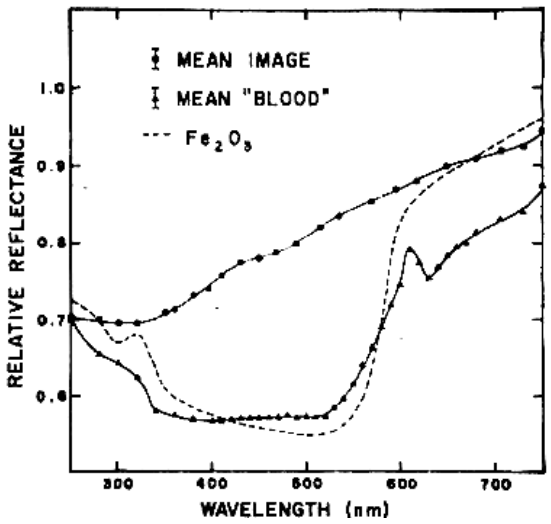
FREQUENTLY ASKED QUESTIONS (FAQs)
By Raymond N. Rogers

1) How do you know that the image was not painted?

The primary goal of STURP was to test the hypothesis that the Shroud's image was painted, as claimed by Bishop d'Arcis in 1389. If it had been painted, some colored material had to be added to the cloth, but the colored material would have gone through the fire of 1532. The pigments and vehicles would have suffered changes in response to the heating, the pyrolysis products, and the water used to put the fire out. No changes in image color could be observed at scorch margins.

We tested all pigments and media that were known to have been used before 1532 by heating them on linen up to the temperature of char formation. All of the materials were changed by heat and/or the chemically reducing and reactive pyrolysis products. Some Medieval painting materials become water soluble, and they would have moved with the water that diffused through parts of the cloth as the fire was being extinguished. Observations of the Shroud in 1978 showed that nothing in the image moved with the water.

The Shroud was observed by visible and ultraviolet spectrometry, infrared spectrometry, x-ray fluorescence spectrometry, and thermography. Later observations were made by pyrolysis-mass-spectrometry, laser-microprobe Raman analyses, and microchemical testing. No evidence for pigments or media was found.



Your eye sees colors when the surface absorbs some wavelengths of light and reflects others. A red surface absorbs all visible wavelengths other than red. Each chemical compound absorbs wavelengths that are characteristic of its chemical structure. The best way to determine the properties of a color is by measuring its spectrum. Reflectance spectrometry was one of the most important contributions of the STURP observations.

The reflectance spectra in the visible range for the image, blood, and hematite are shown in the figure. The image could not have been painted with hematite or any of the other known pigments. The spectrum of the image color does not show any specific features: it gradually changes through the spectrum. This proves that it is composed of many different light-absorbing chemical structures. It has the properties of a dehydrated carbohydrate.

There is no evidence for significant amounts of any of the many pigments and/or dyes that could have been used to paint or touch up the blood stains. We had considered and studied Tyrian purple (6,6'-dibromoindigo) and Madder root dye on an aluminum and/or chromium mordant as well as cinnabar (mercuric sulfide) and ferric oxide pigments.

During and before the 14th Century, gold metal was the most important yellow. That would easily be detected by x-ray fluorescence. Other pigments in common use were yellow

ocher (hydrated Fe_2O_3), burnt ocher (hematite Fe_2O_3) and other ochers, orpiment (As_2S_3), realgar (AsS), Naples Yellow ($Pb_3[SbO_4]$), massicot (PbO), and mosaic gold (SnS_2). Organic dyes included saffron, bile yellow, buckthorn, and weld. Madder root began appearing in Europe from the Near East about that time. Many of the dyes required mordants, which are hydrated oxides of several metals (e.g., aluminum, iron, and chromium). In order to produce the shadings observed in the Shroud's image, the concentrations of pigments would have to vary across the image. No variations in any pigment were observed by x-ray fluorescence spectrometry. The image was not painted with any inorganic pigment of an appropriate color.

2) How do you know that there is real blood on the Shroud?

Alan Adler was an expert on porphyrins, the types of colored compounds seen in blood, chlorophyll, and many other natural products. He and Dr. John Heller, MD, studied the blood flecks on the STURP sampling tapes [Heller and Adler, Applied Optics **19**, (16) 1980]. They converted the heme into its parent porphyrin, and they interpreted the spectra taken of blood spots by Gilbert and Gilbert. They concluded that the blood flecks are real blood. In addition to that, the x-ray-fluorescence spectra taken by STURP showed excess iron in blood areas, as expected for blood. Microchemical tests for proteins were positive in blood areas but not in any other parts of the Shroud.

Several claims have been made that the blood has been found to be type AB, and claims have been made about DNA testing. We sent blood flecks to the laboratory devoted to the study of ancient blood at the State University of New York. None of these claims could be confirmed. The blood appears to be so old that the DNA is badly fragmented. Dr. Andrew Merriwether at SUNY has said that "…anyone can walk in off the street and amplify DNA from anything. The hard part is not to amplify what you don't want and only amplify what you want (endogenous DNA vs contamination)." It is doubtful that good DNA analyses can be obtained from the Shroud.

It is almost certain that the blood spots are blood, but no definitive statements can be made about its nature or provenience, i.e., whether it is male and from the Near East.

3) How do you know that the image was not produced by radiation?

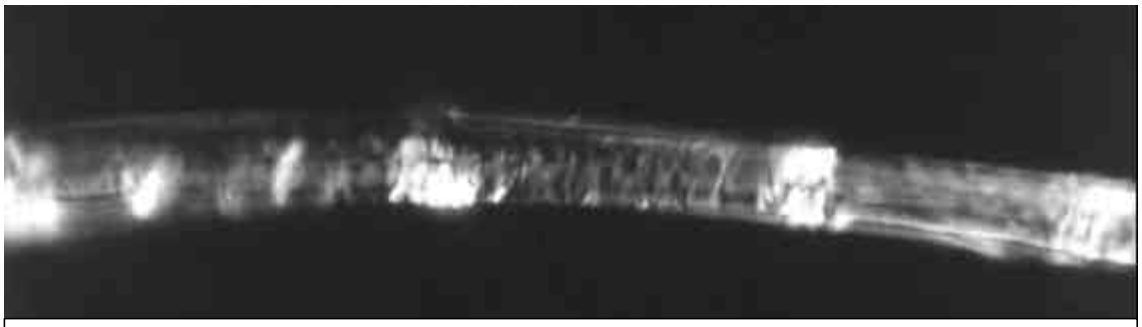
The primary effect of all kinds of radiation is to heat the material it hits. This statement includes electromagnetic radiation (visible, ultraviolet, and infrared radiation); ionizing particles such as protons, electrons, and alpha particles; and non-ionizing particles such as neutrons. You can feel the heat when you hold a lump of plutonium, a flask of tritium, or a recently irradiated accelerator target. Intense irradiation can cause enough heat to explode explosives and burn metals (think of laser effects).

Cellulose molecules are folded back and forth in a fairly regular arrangement, and they show the properties of crystallinity. This is called a "fibrillar structure." When you rotate the stage of a petrographic microscope with crossed polarizers while looking at a linen fiber, straight lengths change from black through colored to black again every 90?. The fiber is birefringent and has an ordered structure.

When cellulose fibers are heated enough to color them, whether by conduction, convection, or radiation of any kind, water is eliminated from the structure (the cellulose is "dehydrated"). When water is eliminated, C-OH chemical bonds are broken. The C? free

radicals formed are extremely reactive, and they will combine with any material in their vicinity. In cellulose, other parts of the cellulose chains may be the closest reactants. The chains *crosslink*. Crosslinking changes the crystal structure of the cellulose, and you can see the effect with a polarizing microscope.

When cellulose starts to scorch (dehydrate and crosslink), its characteristic crystal structure becomes progressively more chaotic. Its birefringence changes, and not all parts of a straight fiber go through clear transitions from dark to light at the same angle. Zones of order get smaller and smaller. It finally takes on the appearance of a pseudomorph and just scatters light. A significantly scorched fiber does not change color as the stage is rotated between crossed polarizers.



Proton-irradiated fibers by Rinaudo. Little, white, straight lines cutting across the fiber are the paths of the protons.

Specific types of radiation cause specific types of defects in the crystals of flax fibers. For example, protons ionize the cellulose as they pass through the fiber. This warps the crystals, making the protons' paths birefringent. You can see where they went in the fiber by the straight lines of their paths (see the "Proton-irradiated" figure).

Not all kinds of radiation ionize the material they penetrate. Neutrons and neutrinos do

Neutron-irradiated fibers from the Lyma mummy wrapping by Moroni. Observe the small, white, vertical streaks made by recoil protons between the bright growth nodes. There is also a faint haze in the background that was made by an associated gamma flux from the reactor.

not have any electrical charge. Neutrinos hardly interact with matter at all, the fact that made

them so difficult to detect. They have practically no chance of being stopped as they shoot through the entire diameter of the earth. The effects of neutrons depend on their energy, but they normally interact with hydrogen-containing materials to produce "recoil protons." They knock a hydrogen nucleus out of the material, producing an ionizing proton. You can see the ionization streaks of these (usually lower energy) protons (see the "Neutron-irradiation" figure).

The crystal structure of the flax fibers of the Shroud shows the effects of aging, but it has never been heated enough to change the structure. It has never suffered chemically significant irradiation with either protons or neutrons. No type of radiation that could produce either color in the linen fibers or change the ^{14}C content (radiocarbon age) could go unnoticed. All radiation has some kind of an effect on organic materials.

This proves that the image color could not have been produced by thermal or radiation-induced dehydration of the cellulose. Image formation proceeded at normal temperatures in the absence of energetic radiation of any kind.

4) How do you know that the image was not a scorch? How do you know that most of the Shroud had not been heated enough to start decomposition?

As discussed in (3) above, the crystallinity of the flax fibers in all of the parts of the Shroud that were not scorched has not been significantly degraded.

The Arrhenius Law describes the effect of temperature on rate constants for all consistent chemical reactions, as follows:

$$k = Ze^{-E/RT}$$

where k is the rate constant at any specific temperature, Z is the Arrhenius pre-exponential (related to the probability that any specific molecule(s) will react), E is the Arrhenius activation energy, R is the gas constant, and T is any specific, constant absolute temperature (degrees Kelvin). If the image were a scorch or any part of the Shroud had been heated enough to make significant changes in the rates of decomposition of any of its components, we would see changes in the structure of the flax fibers and blood. The blood still evolves hydroxyproline on mild heating, and the cellulose crystals are largely undistorted. Image and control fibers show identical crystal properties. The image is not a scorch. The cloth was not heated, not even boiled in oil.

5) How do you know that the radiocarbon sample was not valid for dating the Shroud?

The 1988 radiocarbon age determinations were carefully done. The sample preparation methods, the measurement technologies and procedures, and the data reduction were adequately planned and executed to answer the most important question: was the Shroud produced in the First Century? Damon, *et al*., reported that "The age of the shroud is obtained as AD 1260-1390, with at least 95% confidence." However, that date does not reflect observations on the linen-production technology nor the chemistry of fibers obtained directly from the main part of the shroud in 1978. The independent analyses from the different laboratories scatter more than would be expected for a homogeneous sample, raising other questions.

The 1988 sampling operation was described as follows: "The shroud was separated from the backing cloth along its bottom left-hand edge and a strip (~10 mm x 70 mm) was cut from just above the place where a sample was previously removed in 1973 for examination. The strip came from a single site on the main body of the shroud away from any patches or charred areas."

The use of a single sample, assuming it was representative of the whole cloth, defied normal procedures and protocols established before the radiocarbon study. It was a serious mistake.

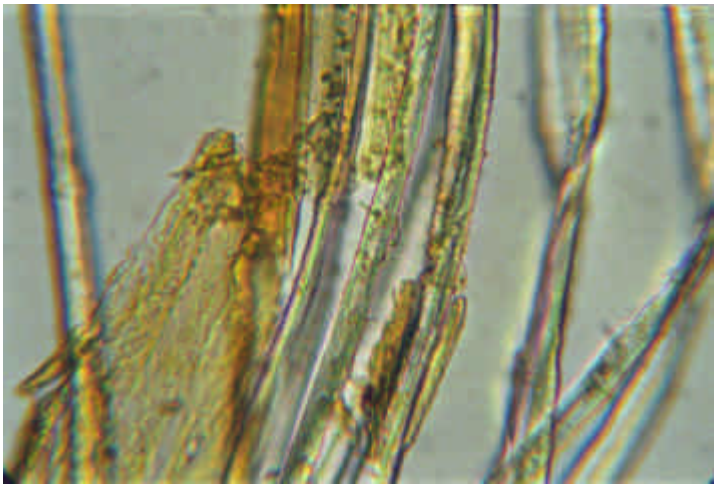
To make matters worse, Mssrs. Franco Testore, professor of textile technology at the Turin Polytechnic, and Gabriel Vial, curator of the Ancient Textile Museum, Lyon, France, approved the location of the radiocarbon sample without any serious attempt at characterizing the sample. No chemical or careful microscopic sample characterizations were made. The 1988 work did not guarantee the validity of the sample.

The area where the radiocarbon sample was obtained had been photographed in 1978 with an ultraviolet source (see "UV fluorescence"). While making the UV photographs, the source was heavily filtered to exclude visible light and the camera was heavily filtered to exclude any effect of the UV on the film. All that appears on the film is the result of pure fluorescence. All fluorescence is a result of the chemical composition of the material.

UV fluorescence photograph of the ^{14}C sample area. The small, white triangle (bottom left) is the location of the Raes sample, which adjoins the radiocarbon sample.

The non-image cloth typically shows weak fluorescence (upper right). When image appears on the cloth, it quenches the fluorescence and gives it a brown color (see "Hands" below). The small, triangular, white area is where the Raes sample was cut in 1973. The radiocarbon sample was cut upward from there about 1 cm to the right of the seam and about 7 cm long. The area where the radiocarbon sample was taken is relatively dark, a fact that is not the result of dirt, image color, or scorching. The cloth is much less fluorescent in that area, brightening into more typical fluorescence to the right. The photograph proves that the radiocarbon area has a different chemical composition than the main part of the cloth. This was obviously not considered before the sample was cut.

Raes and radiocarbon yarn show colored encrustations on their surfaces. Some sections of medulla contain some of the material, showing that it had been able to flow by capillary attraction as a liquid. The encrustation is not removed by nonpolar solvents, but it swells and dissolves in water. There was absolutely no encrustation on either the Holland cloth or fibers from the main part of the Shroud.



Al Adler had found large amounts of aluminum in yarn segments from the radiocarbon sample, up to 2%, by energy-dispersive x-ray analysis. I found that the radiocarbon sample was uniquely coated with a plant gum (probably gum Arabic), a hydrous aluminum oxide mordant (the aluminum found by Adler), and Madder

root dye (alizarin and purpurin). Nothing similar exists on any other part of the Shroud. The photomicrograph shows several fibers from the center of the radiocarbon sample in water. The gum is swelling and slowly detaching from the fibers. Many red alizarin/mordant lakes can be seen, and yellow dye is in solution in the gum. Several cotton fibers are visible, a situation unique to the Raes and radiocarbon samples.

The radiocarbon sampling area had been dyed to match the old part of the cloth. The sample chosen for dating was totally invalid for determining the true age of the Shroud.

6) How do you know that the fire of AD 1532 did not start a long-term autocatalytic decomposition of the Shroud?

Based on the facts of chemistry and current storage conditions, the Shroud of Turin is not now and has never been in imminent danger of catastrophic autocatalytic decomposition. The "restoration" of 2002 was based on an erroneous understanding of chemistry.

Autocatalytic chemical reactions are those in which the rate increases as the amounts of reactants decrease, i.e., while the materials are reacting. The most important single factor in predicting effects is the ***temperature***. When the temperature changes, the rate changes. The only severe heating episode the Shroud has suffered was during the fire of 1532. Any autocatalytic decomposition that occurred then has long since stopped as the Shroud is stored at normal temperatures.

The fundamental chemical-rate equation that describes an autocatalytic process is the following:

$$\frac{d\alpha}{dt} = k\alpha^{p}(1-\alpha)^{q} Ze^{-\frac{E}{RT}}$$

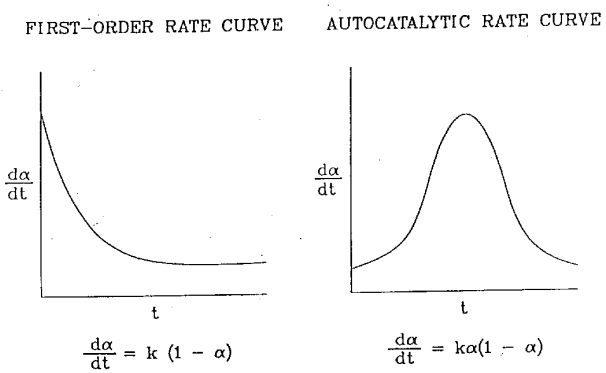
where ? is the fraction reacted at any specific time, t. The derivative, d? ?dt, is the rate of the reaction. E is the "Arrhenius activation energy," and Z is the "Arrhenius pre-exponential." Each applies ***only*** to a single specific, consistent reaction being studied. The value of the "rate constant," k is different at each specific temperature: It is a *constant* only at one temperature, and it applies ***only*** to one specific reaction. The values of E and Z are determined from a large number of k measurements at different temperatures.. Predictions of the Shroud's expected lifetime can not be made on the basis of a single rate constant. Observations made during a scorching event can not be applied to rates at normal temperatures.

E, Z, and k are the most important values in a discussion of rates and associated lifetimes of materials. All of these values have fundamental meaning in the chemical reaction. R is the "gas constant (1.9872)," a universal constant that applies to many disparate physical and chemical processes, and it is known with great accuracy and precision. T is the *absolute* temperature, expressed in degrees Kelvin (0K = -273.2?C). The exponents p and q allow the prediction of the position of the maximum rate in an autocatalytic process, i.e., the amount reacted at the maximum rate - ***at constant temperature***. Exponents higher than 2 are extremely rare.

Examples of simple and autocatalytic rate curves are shown in the figure. Notice that the rate increases with time in the autocatalytic curve, **at constant temperature**, until it reaches a

maximum reaction rate. Then the rate decreases. However, **the initial rate at any temperature is much lower than the maximum rate.** The chemical decomposition rate of cellulose is essentially zero at room temperature. Most long-term degradation of cellulose that is observed in archaeological contexts is caused by microbiological attack.

When cellulose is decomposing autocatalytically at high temperature, the rate can be returned to its initial value by cooling.



Reaction rates in solids, *especially crystalline solids like cellulose,* are much lower than the values for the same material in a solution or melt, because a crystalline lattice is stabilized by its ordered structure. The crystal structure is called "fibrillar" in materials like linen.

A major cause for autocatalysis in cellulose decomposition is the destruction of crystalline order when the material is heated above its melting point, about 260°C. With the exception of the fire of 1532, the Shroud has never faced this danger. Secondary, chemical autocatalysis is discussed below. Rates in the normal cellulose solid phase are essentially zero in the absence of acids, bases, short-wavelength light, or water and microorganisms.

When the crystalline order of cellulose is destroyed by heating, the cellulose melt is also chemically autocatalytic. The possibility for chemical autocatalysis in linen depends on the products of cellulose decomposition. Feigl and Anger [Feigl, F. and Anger, V., 1966, *Spot Tests in Organic Analysis,* Elsevier Pub. Co., New York.] describe the effects of heating cellulose as follows: "When cellulose is heated it decomposes and the resulting superheated steam reacts with unchanged cellulose to produce hexoses, which in turn hydrolyze to give hydroxymethylfurfural." The only important chemical catalyst for the autocatalytic degradation of cellulose at high temperatures is ***superheated steam.*** Superheated steam does not exist at room temperature. There is no "memory effect." The Shroud should be as stable at room temperature as any other sample of linen. The Shroud was in no danger of autocatalytic decomposition.

The decomposition rate of a crystalline solid depends on crystal perfection. When crystals are put under stress, they develop high-free-energy defects, and decomposition is much faster at the defects than it is in the parent material. If autocatalysis were a real problem for the Shroud, significant differences should have been observed around the stressed and strained stitching of the patches. STURP observed those areas, and there was no sign of accelerated autocatalysis, indeed there is no sign of any autocatalysis. Autocatalysis is not a real hazard for the Shroud.

More detailed studies have shown that the major secondary products of the thermal decomposition of cellulose are formaldehyde, furfural (2-furaldehyde), hydroxymethylfurfural (5-hydroxymethyl-2-furaldehyde), levulinic acid (4-oxopentanoic acid), and 3-pentenoic-?-anhydride. None of these are a significant catalyst for the autocatalytic decomposition of linen. Indeed,

formaldehyde, furfural, and hydroxymethylfurfural are reducing agents, antioxidants. Furfural inhibits the growth of molds and yeasts. Scorched areas are less likely to show microbiological attack.

Observations and descriptions of the Shroud through the 470 years since the fire of 1532 do not support fear of catastrophic decomposition of the cloth. There is absolutely no evidence for attack on the cloth by acids, bases, or microorganisms. Samples from all parts of the Shroud were tested for pH by STURP. No impurities that could start autocatalytic decomposition were found, confirming what was observed through the 470 years of history.

If Shroud deterioration is still a worry, one practical way to slow the rate is to keep it cold. That also has the advantage of reducing microbiological attack. As in the case of the use of "inert" atmospheres, storage at reduced temperature should carefully be considered. Too low a temperature could cause physical stress and might cause fibers to fracture. It would probably cause the thin coating of image color on the fibers to be loosened in some areas.

As a rule of thumb according to the Arrhenius expression, rates of normal reactions are increased by a factor between two and three for each 10?C increase in temperature. Some moderate cooling could have a significant effect on prolonging the life of the Shroud. Severe freezing could damage the cloth and image.

7) Why are there bands of different colored linen throughout the Shroud, and what do they prove about image formation mechanisms?

Bands of slightly different color can be seen in Shroud photographs. They are most visible in ultraviolet-fluorescence photographs (see Hands UV). Both warp and weft yarns show this property. Some areas show darker warp yarns and some show darker weft yarns. In some places bands of darker color cross. In other places bands of lighter color cross. The effect is somewhat like a plaid.

Hands UV, showing bands of color and their effect on image color density.

All of the bleaching processes used through history remove lignin and most associated flax impurities (e.g., flax wax and hemicelluloses). The more quantitative the bleaching process the whiter the product. The bands of different color on the Shroud are the end result of different amounts of impurities left from the bleaching process.

Anna Maria Donadoni, a curator at the Museum of Egyptology in Turin, pointed out locations where batches of yarn ended in the weave and new yarn had been inserted in order to continue weaving. The yarn ends were laid side by side, and the weave was compressed with the comb. The ends are often visible, and the overlaps correspond to zones of different color in the weave. The different batches of yarn show different colors.

Where darker bands of yarn intersect image areas, the image is darker. Where lighter bands intersect an image area, the image appears lighter. This proves that the image color is not

a result of reactions in the cellulose of the linen. Some impurities on the surface of the different batches of yarn produced the image color. This observation is extremely important when tests are being made on image-formation hypotheses. If image color is not simply a result of color formation in the cellulose of the linen fibers, image formation must be a much more complex process than we originally thought.

8) How fast does cellulose (linen) decompose (produce a color) compared with the impurities found on the Shroud?

J. L. Banyasz, S. Li, J. Lyons-Hart, and K. H. Shafer [Fuel 80 (2001) 1757-1763] studied real-time evolution of formaldehyde, hydroxyacetaldehyde, CO, and CO_2 from pure microcrystalline cellulose by EGA/FTIR (effluent gas analysis and Fourier transform infrared spectrometry). They detected 10 compounds simultaneously in the gas phase by FTIR. The cellulose decomposition is very complex. The quantity of formaldehyde produced is a function of heating rate, so decomposition mechanisms change depending on how fast you heat the cellulose. That is important in considering image-formation mechanisms and long-term stability vis-à-vis scorching processes.

According to A. G. W. Bradbury, Y. Sakai, and F. Shafizadch, [J. Appl. Polym. Sci. (1979) 23, pp. 3271-3280], the induction process in cellulose can be neglected above 300ºC. They observed two major decomposition mechanisms with the following constants:

$E_1 = 47.3$ kcal/mole $\quad Z_1 = 3.2 \times 10^{14}\ s^{-1}$

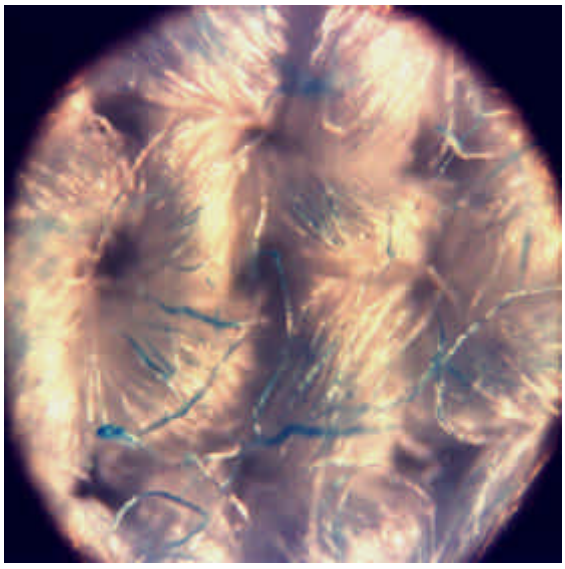
$E_2 = 36.6$ kcal/mole $\quad Z_2 = 1.3 \times 10^{10}\ s^{-1}$

They assumed that 65% of the products in the char-forming chain of reactions went to gas.

Glucose decomposes by a multi-step process. As with all of the other saccharides, the first is a dehydration/condensation reaction. The condensation processes yield carbon-carbon double bonds, which ultimately lead to color formation. Bruce Waymack of Philip Morris measured the kinetics of the first reaction as E = 23.9 kcal/mole and $Z = 1.26 \times 10^{7}\ s^{-1}$. The low-molecular-weight polysaccharides are much less stable than cellulose.

I measured the kinetics of vanillin elimination from lignin as E = 23.6 kcal/mol and $Z = 3.7 \times 10^{11}\ s^{-1}$. It is much less stable than crystalline cellulose.

Results of kinetics studies support a low-temperature image-formation process. The temperature was not high enough to change cellulose within the time available for image formation, and no char was produced.



9) How is it possible to get image only on the topmost surface of the cloth?

Because the cellulose was not involved in image formation, the color must have formed in impurities on the surfaces of the image fibers. Independent observations have proved that all of the image color resides in a very thin layer on the outside surfaces of colored fibers.

Evaporation concentration can explain the superficial nature of the image and the identical properties of the front and back images. It can also explain the "doubly-superficial" image, i.e., the presence of a superficial image on the back surface of the cloth as reported by Ghiberti and Fanti and Maggiolo.

When a solution evaporates at the surface of a porous solid, dissolved solutes are concentrated at the evaporating surface. The principle is illustrated in the photomicrograph with blue dye. A piece of linen was saturated with a dilute solution of blue dye, and the cloth was dried while laying on a sheet of Teflon. All evaporation occurred at the top surface, and the dye concentrated on that surface. It is obvious that most of the dye deposited on the highest parts of the weave and the upward-pointing fibers of the nap. A sheet of cloth that contained sugars and starches would deposit those impurities at the very topmost part of the weave after washing and drying.

10) Can some simple, natural process explain a doubly-superficial image?

When a cloth is dried on a line, impurities concentrate on both evaporating surfaces; however, more impurities will deposit on whichever surface dries faster. Any concentration of impurities can take part in the image-formation reactions. This can explain the "doubly-superficial" image.

11) How fast does a human body begin to decompose, and what are the products?

The University of Tennessee maintains an experimental area where observations are made on decomposing corpses. They find that flies lay their eggs in wounds on dead bodies, and maggots appear before 30 hours at about 23ºC. This approximates the time required for liquid decomposition products to begin to appear on the surface of a body. We could not find any evidence for the migration of liquid decomposition products through the cloth; therefore, the cloth could not have been in contact with the body for very long.

Decomposing bodies start producing ammonia (NH_3) in the lungs quite soon after death, and the ammonia diffuses outward through the nose and mouth. Ammonia is lighter than air, and it diffuses rapidly. The rate of production of ammonia decreases with time after death.

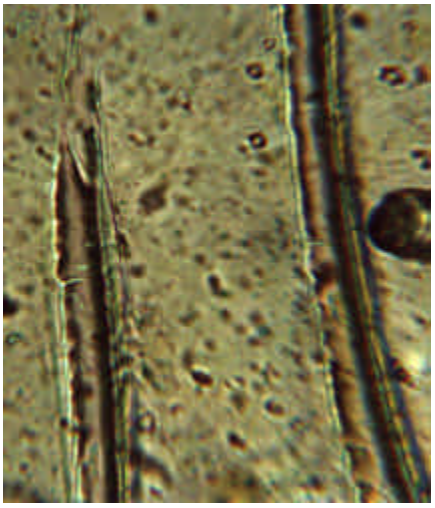
Within a few hours, depending on weather conditions, a body starts to produce heavier amines in its tissues, e.g., putrescine (1,4-diaminobutane), and cadaverine (1,5-diaminopentane). These amines are much heavier than air, and they diffuse relatively slowly. Experiments prove that slow diffusion relates to increased resolution in image formation. The early appearance and rapid diffusion of low-molecular-weight ammonia from the nose and mouth might help explain the greater amount of image color between the nose and mouth, in the beard, and into the nearby hair. It will also diffuse through the cloth more quickly and reach the back side of the cloth in greater concentration. Ammonia will diffuse about 20 cm through air while cadaverine is diffusing only 6 cm.

12) How do you know that the flax fibers were not involved in image formation?

Prof. Alan Adler of Western Connecticut University found that the image color could be reduced with a diimide reagent, leaving colorless, undamaged linen fibers behind. This confirmed spectral data that indicated that the image color was a result of complex conjugated

double bonds; however, it proved that image color was found *only* on the outer surfaces of colored image fibers. Until this time, we had assumed that the image color was a result of chemical changes in the cellulose of the linen. The most likely change would involve the dehydration of the cellulose to produce conjugated-double-bond systems Adler's observations proved that the cellulose was not involved in image formation. ***This is an extremely important observation.***

This fact was confirmed by the observation that the image color on some fibers had been stripped off of their surfaces by the adhesive of the sampling tapes. The photomicrograph shows the places where two fibers were pulled out of the adhesive leaving their colored coating behind. The coating is too thin to measure accurately with a standard microscope; however, it appears to be 200-600 nanometers thick (in the range of a wavelength of visible light).



The bands of color and the fact that all of the image color appears only on the outer surfaces of the fibers, suggested that image formation involved a thin layer of impurities. Because the cellulose was not colored, the impurities had to be significantly less stable than cellulose.

This also suggested that the impurities were the result of cloth-production methods, and they should appear on all parts of the cloth. A search for carbohydrate impurities on the Shroud confirmed McCrone's detection of some starch fractions. Starch and low-molecular-weight carbohydrates from crude starch would color much more easily than would cellulose as a result of either thermal dehydration or chemical reactions.

Any image-formation mechanism that would result in color formation ***inside*** the linen fibers must be rejected. Some "theories" that have been mentioned that would cause coloration inside fibers are penetrating radiation, high temperature scorching (hot statue, painting with a torch, etc.), and catalyzed dehydration of the cellulose. ***Image fibers are colored only on their surfaces.***

13) Are there any other ways than radiocarbon to date the Shroud?

Archaeologists use many different methods to estimate the age of artifacts and/or soil strata that contain artifacts. One of the most important ways is to observe changes in technology: methods used to make tools change with time. There is a big difference between the hand axes made during the Paleolithic and fine arrow points made a few hundred years ago. The technology used to make the Shroud was much different than that used during medieval times or modern times.

Stone tools hydrate and form a patina. Its thickness indicates age. Similarly, all organic materials tend to decompose or change structure with time. Proteins undergo "racemization." Their amino acids change their optical properties. This would apply to the blood on the Shroud.

The DNA in blood and tissue samples degrades with time. The DNA in Shroud blood samples shows the effects of significant aging: only short lengths of the chain remain intact. The reported ABO typing results are very suspect and probably not valid. However, the results prove appreciable age for the Shroud.

Crystalline materials undergo damage that is caused by natural sources of radiation, and Shroud fibers show some evidence for changes in their crystal structure.

Some compounds like lignin change composition with time. The lignin in the Shroud does not give the normal microchemical test for vanillin, indicating that it is quite old. Measurements of the chemical rate for loss of vanillin estimates an age for the Shroud of more than 1300 years, depending on storage conditions.

14) What could be observed about image properties by looking at the damage from the fire of 1532?

See FAQ 15 below.

15) What options for future scientific study of the Shroud's history and image were lost as a result of the "restoration" of 2002?

Although the fire of 1532 nearly destroyed the Shroud, it created opportunities for many types of chemical studies. We would never use the same destructive methods of observation on an undamaged relic, but misadventure gave us many unexpected options. The important fact is that, before the restoration, we could look at the chemistry of specific locations on the Shroud where scorches intersected image, blood, serum, and water stains. The restoration destroyed much chemical information at those intersections.

If the image had been painted or retouched, some foreign materials had to be added to the cloth. The pigments and vehicles (e.g., the ochers, realgar, orpiment, mosaic gold, glair, gums, and glues) would have been subjected to a violent "chemical test" during the fire. The temperatures, temperature gradients, pyrolysis products, and water used to extinguish the fire would have changed the chemical composition of most foreign materials. Before going to Turin in 1978, we did many experiments on the stability of the painting materials. We had hoped that future observations on the Shroud could compare predictions with reality. The restoration disturbed exactly the areas of most chemical importance.

The persons involved in the restoration of June and July 2002 did not appear to be familiar with previous scientific observations, and they did not consult chemists with different areas of experience or chemically-oriented textile conservators. The restoration destroyed much of the chemical information that could have been recovered as a function of position on the surface of the Shroud.

The fire of 1532 produced many extremely reactive pyrolysis products, and the fire was extinguished with water. All paints that were used during or before medieval times (except gold) are changed by heat and/or the chemically reducing and reactive pyrolysis products of the cloth (e.g., formaldehyde, furfural, organic acids, CO, etc.). For example, red hematite would have been reduced to black magnetite. This fact provided one basis for refuting McCrone's claim that the image was painted with hematite. We planned to look for the products of such reactions. Some medieval painting materials become water soluble, and they would have moved with the water. A huge amount of chemical information existed in the scorches.

Most organic colors are much less stable than cellulose (linen) and the normal inorganic pigments. Experiments in 1978 showed that scorch lines in impurities precede the scorches in pure linen. Most organic materials, including natural products, change in predictable ways in

response to heating and the known products of cellulose pyrolysis. We even tested squid ink, which had been reported being used in ancient times.

It might still be possible to extract the products of the reactions from the materials recovered during the restoration, assuming that samples were segregated and locations were recorded. Such information could be important for suggesting the chemical composition of the image. Most possibilities for directly studying the effects of the fire on image materials were destroyed by the restoration of 2002.

Visual and microscopic observations on the Shroud in 1978 indicated that image color or its reaction products did not move with the water. Other unidentified products did move. Aldo Guerreschi has suggested that two different sets of water stains exist on the Shroud. They could contain interesting chemical and historical information. We had counted on the tape samples and possible future direct studies on the scorch/water-stain areas of the Shroud for detailed chemical confirmation of what did and did not move with the water. Now the tape samples are kept from scientific study by the officials in Turin, and scorches were destroyed by the "restoration."

The Shroud showed many locations where scorches of different severity intersected image and/or blood. Thermal gradients can be estimated on the basis of scorch colors. Temperatures are the most important factors in calculating chemical rates. We made predictions on the kinds of products that might appear in image areas as a result of reactions between its components and the pyrolysis products and water. These predictions could be used to test many of the hypotheses that have been proposed for image formation.

I took samples from many scorch/water/image intersections in 1978, but observations on them generated more questions. Answers required additional observations and/or samples. The samples are now secreted in Turin. As a result of the restoration, any future studies will be much more difficult and expensive: Some will be impossible.

The Shroud is a structure composed of chemical compounds, and all of the main ones have been studied in detail. They are published in chemical text books. Chemical analyses can yield considerable definitive historical information. All manipulations of the Shroud should be considered in detail in order to preserve as much information as possible.

Linen-production technology has changed through the centuries. We have assembled chemical information related to the technology, and we have consulted textile experts who have done detailed chemical research that relates to the composition of the Shroud. Our detailed analyses suggested that the cloth had been prepared by technology common before about AD 1200. It best resembles linen made in the Near East during Roman times. These results do not agree with the date published in 1989. The differences can be explained on the basis of samples from the radiocarbon area, but all scientific observations should be confirmed. Samples from the restoration might help confirm the properties of the radiocarbon sample; however, the persons involved in the restoration fight any attempt to test and confirm the truth. No scientist in Torino will discuss the problem, and the custodians refuse to recognize the problem. Ethical science is impossible in such an environment.

Lignin is a structural polymer that is found in all plants, including flax. Linen is bleached in an effort to remove as much lignin as possible, but some lignin always remains in linen. Lignin slowly ages with the loss of vanillin (4-hydroxy-2-methoxybenzaldehyde). A very sensitive microchemical test exists for the detection of traces of vanillin. It is easy to detect vanillin in modern lignin, it is harder to find in Medieval linen, and no test can be obtained from the few Shroud fibers that are still available for study. The lignin in samples from the Dead Sea scrolls (ca. AD 70) does not give the vanillin test. This observation would suggest that the linen

of the Shroud is very old, casting doubt on the accuracy of the 1988 date. Observations on the lignin could be confirmed with samples from the "restoration"; however, such samples are jealously guarded in Turin.

The tape samples show that much of the charred material is elemental carbon. It is very inert chemically. It would not have changed during the 470 years since the fire. Published concerns about isotope fractionation during the fire are nonsense. The carbonized material can easily be chemically cleaned of any organic deposits that might have appeared after the fire, making it an ideal material for radiocarbon dating. Before the restoration, the carbon from specific areas could have been dated separately, giving critical information about the homogeneity of the cloth as well as "clusters" of dates. Clusters of dates are more reliable than dates on single samples.

Dr. Max Frei took tape samples to recover pollen grains from the surface of the Shroud in 1973 and 1978. Sweeping claims have been made on the basis of Frei's samples, but published photomicrographs do not support the claims. Other reports suggest that there were major changes in the number of grains found on Frei's tapes between the time of his death and more recent publications. The pollen data badly need confirmation. The restoration totally destroyed any chance to take valid additional pollen-grain samples from the surface of the Shroud. A suspicious person might wonder whether the "restoration" was rushed through to prevent ethical work on confirming both chemical and pollen observations.

Biblical accounts suggested several types of compounds that might have appeared on the cloth (e.g., aloes, myrrh, sebaceous secretions, etc.). We planned and executed chemical analytical methods that could detect them in 1978. Those methods were extremely sensitive, but they did not detect squalene or myrrh. These results could have been confirmed by additional tests on the Shroud, but the "restoration" has totally changed the Shroud's surface.

The surface of the Shroud could have been analyzed by Electron Spectroscopy for Chemical Analysis (ESCA), which observes the top few nanometers of the surface. Now that the surface has been disturbed, that powerful technique will be much more difficult to apply, and results will be ambiguous. This is a terrible, discouraging loss for Shroud chemists.

The problems associated with surface analyses are now compounded by the fact that thymol was used to sterilize the reliquary after the 1988 sampling operation. Thymol is a phenolic compound that will react with many functional groups on the Shroud. This will confuse image analyses, and it may result in damage to the cloth. As one example, we found a significant amount of iron in the Shroud's cloth. Iron reacts with phenolic compounds to form complexes, and some of them are intensely colored. I would urge the custodians of the Shroud to consult with chemists before taking other irreversible actions.

One justification for the hurried, secretive restoration was a fear of "autocatalytic" degradation of the cloth. No experts on chemical kinetics were consulted. The Shroud has not been and is not now in danger of autocatalytic degradation (see FAQ 6).

Chemical autocatalysis is responsible for the destruction of books that are made with cheap, acid paper. Claiming analogy with the Shroud is mischievous. Adler and Schwalbe made the following comment: "Previous chemical reactions on the cloth, e.g., the retting process in manufacture of the linen, the known historic fire and its extinguishment, and previous display and storage procedures, have left a variety of chemical structures on the surface that can act as oxidants and also as catalysts. For example, the acidic structures produced by previous oxidative activity can strongly promote various types of autocatalysis" [A. D. Adler and L. A. Schwalbe, "Conservation of the Shroud of Turin," Shroud Spectrum International, No. 42, December 1993,

Indiana Center for Shroud Studies]. Such claims led to the secret restoration. Secrecy is never productive, and the plans for a restoration should have been reviewed with as large a group of scientists as possible. The restoration was a terrible mistake.

16) What are the optical and physical properties of flax fibers (linen)?

Flax fibers look like small lengths of bamboo under a microscope.

The gross internal composition of a flax fiber is shown in the figure (after Cardamone).

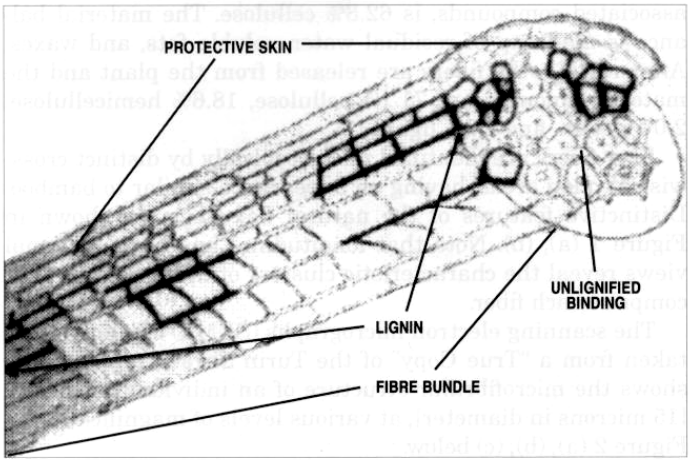


Fig. 1 (b)
Microscopic details of the lengths and cross-sections of typical flax fibers.

The cellulose molecules in flax fibers are folded back and forth in a fairly regular arrangement, and they show the properties of crystallinity. The fibers are composed of closely packed "ultimate cells" of the fibrillar structure that are cemented together with holocellulose and lignin. You can see the ultimate cells under a microscope, and abraded fibers often show ultimate cells sticking away from the surface. These were the structures that were mistaken for "filamentous bacteria" by Garza-Valdes.

When you rotate the stage of a petrographic microscope with crossed polarizers while looking at a flax fiber, straight lengths change from black to colored every 45?. The fiber is birefringent and has an ordered structure. Most of the cellulose of the fibers is in a crystalline structure. In structures like flax, it is called a "fibrillar" structure.

McCrone ignored our agreements for work on the STURP sampling tapes: he stuck them all down to microscope slides. This made observations much harder; however, flax and cotton fibers can still be distinguished by their indexes of refraction.

Crystallographic observations must be made on the specific fibers that reach extinction at the same angle as the tape (while everything is black). The index of refraction of a normal linen fiber parallel to its length is nearly identical to that of the adhesive on the sampling tapes (it nearly disappears). That index is very close to 1.515. The index across the fiber is appreciably lower than the adhesive. The indexes of refraction and crystallinity of image fibers are identical to unaffected fibers. Bent, crushed, or otherwise damaged fibers show strain dichroism and will give an erroneous index. Most flax fibers show intense birefringence colors when they are viewed at a 45º angle from the plane of polarization of the microscope.

Cotton has a low birefringence, usually appearing white (first-order white), and it is a thin, wide tape that shows periodic reversals (twists).

17) What image properties have been observed objectively by scientific methods?

The image is extremely faint and difficult to see. Much more detail can be seen in contrast-enhanced and ultraviolet photographs; however, they are somewhat misleading to

studies on image formation. Whatever produced the image color did not produce very much color. Scientific observations were planned in order to learn as much as possible about the image distribution and chemical composition.

The Shroud was observed by microscopy, visible and ultraviolet spectrometry, infrared spectrometry, x-ray fluorescence spectrometry, and thermography. Later observations were made by microchemistry, petrographic microscopy, scanning-electron microscopy, energy-dispersive x-ray analysis, pyrolysis-mass-spectrometry, and laser-microprobe Raman analyses.

Without making any assumptions that are based on the appearance of the image, some statements of fact can be proved from the scientific observations.

1) Reflectance spectra, chemical tests, laser-microprobe Raman spectra, pyrolysis mass spectrometry, and x-ray fluorescence all show that the image is not painted with any of the expected, historically-documented pigments and media.
2) No painting pigments or media scorched in image areas or were rendered water soluble at the time of the AD 1532 fire.
3) Direct microscopy showed that the image color resides *only* on the topmost fibers at the highest parts of the weave.
4) The color density of any specific image area depends on the batch of yarn that was used in its weave. The cloth shows bands of slightly different colors of yarn.
5) Adhesive-tape samples show that the image is a result of concentrations of yellow/brown fibers.
6) The image does not fluoresce under ultraviolet illumination.
7) The image of the dorsal side of the body shows the same color density and distribution as the ventral, and it does not penetrate the cloth any more deeply than the image of the ventral side of the body.
8) Thermography proved that the emittance of the image was the same in all areas. The entire image formed by the same mechanism. Spectra and photography confirmed this observation.
9) The only image color easily visible on the back side of the cloth is in the region of the hair. Fanti and Maggiolo were able to show traces of face and hand images by image processing.
10) No image formed under the blood stains.
11) The image-formation mechanism did not damage, denature, or char the blood. The blood can be removed with a proteolytic enzyme. The blood produced hydroxyproline at low temperatures in the pyrolysis/ms spectra. It was never heated significantly. Image formation had to be a low-temperature process.
12) Image color can be chemically reduced with diimide, leaving colorless cellulose fibers. All image color resides on the outer surfaces of the fibers.
13) The medullas of colored image fibers are not colored: *The cellulose was not involved in color production.*
14) The color of image fibers was often stripped off of their surfaces, leaving molds of the fibers in the adhesive. Growth nodes can be seen in the molds. The colored layers show all of the same chemical properties observed on intact image fibers (see 12 above). All of the color is on the surfaces of the fibers. The colored layer is 200-600 nanometers thick.
15) Chemical tests showed that there is no protein painting medium or protein-containing coating in image areas. The image was not painted with glair, and it follows that microbiological activity did not produce the image.
16) Microchemical tests with iodine detected the presence of starch impurities on the surfaces of linen fibers from the Shroud. An impurity layer could be seen by phase-contrast microscopy.

17) There is no evidence for tissue breakdown (formation of liquid decomposition products of a body). Body fluids (other than blood) did not percolate into the cloth.
18) Any radiation that is energetic enough or sufficiently intense to heat the cloth enough to cause the initial dehydration reactions of cellulose would penetrate into a fiber to a distance determined by its energy. Simple heating would change both the cellulose and blood. Both protons and neutrons leave characteristic tracks in flax fibers. The image fibers could not have been colored by energetic radiation.
19) Rapid heating, as when linen is scorched with a torch, leaves characteristic, small balls of solidified melt at the ends of fibers. No such features can be observed on the Shroud.
20) The cloth does not show any phosphorescence.
21) The blood on the cloth is still largely red. Old blood is normally black. Blood that has been hemolyzed remains red for a long time.
22) Neither aloes or myrrh could be detected on the cloth.

18) Can the presence of a "bioplastic polymer" coating anywhere on the Shroud be confirmed? Could it affect the radiocarbon age determination?

No**.** Stephen Mattingly of the University of Texas has proposed a hypothesis that a "bioplastic" coating on the Shroud produced an error in the ^{14}C analysis that was used in obtaining the 1988 age estimate for the Shroud of Turin. He also proposed that common skin bacteria produced the image. I believe that there are several things wrong with these hypotheses.

Even assuming that the coating formed all at once in the 20th Century during a high-fallout time, when bomb-produced ^{14}C was high, an observable error in the age determination would require the addition of a significant amount of material to the surface of the Shroud. Mattingly proposes that the added material is a product of microbiological action. Such microbiological processes require fixed carbon, nitrogen, phosphate, sulfur, etc., to produce the products observed as biopolymers. The chemical components of biopolymers can be detected with great sensitivity.

Joan L. Rogers took authentic Shroud fibers, which she laboriously extracted from the STURP sampling tapes by washing them free of adhesive with xylene (not a solvent for any "bioplastic polymers"), to Metuchen, NJ, for laser-microprobe Raman analysis. The analysis is extremely sensitive, but nothing was observed that would indicate a "bioplastic polymer."

She also took fibers to the NSF Mass Spectrometry Center of Excellence at the University of Nebraska. They did pyrolysis-mass-spectrometry on the fibers. Their system was sufficiently sensitive to detect traces of the oligimers (low-molecular-weight polymers) from the polyethylene bag that Professor Luigi Gonella of Turin had used to wrap the Raes samples; however, the polyethylene never touched the samples. They were protected inside acid-free conservator's paper.

The NSF facility observed the pyrolysis products of polysaccharides as a function of their relative temperatures of decomposition. For example, they detected traces of furfural from the anomalous pentosan gum layer in the radiocarbon-sample area. They easily detected hydroxyproline from the proteins of the blood spots. No evidence for a bioplastic polymer was detected on either non-image or image areas.

R. Rogers, J. Rogers, and A. Adler spent many hours looking at samples from the Shroud under microscopes and running microchemical spot tests. There were no anomalous indexes of refraction, there were no amorphous materials cementing fibers (except for the blood/serum and

some pentosans on yarn segments taken from the Raes and radiocarbon samples), and there were no sulfur compounds on the surface (except in the blood/serum areas). No "bioplastic polymers" are absolutely devoid of amino acids (proteins) and sulfoproteins. There is no significant amount of bioplastic polymers on the main part of the Shroud.

In order to change the carbon date, the organisms Mattingly postulates *must* be utilizing carbon dioxide from the atmosphere. A ^{14}N n-p ^{14}C nuclear reaction in the upper atmosphere is the source for ^{14}C-containing carbon. The addition of modern carbon is the only way to decrease the apparent age of ancient carbon-containing material. The organisms that fix CO_2 are photosynthetic, and they are "obligate aerobes." They must have oxygen in their atmosphere as well as CO_2. They need a source of energy. They get that energy by absorbing light into complex colored molecules that then provide electrons for the chemical reactions that involve the carbon and other reactants. The final products of photosynthesis are sugars, polysaccharides, nucleic acids, proteins, etc. Nature builds flax (linen), trees, grass, and little colored microorganisms by photosynthesis. All of the ^{14}C in our bodies comes originally from photosynthetic organisms. The most important organisms that fix CO_2 are plants, mostly green plants.

Mattingly's postulation of an appreciable amount of slime/biopolymer requires photosynthetic aerobes. They all use water, CO_2, and light, and they produce fixed carbon and oxygen. The oxygen we breathe comes from photosynthesis. Appreciable photosynthesis would not be expected on the Shroud, because historically it was stored dry in a dark place.

All photosynthetic organisms contain intensely colored pigments, for example chlorophyll. All such pigments absorb visible light and reflect intense colors. They all show distinctive spectra. Some of the most important observations made by STURP in 1978 were the reflectance spectra of the image, blood, and non-image areas of the Shroud. We could not have missed any pigments that are involved in photosynthesis.

If the organisms involved in biopolymer production (like fungi) used only the carbohydrates in the Shroud for their metabolic purposes (we call it "rotting") and did not fix atmospheric carbon by using pigments, the biopolymer product would show the same carbon age as the Shroud. Such effects have been observed. The organisms would use fixed carbon (e.g., the sugar units of cellulose) and yield carbon dioxide and cell components. Only part of the metabolized carbon would end up in a slime/polymer layer, and the cloth would tend to disappear much faster than the polymer appeared.

All biopolymers are products of living organisms. They contain proteins, amino acids, and nucleic acids. Algal cells contain 3.9% nitrogen and 3.3% phosphorus. Fungal cells contain about 0.9% phosphorus and 2.9% nitrogen. Compounds containing these elements can be detected by several of the analytical methods STURP used. The polymers can be nearly pure polysaccharides, but they all give protein spot tests.

STURP used all of the protein spot tests, e.g., Hycel biuret followed by Fisher Folin reagent, biuret Lowrey, amido black, iodine-azide to look for sulfoproteins, and a sensitive pyrolysis test that detects the purine from proteins. There was no protein in areas other than the blood flows. There was no bioplastic-polymer coating.

Mattingly and Garza-Valdes presented a photomicrograph of a linen fiber from the radiocarbon sample. It shows a thick coating and what are indicated to be "filamentous bacteria, a snake-like growth." They did no analyses to support their claims, and they apparently know nothing about the structure of linen. Features identical to the "filamentous bacteria" are common in linen samples. They are what are called "ultimate cells."

Linen fibers are made of parallel bundles of these cells, cemented together with lignin and hemicelluloses. Details can be found in a paper presented by Jeanette Cardamone ["The Turin Shroud Past, Present and Future," International Shroud Scientific Symposium (Torino 2-5 March 2000)]. There are images of flax fibers, drawings, and text explanations. She has said that: "Any fuzziness could be due to abrasion that causes micro-fibers to develop on the surface of the fiber and, critically, remain attached to it." In other words, things that look like filamentous bacteria are to be expected on linen fibers.

Ultimate cells are easy to differentiate from bacteria, because the ultimate cells are crystalline and birefringent. It is too bad that the "bioplastic-polymer" proponents did not do any analyses of their samples. They have caused massive confusion and mischief.

19) Could a "bioplastic polymer" affect the radiocarbon age of the Shroud?

A good discussion of this problem was presented by Harry Gove in the paper that presented the bioplastic-polymer hypothesis [Gove, Mattingly, David, and Garza-Valdes, Nuc. Inst. and Methods in Physics Res. B, 123 (1997) 504-507].

It would be important to know when the contamination appeared in order to know how much effect it would have on the date. Obviously, if all of the contamination occurred in about AD 33, there would be no change in the apparent age. If all of the contamination appeared at the time of the fire of 1532, 79% of the carbon in the Shroud would have to have been from the contamination and only 21% from the original cloth in order to give a date of 1357.

This problem applies to all postulated types, amounts, and ages of possible contamination. Contamination had little or no effect on the age reported by Damon et al.