PYROLYSIS/MASS SPECTROMETRY APPLIED TO THE SHROUD OF TURIN

Raymond N. Rogers
Fellow
University of California, Los Alamos National Laboratory
Los Alamos, NM, USA

Our primary goal in undertaking pyrolysis-MS analyses on samples from the Shroud of Turin was the detection of impurities (e.g., painting materials). Most of the structural materials and probable impurities in Shroud samples were carbohydrates. We wanted to see traces of materials that were not carbohydrates.

The samples were run at the Midwest Center for Mass Spectrometry (MCMS), University of Nebraska-Lincoln. This is a National Science Foundation "Center of Excellence," and it ranks among the foremost facilities in the world.

Walter McCrone had ignored agreements on how the STURP samples were to be observed, and he contaminated all of our samples by sticking them to microscope slides. All of the fibers were immersed in the tape's adhesive, Joan Janney (now Joan Rogers) laboriously cleaned and prepared Shroud fibers for analysis at the MCMS.

Mass spectrometry is based on the fact that charged particles in motion have their trajectories bent by electric and/or magnetic fields. Molecules in a high vacuum can be ionized (charged) by electron impact or chemical ionization. Chemical ionization uses collisions with excited atoms or molecules to ionize the sample, and it gives a much simpler mass spectrum than electron impact. Since we desired detection sensitivity rather than high resolution, we used a machine with moderate resolution, chemical ionization, and high sensitivity.

The method was sufficiently sensitive to detect traces of the low-molecular-weight fractions (oligomers) of the polyethylene bag that Prof. Luigi Gonella had used to wrap the Raes threads. It did not detect any unexpected pyrolysis fragments that indicated any Shroud materials other than carbohydrates. That is exactly what would be expected from a piece of pure linen. This helped confirm the fact that the image was not painted.

The oldest known paintings appeared in prehistoric times (ca. 30,000 BC), and they are found in the caves of France, Spain, and Africa. They were done in natural materials, e.g., red and yellow ochre and charcoal. There is evidence that the pigments were mixed with animal fat for application to the irregular cave surfaces. Tempera painting appeared early in history. It involves powdered pigments mixed with egg, plant gums, and/or glues. Aside from fresco, tempera was the principal painting medium before the introduction of oil paints.

The Flemish brothers Hubert and Jan van Eyck are generally (probably incorrectly) credited with the invention of oil painting. Their careers are well documented between about 1422 and 1441. They normally worked on canvas that was made from either linen or a linen-cotton blend. It would be extremely unlikely that oil paints had been used to hoax the image during or before the 14th Century; however, we planned observations that would detect such materials. Oils were the favorite vehicles for pigments during the time of the 1532 fire. They could have been used in an attempt to reproduce the Shroud, if it had been totally destroyed in the fire.

The matrix of samples that were analyzed at the MCMS is shown in the table. We attempted to get representatives of all of the different areas of the Shroud.

Slide Number	**Image**	**Scorch**	**Blood**	**Water**
6BF	yes	light scorch	yes	no
3EF	yes	no	yes	no
Zina heel	yes	no	yes	no
Raes #3	no	no	no	no
1EB	yes	no	no	no
2CF	yes	no	no	yes
Edgerton modern	no	no	no	no

Materials that are heated in the absence of air (oxygen) tend to produce pyrolysis products that are characteristic of the sample. Organic materials pyrolyzed in air tend to produce heat, light, carbon monoxide and/or carbon dioxide, and water. It was fortunate that the Shroud was stored in a closed reliquary in 1532. The lack of oxygen in the heated reliquary made the intersections of scorches with image, blood, and water-stains important for a chemical study of the cloth.

These same pyrolysis products can also be produced in the inlet of a mass spectrometer (MS), and they can be separated and identified. The MCMS pyrolysis system covered a wide range of temperatures, and most organic materials would have been detected.

The pyrolysis-MS analyses did not detect any nitrogen-containing contaminants. This seemed to rule out glair (egg white) as well as any significant microbiological deposits, confirming microchemical tests that were also made. They did not detect any of the sulfide pigments that were used in antiquity, e.g., orpiment, realgar, mosaic gold, and cinnabar (vermilion, mercury sulfide, HgS). The Shroud's image had not been painted with any known vehicles and pigments.

Many of the pyrolysis fragments observed by pyrolysis-mass-spectrometry would be the same products of thermal degradation whether they came from cellulose, hexose sugars, pentose sugars, or starches. However, the ratios of products can be characteristic and important.

The major products of the thermal decomposition of cellulose and other carbohydrates in the absence of oxygen are formaldehyde, carbon monoxide, furfural (2-furaldehyde), hydroxymethylfurfural (5-hydroxymethyl-2-furaldehyde), levulinic acid (4-oxopentanoic acid), and 3-pentenoic-γ-anhydride. Pentoses (sugars composed of five-carbon rings) do not produce any hydroxymethylfurfural. Hexoses, as in the cellulose structure (six-carbon sugars), produce copious hydroxymethylfurfural. The hydroxymethylfurfural deformylates (loses a formaldehyde fragment)

in a series reaction, producing some furfural. Therefore, a pure hexose system will show some furfural, but a pure pentose system will not show any hydroxymethylfurfural.

In addition to different products, the different carbohydrates produce pyrolysis products at very different rates. Rates of all kinds of reactions are modeled with an exponential equation called the Arrhenius expression:

$$\frac{da}{dt} = kf(a)Ze^{-E/RT}$$

Rates can be predicted from amounts of reactants (a is the fraction reacted at any time t) and known, measured chemical kinetics constants (k, the rate constant; Z, the Arrhenius frequency factor; E, the Arrhenius activation energy; R, the gas constant; and T, the absolute temperature in degrees Kelvin). Any chemical process involved in Shroud aging and pyrolysis or image formation will have properties in accordance with this equation.

Cellulose decomposes much more slowly than a plant gum that is composed of pentose units. Cellulose has the following kinetics constants (personal communication from Bruce Waymack, Philip Morris Co.): E = 52.6 kcal/mole and Z = 3.16 X 10^{16} s^{-1} early in its decomposition at slow heating rates (as in the pale-scorch areas from the fire of 1532). Pure glucose shows the following constants: E = 23.9 kcal/mole and Z = 1.26 X 10^{7} s^{-1}. Arabinose, a pentose, has an activation energy of only 19.7 kcal/mole: it would decompose much more rapidly than the major components of linen.

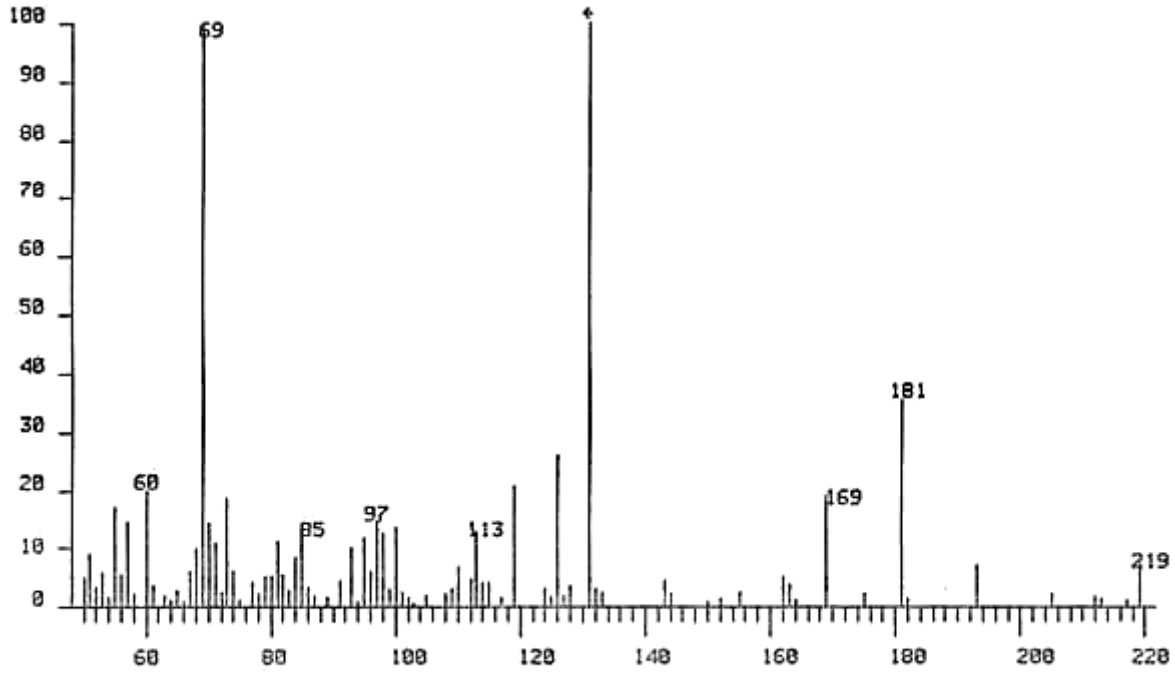


Figure 1: Mass spectrum obtained from a low-temperature pyrolysis of Shroud image sample 1EB.

The ordinate of the graph shows the relative ion intensity for each product produced at that temperature. The abscissa shows the mass of the ion.

The Shroud is nearly pure linen. Notice that the hydroxymethylfurfural signal at m/e 126 is quite large: the furfural signal at m/e 96 is quite small.

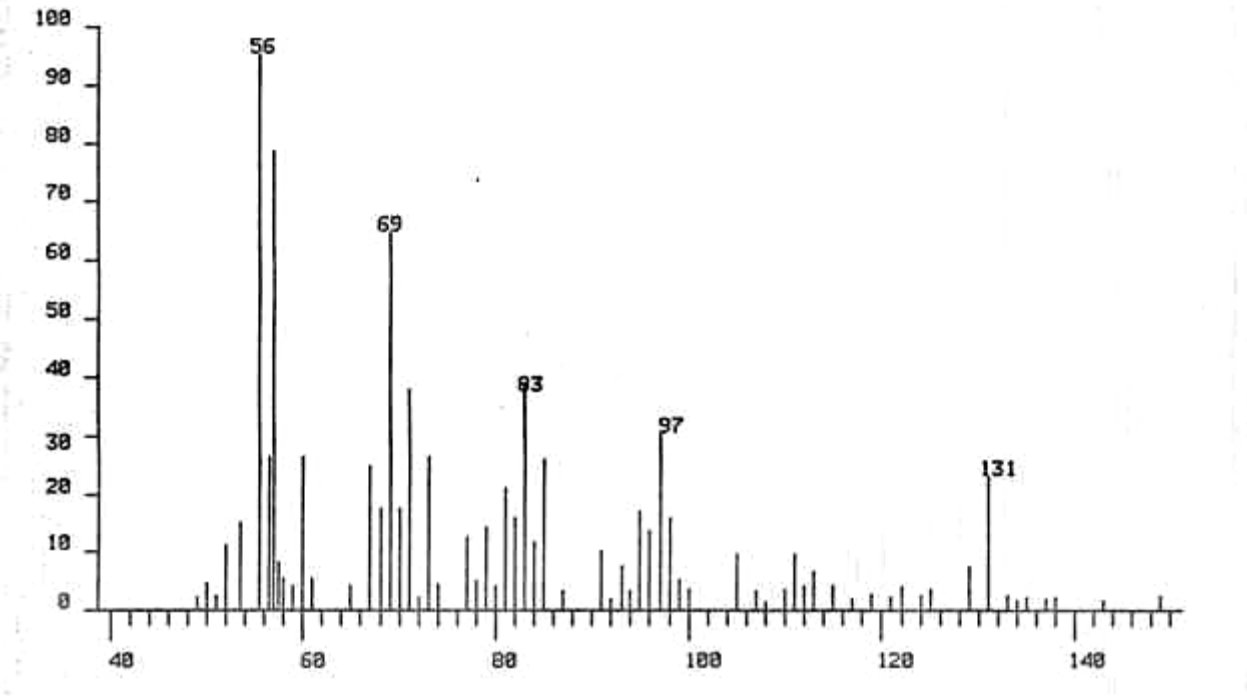


Figure 2: Mass spectrum of the low-temperature pyrolysis of fibers from Raes sample #3.

The spectrum obtained for the Raes sample (cut in 1973 from the area adjoining the radiocarbon sample of 1988) shows absolutely no m/e 126 signal: the cellulose of the sample had not yet started to pyrolyze. There is, however, a significant m/e 96 signal: furfural was being produced at this temperature. This proves that the sample contained some pentose-sugar units. This is unique among all of the Shroud samples: no other area showed this pentose signal.

Chemical analyses have proved that the Raes samples are coated with a gum/dye/mordant system that has been used for millennia to color cloth. It is stained with a synthetic system. Apparently the intent was to make these threads look like the old, sepia yarn of the main part of the cloth.

The pyrolysis/mass spectrometry system at MCMS is equipped with a pulsed source with a time resolution of 100 nanoseconds. It can present a series of complete mass spectra as the sample heats up. Figure 3 shows the "map" for image sample 1EB.

The axis numbered 0 - 50 shows the time/temperature for the corresponding mass spectrum. The mass spectrum at each temperature is shown on the 50 - 500 axis, the numbers indicating the

mass of each fragment. The height of each signal indicates the relative concentration of that ion. Notice that there are no major peaks at masses less than 100 between 30 and 40.

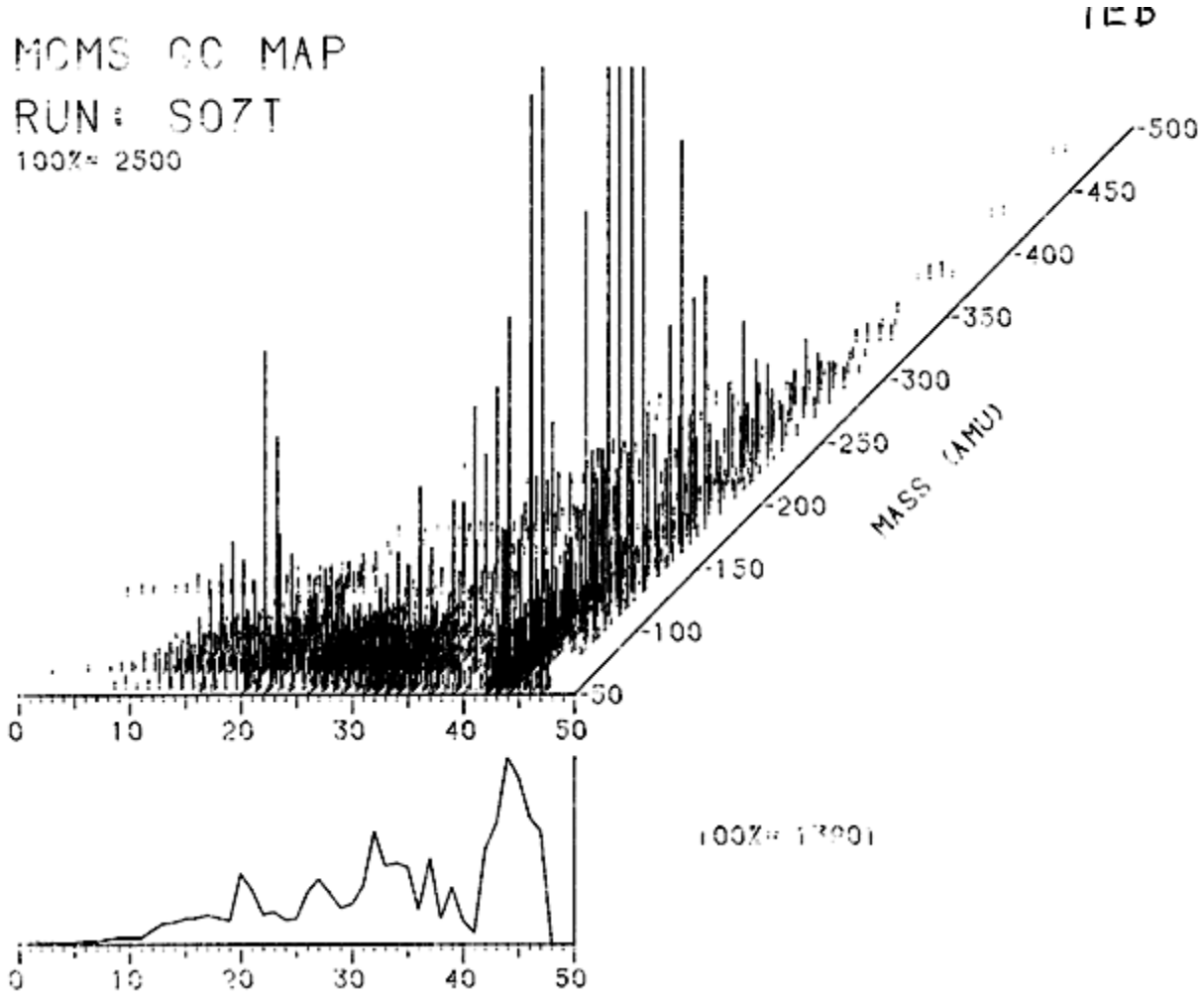


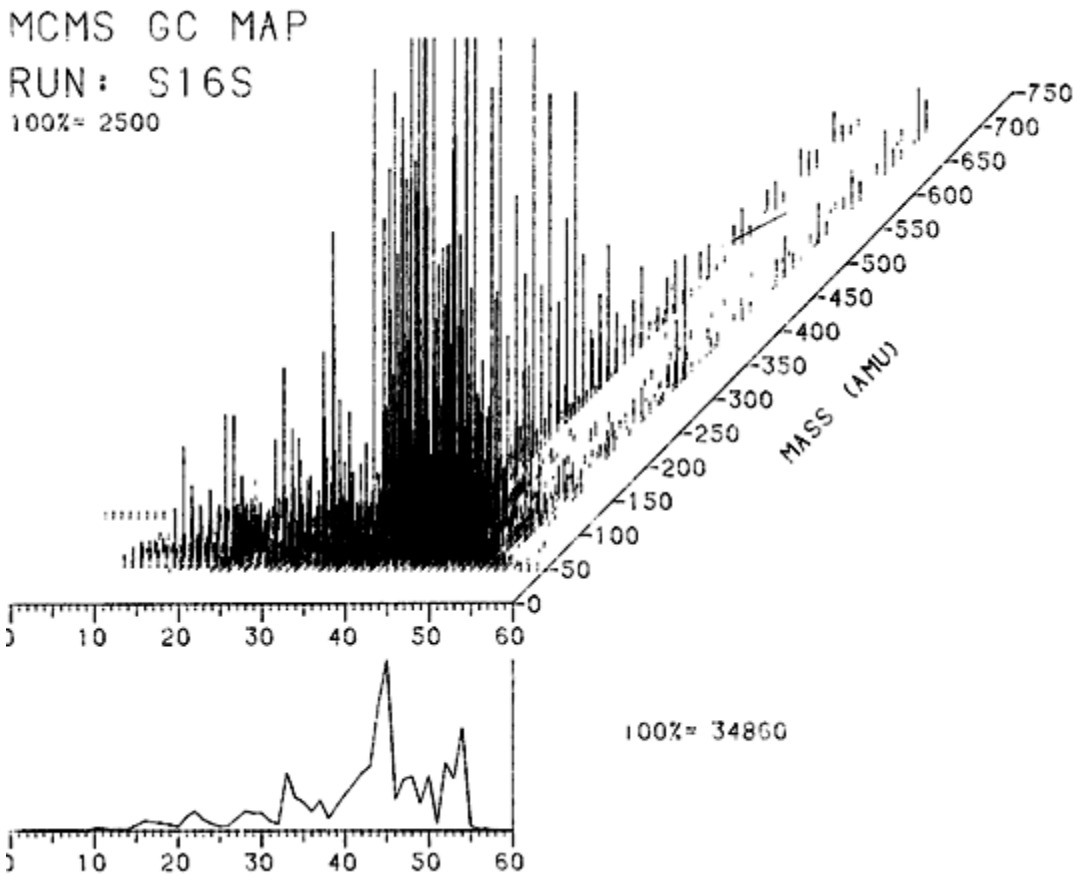
Figure 3: A mass/scan/concentration map of the pyrolysis products from tape sample 1EB, the image of the back of the ankle.

The small graph below shows the total ion current at each time/temperature. The largest amount of products is evolved at the highest temperatures, as would be expected. The map shows some contamination with the xylene that was used to wash adhesive off of the fibers.

The same kind of map for the Raes sample is shown in figure 4. The primary product early in the pyrolysis (e.g., between 35 and 40) is m/e 96, furfural. No xylene was used to clean the fibers, because they were not obtained as part of the tape sampling; therefore, product evolution was much lower before scan 30.

Maps of all of the other samples were also obtained. They all showed the same difference in product ratios: the Raes sample was unique. It was contaminated with some material that produced pentose pyrolysis products at relatively low temperatures.

Figure 4: A mass/scan/concentration map of the pyrolysis products from tape sample 1EB,



the image of the back of the ankle.

Conclusion:
The pyrolysis/MS data confirm the identification of a gum coating on the Raes threads.