for the cotton cheesecloth standard.

The fiber is definitely not linen

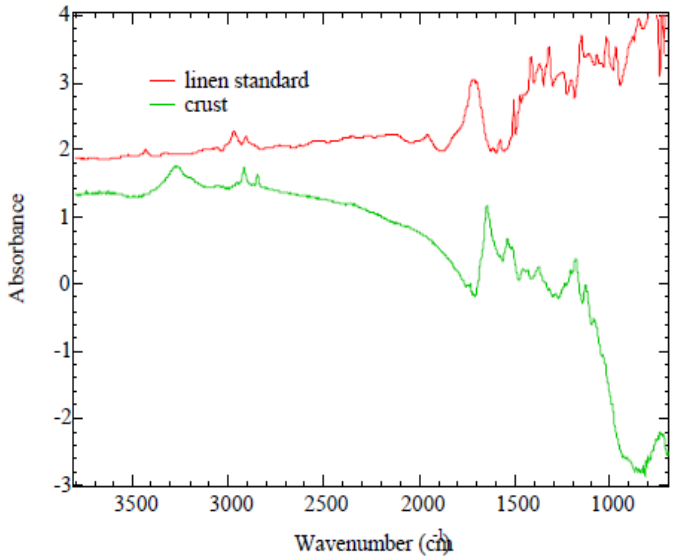
Brown Crust – Larger Bulk Sample



Data taken from a large piece of crust are quite similar to data from the Shroud thread.

Spectrum may be dominated by embedded fibers.

Brown Crust – Thin Fragment



What appeared to be a thin fragment of crust gave a very different spectrum

Dominated by:

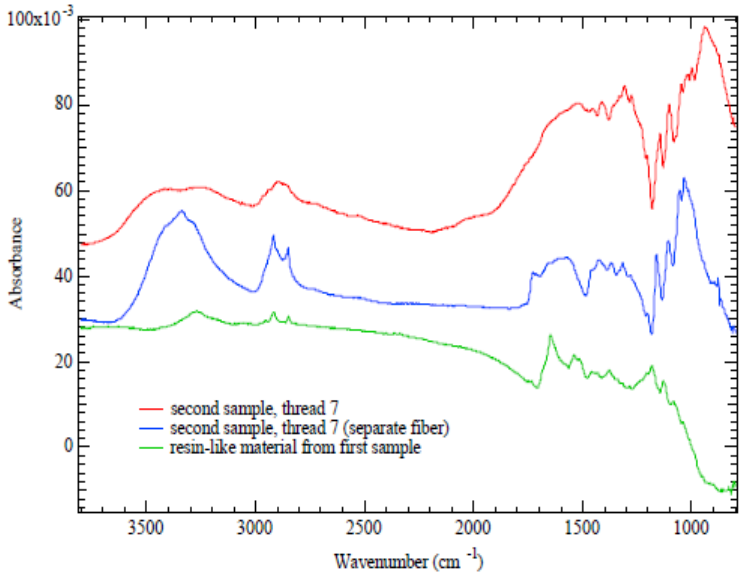
- sp^3 -CH_2-
- smaller olefinic CH_n features
- olefinic C=C
- -OH

Not linen

Possibly a terpene-based resin

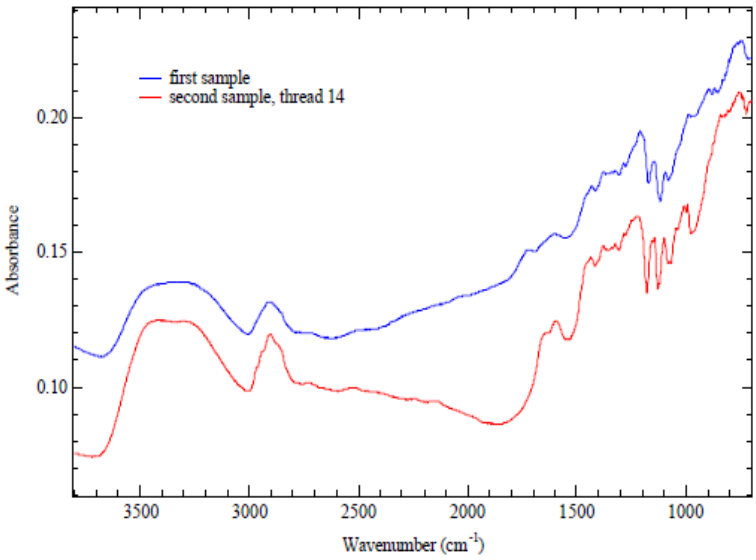
(Editor's note: Terpene is contained in the Myrrh)

FTIR Analysis of Thread 7



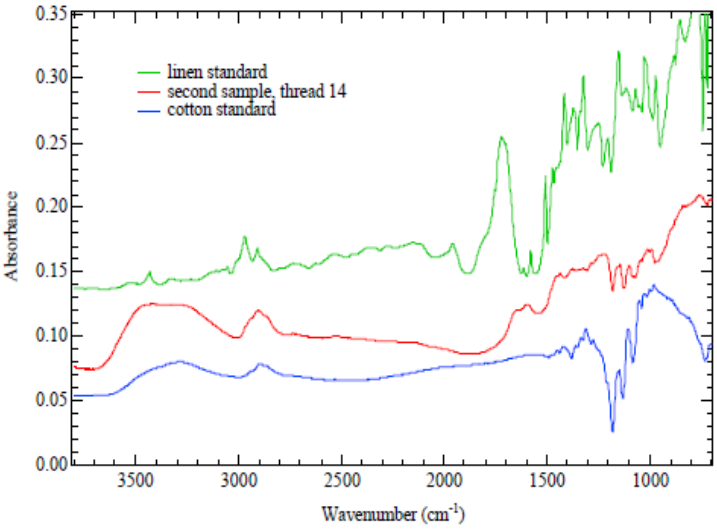
Thread 7 also appears to be cotton. Many of the individual fibers in this sample appear to have a small residue from the resin-like material included in the first sample set.

FTIR Analysis of Thread 14



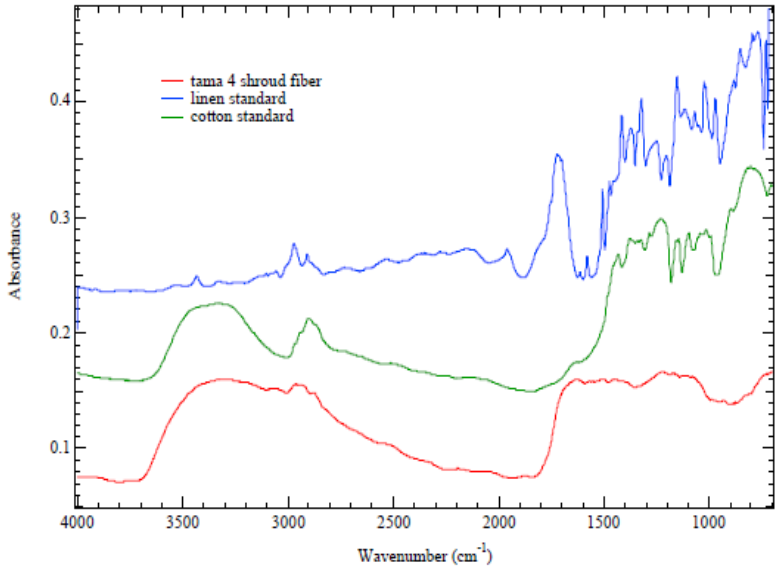
Spectra from thread 14 are a good match to those from the first sample set

Comparison of Thread 14 with Reference Standards



As with the first sample set, thread 14 appears to be a reasonable match to cotton. It is definitely not linen.

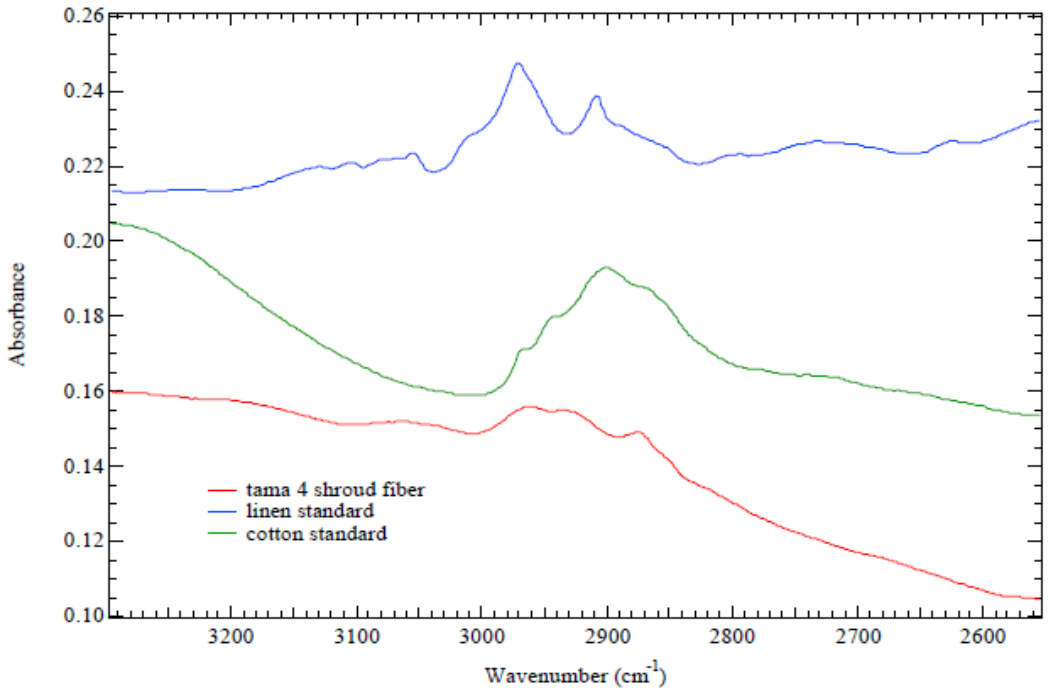
FTIR Absorption Data for Tama 4 "Shroud Fiber?"



As seen on this page and the next, data from the thread labeled Tama 4 are not a good match for either the cotton or linen standards. This may be the result of aging effects, or the material may be something different entirely.

FTIR Data Expanded

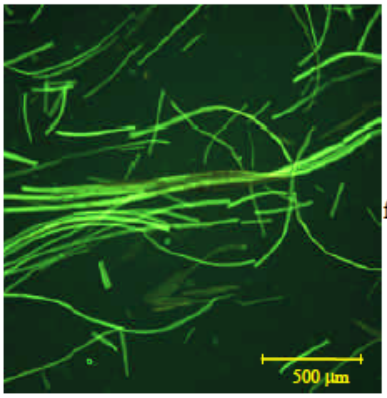
Data focusing on the $sp^{2,3}$ CH_n stretch region



Sticky Tape Sample from Shroud Area

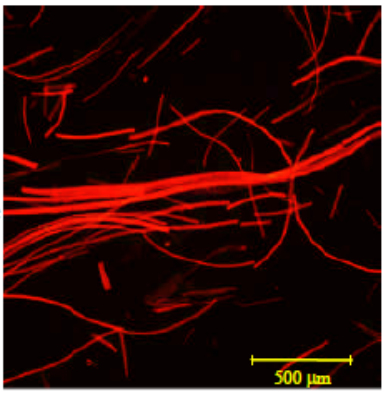
125x

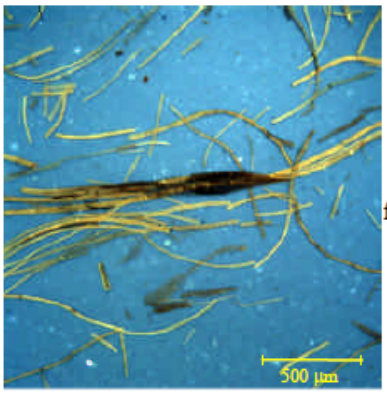
white light



blue fluorescence

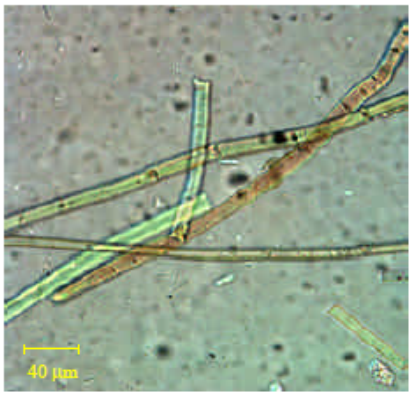
green fluorescence



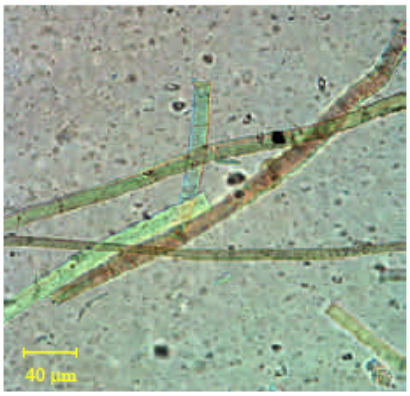


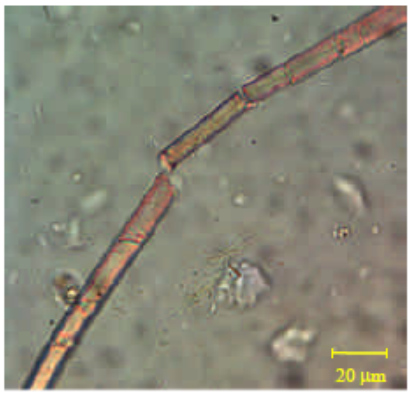
UV fluorescence

Sticky Tape Sample Featuring Individual Strands



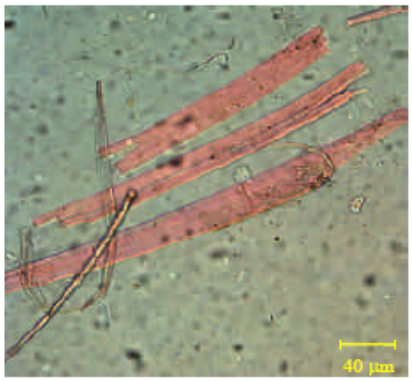
500x



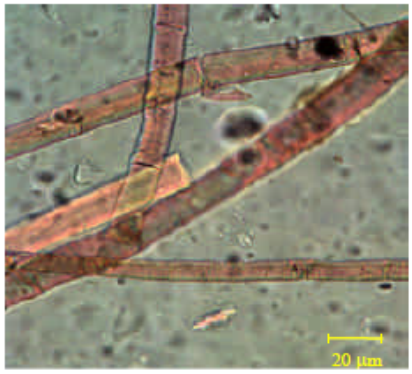


1000x

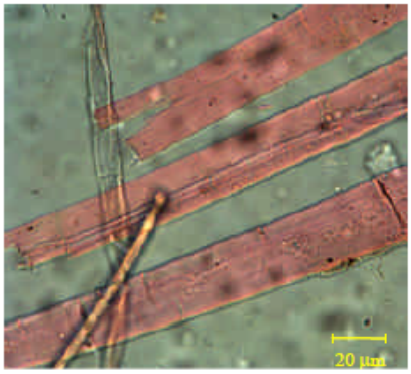
Sticky Tape Sample Indicating Flattened Fibers



500x

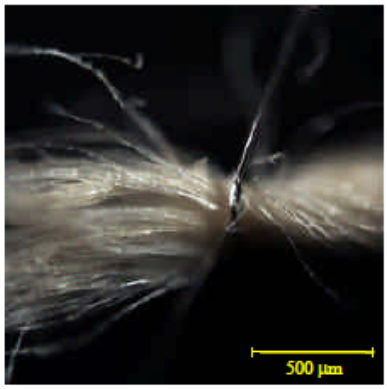


1000x



Fiber 14 with Nickel Wire Wrap

Fiber 14

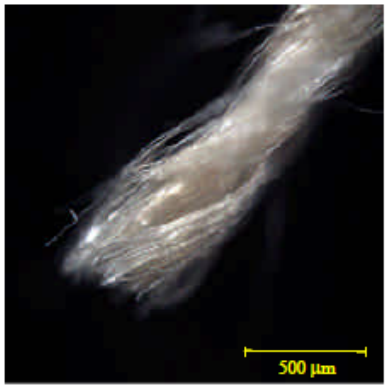


100x

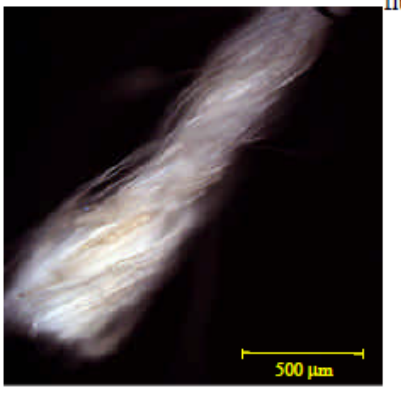
middle

white light

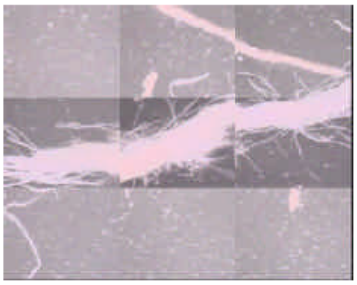
UV fluorescence

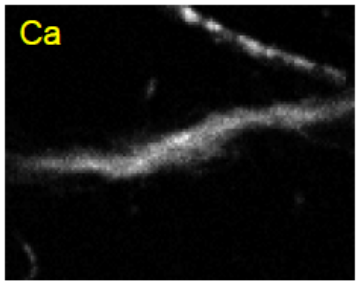


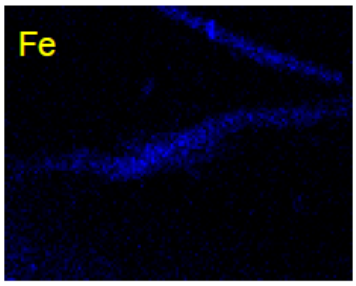
bottom

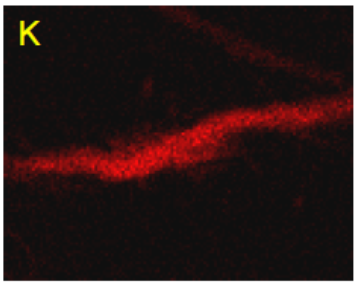


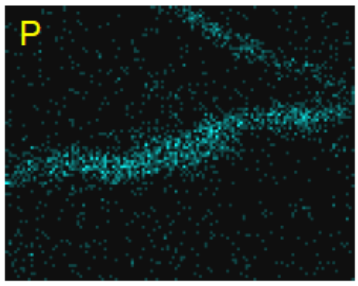
Elemental Images



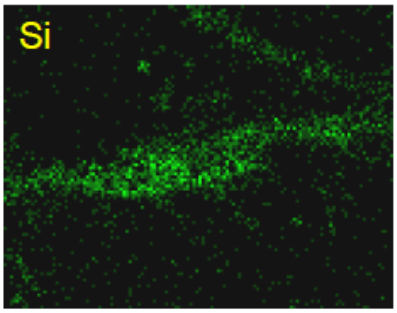


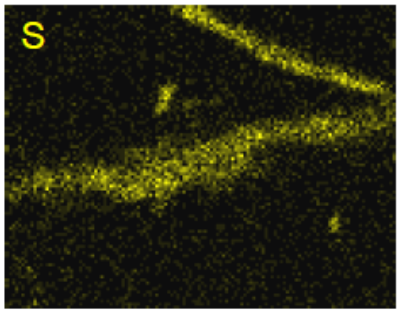




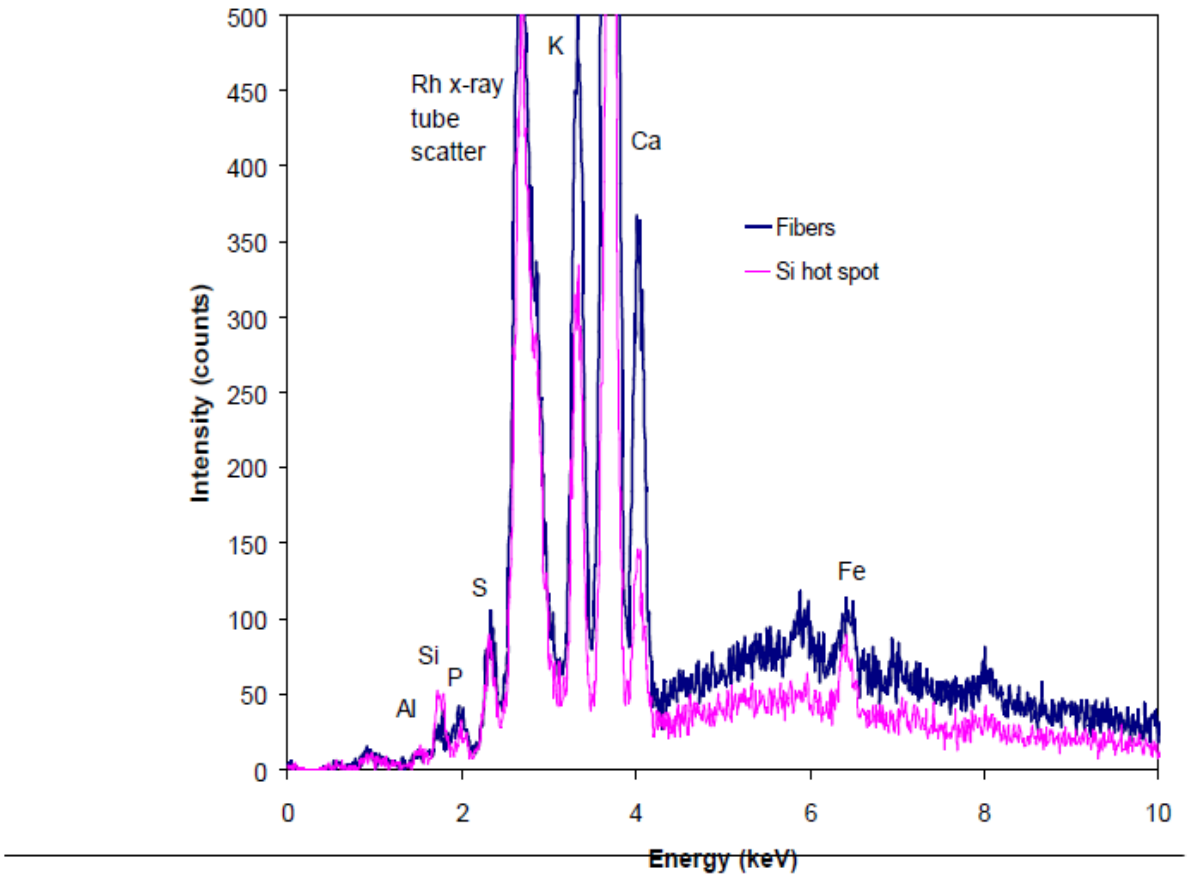


Elemental Images





Shroud Fiber Spectra



Calculated Composition (wt. %)

	Composite	Multi-fiber Thread	Si Hot Spot	Fe Hot Spot
Si	2.1	0.81	4.69	2.43
P	0	0.59	0.84	0.53
S	1.6	1.15	2.09	3.09
K	14.2	11.38	16.62	1.88
Ca	77.8	83.88	70.01	62.72
Fe	4.4	2.19	5.67	29.36

Discussion

- **GOAL: To analytically determine the identity of the cloth on the Raes and C-14 sampling corner by analyses of three threads taken from that area.**
- **APPROACH: To determine the identification of each of three sample threads by analytical methods and to confirm the identification by comparison to cotton and linen (flax) standards.**
- **OBJECTIVES:**
  - To establish list of analytical instrumentation that is appropriate and available for conducting study.
  - To determine the relative effectiveness of analytical methods for material identification of three threads.
  - To conduct the studies non-destructively and without contaminating the samples.
- **GIVEN: The main original Shroud cloth is linen (flax). We received and analyzed three threads ~8-10 mm in length and ~0.2 mg weight.**
- **LIMITATIONS AND ASSUMPTIONS:**
  - We did not have actual Shroud linen standard.
  - The three thread samples analyzed are representative of Raes and C-14 sample areas.

Conclusions

- **Introduction: All the conclusions from this study are from actual analytical data of three samples taken from the Raes (1973) and C-14 (1988) sampling corner (lower left corner of frontal image area of the Shroud).**
  - The many strands of fibers from the three threads analyzed gave FTIR signatures (spectra) of cotton and definitely did not give evidence of linen (flax) fibers.
  - The FTIR data confirms the Ray Rogers assertions:
    - "The material from the radiocarbon area of the Shroud is significantly different from that of the main cloth, and
    - The radiocarbon sample was thus not part of the original cloth and is invalid for determining the age of the Shroud." (Thermochemica Acta 2005)
  - The samples taken for the C-14 dating of the Shroud in 1988 were77 all from the same corner and were not representative of the main Shroud. What was true for the part was not true for the whole.
  - Therefore, the approach used for conducting the age dating was flawed and the results are invalid.
- **Recommendation: A new age dating must be conducted on samples that are representative of the Shroud image area.**

Acknowledgements

The following scientists and spectroscopists from Los Alamos National Laboratory were key in pursuing analyses of the Shroud threads. All the scientists listed are PhD's and are experts in their technical fields. We appreciate their efforts and knowledge in analyzing the Shroud samples in a scientific and meticulous manner.

Steve Doorn	Brian Patterson
Doug Farr	Jon Schoonover
George Havrilla	Roland Schulze
Kevin Hubbard	Warren Steckle