

## THE SHROUD FABRIC AND THE BODY IMAGE: CHEMICAL AND PHYSICAL CHARACTERISTICS

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### Abstract

A variety of investigative techniques has been applied to the study of the fabric of the Shroud of Turin and the frontal and dorsal body images on its surface by a variety of independent experienced investigators. These investigations include photographic studies (reflection, transmission, IR thermographic, and ultraviolet emission), computer image analysis, spectroscopic studies (X-ray transmission and fluorescence, electron microprobe, reflection ultraviolet-visible spectroscopy, infrared spectroscopy, micro-FTIR spectroscopy, various types of optical microscopy), and wet chemical testing (including enzymatic and immunochemical analysis) of materials removed from the surface of the Shroud. These researches at both the macroscopic and microscopic level confirm, complement, and supplement one another so as to provide us with a consistent set of observed physical and chemical characteristics for the Shroud fabric and the body images on its surface. The images are anthropometrically correct for a Semitic adult male human being, as supported by the immunological and forensic studies. The mechanisms to form the body and blood images (contact) are different, with the blood images going onto the cloth first and out of stereoregister with the body images. The body images were produced by some as yet unknown collimated information projective process that upon computer image analysis demonstrates that the cloth enfolded a forensically correct three-dimensional human male body shape. The body images are superficial and lie only on the top exposed fibers of the threads comprising the weave of the cloth, do not penetrate the cloth, nor show capillary flow under the unexposed threads of the weave. The image fibers are brittle, show evidence of some corrosive process and no evidence of applied coatings and/or particles under microscopy, are not cemented to one another, and show a uniform absorbance at the microscopic level. Therefore the shading of the observed macroscopic image is formed by the number of image colored fibers per unit area, an areal density image, and not a pigment concentration gradient image. The chemical, microscopic, and spectroscopic studies show no evidence for any applied particles, stains, dyes, or pigments either comprising the image or contributing to its formation. The chromophore of the image consists of conjugated carbonyl functional groups intact with the cellulose structure of the linen and formed by some type of dehydrative oxidation mechanism. The details of this chemical process are as yet undefined. These established criteria have been used to evaluate a number of conjectures and hypotheses concerning the Shroud and in particular have been employed to invalidate a large number of recent proposals claimed to explain the

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mechanism of the formation of the body images on the Shroud of Turin. They are also invaluable guides in our exploration of measures that must be undertaken in order to best preserve and conserve the cloth and its unique images.

## **Introduction**

The 4.3x1.1 meter image-bearing linen cloth known as the Shroud of Turin became an object of religious and historical dispute following its display in the mid-1350s at Lirey by the de Charny family, as they declared it to be the authentic burial cloth of Jesus. It first became scientifically polemical after the 1898 Exposition in Turin, when for the first time it was photographed by Secondo Pia.<sup>1</sup> Scientific interest was aroused due to the observation that the plate bearing the photographic negative of the body showed details more clearly and gave a more natural appearance to the body images than the visually observed image on the cloth, although the blood images behaved as expected. As its known history predated the invention of photography, this fact stimulated scientific inquiry, hypothesis, and controversy.<sup>2-6</sup> A large variety of investigative techniques carried out by many types of independent investigators have created a large corpus of scientific information on the Shroud. This has been reported in many general and specialized reviews, monographs, conference proceedings, and professional journal publications.<sup>7-19</sup>

## **Science and the Shroud**

The validation of scientific conclusions differs from the criteria used in historical arguments in that hypotheses must be testable by a reproducible experiment. For example, determining the chemical structures comprising the body images on the cloth can test whether or not it is a painting. On the other hand, scientific studies cannot establish the authenticity of the Shroud as Christ's burial cloth, but only its disauthenticity, as no acceptable laboratory experiment exists yielding the identity of the human image seen on the cloth. However, evidence that it is a painting would disauthenticate it. Furthermore, initial test results supporting a hypothesis do not necessarily prove it. An alternative hypothesis equally well supported by the observations is always possible, e.g., the presence of interferences can lead to false negative or positive conclusions. The test may not be sensitive enough to draw a proper conclusion or it may be so sensitive that it will give misleading conclusions. There also exists the problem of errors, both random (affecting precision, i.e., reproducibility) and systematic (affecting accuracy), particularly for quantitative measurements. The investigator must carry out enough measurements to establish precision and enough control experiments to distinguish which of all reasonable possible testable explanations best fits all the data. One must not simply select or delete data that favors what might seem to be an obvious acceptable conclusion. Scientific truth becomes a matter of relative probabilities to which one approximates by continued application of the scientific method utilizing further testable hypotheses and experiments.

## **Image Investigations**

Vignon was the first to investigate the images on the Shroud.<sup>2, 3, 7</sup> He noted that, while the body images appeared "reversed" to what was expected, the blood

images were as expected. This suggests that these two types of images got onto the cloth by different processes. He demonstrated that both painted images and contact images did not reproduce the appearance of the Shroud images. He noted that the body images appeared to be projected onto the cloth, while the blood images were forensically correct for those of clotted wounds and not fresh flowing blood. Vignon also initiated the iconographic theory relating the Shroud images to previous artistic works to indicate the historic antiquity of the images.

Several different types of photographic studies have been conducted on the Shroud and in several regions of the electromagnetic spectrum.<sup>7</sup> These photographs were further subjected to several forms of analysis by different types of computer algorithms. These studies have then been compared to the microchemical and spectroscopic investigations to test the consistency of the conclusions drawn.

Using appropriate light sources and filters a series of ultraviolet fluorescent photographic images were made of the Shroud and compared to color reflectance photographic images taken of the same areas.<sup>20</sup> The waterstains, scorches, body images, and blood marks all appear as red brown to brown yellow images of approximately the same range of intensity variation in the color reflectance photographs. However, these images all appear quite differently in the ultraviolet emission and absorption photographs. The background cloth shows a light greenish yellow emission not always seen in other known older linen cloths and perhaps suggesting the presence of some type of thin coating of a fluorophore such as pectic substances left over from the retting of the original linen. The scorches show the typical reddish orange fluorescence associated with scorched cellulosic fabrics. The assignments of these two types of emission are in agreement with control studies on other linen fabrics.<sup>33</sup> The body images absorb somewhat more strongly than in reflectance, but do not show any emission characteristics. Therefore the body images were not produced by a scorching type process, but their mechanism of production did chemically modify and quench the background cloth fluorophore. Like the body images, the waterstains also appear somewhat darker than in reflectance and show no emission. However, they now show more color variation than in reflectance, as might be expected for images of some type of chromatographic diffusion process. The blood marks have their own characteristics.

A series of color microphotographs of the different types of image areas on the Shroud were made at magnifications ranging from 3.6x to 36x.<sup>21</sup> Utilizing the microscope employed in making these image area photographs, a visual mechanical examination of these same image areas was also conducted with the aid of a probing needle.<sup>9, 10</sup>

In contrast to the blood area images, the body image areas, though not as lustrous as the non-body background image areas, still retain some of the typical luster characteristic of linen.<sup>22</sup> They also do not show any evidence of abrasion or cementation to one another. Examination with the probing needle confirms that there is no cementation, that the body image fibers are more brittle than those of the non-body image background fibers, no evidence for any coatings, and that there is no evidence of capillarity.<sup>9, 10</sup> Thus there is no evidence for an artist's

pigment binder. The body image coloration does not appear under the crossing threads of the weave (no capillarity) or penetrate the cloth, but it actually goes only one fiber deep into the threads of the weave. The body image literally lies only on the very top exposed fibers of the weave of the cloth leaving the unexposed fibers of the threads of the weave unchanged in color from that of the background. Furthermore all the modified (colored) portions of the fibers show a uniform straw yellow coloration, as confirmed by a densitometric study of these photoimages, yielding a less than 2% variation in the absorbance of the individual colored body image fibers.<sup>9</sup>

This uniformity of color of the body image fibers again argues against the body image being a painting. To provide shading and detail in a painting, an artist varies the concentration of an applied pigment thus creating a variation in color by a pigment concentration gradient. However, the body images seen on the Shroud are provided by varying the number of uniformly colored fibers per unit area, i.e., it is an areal density image.<sup>9</sup> Thus the presumptive painter would have to monitor the number of fibers he paints per unit area of his painting while visualizing in his mind's eye the macroscopic image he is trying to create. Note that a single linen fiber is about half the thickness of an average human hair, putting rather severe restrictions on the size of the artist's brush and the time required to produce a finished painting. This uniformity of the colored fibers might be possibly construed as evidence for a dry powder contact transfer process. However, there is no evidence seen in the microscope for the presence of the particle particulates required and the color of these body image fibers cannot be removed by rubbing or brushing with the probing needle. In particular it should be noted that this straw yellow color of the body image fibers does not match the color of any of the known forms of ferric iron oxides.<sup>23</sup>

The burn, scorch, and waterstain marks all penetrate the cloth and the low power microscopic image examination of their areas of intersection with body image areas provides further confirmation of Vignon's arguments against the body images being a painting.<sup>9, 24</sup> Though the scorches can be seen to clearly have conducted heat into the body image areas, there is no evidence of any color change along the heat gradient as would be expected if the body image chromophore was an organic pigment or/stain or if it was a yellow hydrated form of ferrous iron oxide. Similarly, while the waterstain margins give the appearance of chromatographic diffusion of material to these edges, the body images within the waterstains show no change in their color, arguing against the presence of any water soluble pigments, stains or applied powders as the chromophore. It is of interest to note that the margins of the waterstains have a 'rusty' appearance in these microphotographs.

Further evidence for the body images being only one fiber deep is demonstrated by a transmission photograph of the Shroud.<sup>9</sup> This photograph was produced by placing the light source behind the suspended cloth and recording the image of the radiation transmitted through the cloth. In the usual reflectance photographs of the Shroud the light source is placed in front of the cloth and the recorded image is then that of the radiation reflected from the surface of the cloth. In the reflectance photographs the images of the waterstains, scorches,

body and blood images are all approximately of about the same intensity. In the transmission photograph the waterstains, scorches, and the blood marks are all still clearly evidenced, confirming that they do penetrate the cloth. However, the body images have almost completely disappeared. In the reflectance mode the colored body image fibers produce 100% of the reflected radiation recorded, but in the transmission mode they only contribute about 1% of the radiation recorded, thus confirming their superficial one fiber deep nature.

X-ray radiographs of the Shroud were taken employing a medical type diagnostic instrument.<sup>25</sup> The waterstains, burned areas, and the details of the weave were all that were evidenced in this study. The body images (and also the blood marks) are not seen. Under the conditions employed one expects strong absorption characteristics for the element calcium, the presence of which is confirmed chemically<sup>24</sup> and also spectroscopically<sup>26</sup> to be in the linen fibers. This explains why the cloth weave is seen clearly and also explains why the waterstain margins show up strongly, as one would anticipate chromatographic concentration of this element in these margins under the conditions imposed by the 1532 fire.

Infrared thermographs of the Shroud were also taken.<sup>27</sup> This technique has been applied in the examination of paintings to detect evidence of any underlying paint structures or to detect evidence of a painter outlining his composition. Neither of these types of evidence was seen, again in agreement with the conclusion that the body images are not paintings. However, the body images, blood marks, and burned areas can be distinguished from one another and from the background cloth, indicating differences in chemical composition between these different areas due to differences in the infrared spectral characteristics.

Several types of computer studies employing various types of algorithms have been carried out on the photographic images of the Shroud.<sup>28, 29, 30</sup> For example, the black and white images were scanned into a computer with the intensities at each pixel being assigned a gray scale value. The program then removed the pixels at each descending gray scale value a level at a time until only the cloth weave pattern remained. At each gray scale level the pixels were observed to disappear at random with no evidence of a directional pattern. This demonstrates that there is no evidence for a brush mark pattern as would be expected for a painting.

The body images were also examined with a VP-8 image analyzer.<sup>30</sup> This instrument treats the intensity of the image at each pixel point as if it were a projection from a surface to a receiving surface. The algorithm employs an inverse distance function analyzer such that darker pixels are translated into points closer to the receiving surface and pixels of lighter intensity are translated into points farther away. The shape of this distance projection is then displayed on a video screen. When the Shroud image is analyzed with this instrument an excellent correlation of the image intensities to the three dimensional shape of a human male body is revealed, i.e., true 3-D information is encoded into the Shroud's body images. The same results can be obtained using other types of image analysis programs.<sup>28, 29</sup> It should be noted that the first evidence for encoded 3-D information in the Shroud images was worked out using sheets of tracing paper.<sup>31</sup>

Further refinements of this analysis<sup>30</sup> show that the distances encoded are not from a body surface to a taut cloth simply stretched over the body, but to a cloth surface actually draped over the body. Further, the information transfer process was shown to be collimated (not isotropic), as is consistent with the absence of any body image between the heads of the two body images, i.e., the top of the head is not seen. This implies the presence of some type of imposed linear field being involved in the mechanism of image formation. Therefore the process producing the body images must involve some type of collimated radiational mechanism, transferring energy from a human body shape to draped cloth covering this body shape, and with the amount of energy transferred at each point in a collimated process to produce an image that is inversely proportional to the distance between the two surfaces at each point. Since the image is seen at points where there is no contact between these two surfaces, this process cannot be one involving some type of contact transfer mechanism. Note this supports Vignon's conclusions that the body images and the blood marks have gotten onto this cloth by distinctly different mechanisms. In fact a more recent experiment with the frontal head blood images demonstrates that the two types of images are not in stereo-register as would be required.<sup>32</sup> Common sense suggests that no medieval artisan would be able to visualize how to do all this at a time in history almost a century away from the recognition of perspective and its incorporation into artistic depictions.

Although no one has as yet discovered a mechanism that accurately reproduces this VP-8 characteristic of the body images, it can be utilized to test any proposed body image formation mechanism. A large number of various artistic rendition techniques have been so tested and all have failed to meet this strict VP-8 criterion.<sup>30</sup> These include albedo (simple reflection) images from a bust of a bearded head, phosphorescent emission images from this same bust, artistic sketches and paintings of various sorts (including copying from a photo of the Shroud face), chemical contact images, thermal imaging, diffusion images, electrostatic imaging, bas reliefs, dry powder contact images, scorching contact with an engraving, and various hybrid mechanisms. While these tests do not preclude the possibility that some form of artistic rendition has been employed to produce the Shroud, they severely restrict any proposed methods to those that have not already been shown to be inadequate. Note one must also explain how this proposed process has been properly incorporated with the blood marks, which have gone onto the cloth first and are out of stereoregister with the body images.<sup>33</sup>

A polarized image overlay technique has been utilized to facilitate and better quantify the comparisons of images in iconographic studies.<sup>34, 35</sup> This technique requires the use of two projectors with one mounted above the other. The two images one wishes to compare are projected onto one another and by means of zoom lenses brought to the same magnification and into an overlapping register. Plane polarizing sheets are then mounted in front of each projector, but in a crossed configuration to one another's planes of polarization. By rotating a third polarizing sheet while viewing the superimposed images through it, one can very readily visualize the degree of congruence of the two images. Using this technique iconographic comparisons have been successfully verified and

extended to coins as well as to the usual Mandylion type icon image comparisons of various sorts to the facial image on the Shroud.

### **Chemical Investigations**

The chemical testing of the Shroud has been conducted on material removed from it by various sampling techniques, but mainly by 'sticky tape' sampling.<sup>9, 10, 24</sup> At the time of the 1978 STURP investigation, samples were removed from designated and documented locations by means of a special tape holder providing a controlled pressure and supplied with a mylar tape coated with an inert hydrocarbon adhesive. Microchemical testing was then carried out on specimens removed from these tapes at off-site chemical laboratories. However, this type of sampling provides some difficulties in deciding which materials collected are actually typical of the designated location.

There is the problem that the mechanical folding and rolling of the cloth will displace abraded material (e.g., blood mark material) and brittle body image fibers from an original site to an inappropriate location, e.g., some abraded material from the blood marks are found in non-blood image locations. There is also the problem of obvious contaminants, e.g., red silk fibers from the protective covering cloth in which the Shroud was previously rolled up (before the present conservation measures were taken) are found on every sample tape. Occasional airborne materials that have fallen on the cloth can also be seen, e.g., dust, industrial soot, insect parts, hairs, tiny fragments of siliceous materials, modern synthetic fibers, etc. A somewhat more serious type of contaminant is the occasional appearance of materials that can be clearly identified as artistic pigments such as rose madder or cinnabar, etc. Historical studies have established that over four dozen painted copies of the Shroud have been produced and that almost all these finished copies were 'sanctified' by pressing the copied image to the original and thus unwittingly providing some contact transfer between the two cloths.<sup>36</sup> Therefore, unless such materials can be shown to be present in predominating amounts, they cannot be construed as evidence that the Shroud images themselves are paintings, but only that the cloth has been contaminated by artists copying the images and sanctifying them.<sup>8, 24, 36</sup> It should be noted that none of these known artistic copies show any of the forensic or image characteristics that typify the Shroud of Turin.

For a given tape, an arbitrary minimum threshold of 15 specimens of a particular type of visually identifiable characteristics (mainly color and surface appearance under phase contrast microscopy) was set to constitute a class of fibers or particles assignable to a specific location on the cloth to be subjected to chemical testing. When removed from the tape and cleaned of adhesive material the specimens can be further classified by their fluorescence characteristics (both the tape and the adhesive are fluorescent and therefore interfere if specimens are not first removed from the tape) and also for their polarization characteristics (the mylar tape is form birefringent and again interferes unless the specimen is removed from the tape as this is a vector property of materials). Carrying out this prescription excluded all the various types of contaminants discussed above and yielded 11 classes of sample objects for testing.<sup>24</sup> Usually at least 5 of each of these types

of objects were tested and were always compared against appropriate controls prepared from laboratory grade chemical samples, modern linen, a sample of 17th century Spanish linen, heated linens, protein coated linens, etc.<sup>24</sup>

Twenty-two different types of microchemical spot tests for 17 different common metallic elements that could be conjectured to be involved in the formation of images on the Shroud were checked against chemical controls and also checked for possible interferences and then applied to the sample objects and any appropriate linen controls as well. All the types of Shroud fibers gave positive tests for only two elements, calcium and iron. However, these elements do not derive from the presence of iron oxides or calcium carbonates on the fibers in a binder, as positive tests are obtained without the need for prior acidic digestion. Therefore these elements can be considered as being coordinately covalently bound to the linen's cellulosic structure. Other samples of old linens (and even modern "craft" linens) show the same type of results. Therefore the presence of these elements can be ascribed to chemistry arising during the manufacture of linen from flax, e.g., the vetting process being carried out in naturally occurring 'hard' waters. Since these tests are ubiquitous and uniform for both body image and non-body image fibers, it demonstrates that the body image chromophore cannot be ascribed to the presence of a metallic element. It should be noted that none of the trace elements associated with iron of a mineral origin were detected.

One class of the test objects can be clearly identified as ferric oxide particles. They are reddish, birefringent, pleochroic, give a positive spot test for iron only if predigested with hydrochloric acid, etc. They were found only predominantly in the scorched blood areas and the waterstain margins. As the combustion of blood is known to produce ferric oxide, its presence in the scorched blood area is expected. A chromatographically induced reaction under the conditions of extinguishing the 1532 fire that produced the waterstains has been proposed and tested by control experiments with the Spanish linen. It produced iron oxide particles of the same appearance and properties as those found in the water-stain margins and therefore suffices to explain their presence at these locations. It should be noted that the waterstain margin fibers test negatively for the presence of protein as a possible paint pigment binder and that particles of this iron oxide type are not found in the body image area samples.

A series of 22 microchemical spot tests for 16 different organic structures or functional groups postulated as possible stains or dyes that could account for the body images were also carried out, again by comparison with appropriate controls. The only positive results were seen for the presence of aldehydes and cellulosic carboxyl functional groups. These results argue against the body images being the result of painting with some type of applied stain or dye, but suggest instead that the image was produced by some type of chemical process yielding a dehydrative oxidation of the cellulosic structure of the linen itself. Note this is consistent with the corroded surface appearance as seen in phase contrast and the brittleness of the body image fibers as observed in the microscope studies. Thus the chromophore accounting for the body image fiber color would be a mixture of conjugated carbonyl structures generated within the cellulose polymer itself.<sup>9, 24</sup> It should be noted that this type of chemistry accounts for the natural



yellowing of linen as it ages. Therefore the body image chemistry can be thought of as some type of selective differential accelerated aging process. No one as yet has experimentally demonstrated a chemical mechanism that would yield this type of chromophore and at the same time be consistent with the observed physical properties of the image.<sup>33</sup>

A series of microchemical tests for the detection of the presence of proteins was also carried out on the appropriate test objects. Control studies revealed that many of the basic dyes usually employed for these purposes, e.g., amido black, bromthymol blue, etc., also stain oxidized cellulosic structures, as they are acidic, and whose presence therefore constitutes an interference. Similarly, it was found that the presence of covalently bound iron interferes with the usual ninhydrin tests. However, the use of fluorescamine tested against controls not only proved to be specific, but was sensitive under the test conditions to the picogram level. Only the blood particles and the serum coated fibers from the margins of the blood marks gave positive responses. All the other test objects gave negative results, including specifically the body image fibers, which therefore are not coated with an artistically applied protein pigment binder. Proteases were also employed to enzymatically confirm these results and yielded the same conclusions. While treatment of the body image fibers with proteases yielded no changes even after several hours of treatment, in less than 20 minutes it removed the coating of the serum coated fibers to reveal a smooth and uncorroded surface. This interesting observation suggests that the blood marks were on the cloth before the image producing process took place and protected the blood mark areas from this process. This further confirms that there were two separate processes involved in generating the images seen on the Shroud of Turin. Note that any proposed image forming mechanism must account correctly for both sets of images.

More recently, due to their specificity, another series of enzymatic tests was carried out on some Shroud fibers and appropriate controls.<sup>33</sup> The above protease tests were confirmed. Positive pectinase tests demonstrated that the conjecture that the fluorescence of the background non-image fibers was due to the presence of pectic substances not completely removed during the retting process is correct.<sup>37</sup> As pectic substances react with basic dyes and may be easily confused for other types of coatings, this explains some of the misinterpretations that have been made in microscopic studies that did not consider alternate hypotheses.<sup>30</sup> Negative tests with estrases and lipases revealed that no polyester coatings are present, consistent with the chemical and spectroscopic studies.<sup>33</sup>

The body image fibers were also tested with 21 different solvents and test reagents to see if the color could be extracted or modified.<sup>24</sup> Although the solvents employed covered the entire solubility scale, none of them could remove the yellow color. Only very strong oxidants or reductants could bleach the yellow color. These results are consistent with the conclusion that the chromophore is a conjugated carbonyl structure integral to the cellulosic polymer itself. In the course of these tests it was discovered that treatment of modern linen fibers with concentrated sulfuric acid produces a simulacrum for body image fibers with many of the same observed chemical and physical properties. Since concentrated

sulfuric acid is both a strong dehydrating and oxidizing agent this is not really surprising, but it further supports the identification of the chromophore.

Thus the chemical investigations are in complete agreement with the image studies in concluding that the body images are not composed of applied pigments, stains, or dyes and have been produced by a different process from that of the blood marks. Note that if one ignores the results of other investigators, does not consider alternative hypotheses and proper control tests, but simply microscopically observes protein covered fibers, iron oxide particles and the presence of other occasional artistic materials, one could incorrectly conclude that the Shroud is simply a painting.<sup>33</sup>

### **Spectroscopic Investigations**

An X-ray fluorescence investigation<sup>26</sup> was carried out on the Shroud to complement the X-radiographic study.<sup>25</sup> The calcium content was shown to be more or less uniformly distributed over the whole cloth supporting the chemical conclusion that it derives from the manufacture of the linen from flax. Similarly, the iron distribution also was uniformly distributed over the whole cloth with a few notable exceptions, again supporting the chemical conclusion that the iron content is in a covalent form and like the calcium derives from the flax-to-linen conversion process. Again there is no evidence for the trace minerals associated with mineralogical forms of iron oxides, such as cobalt or nickel. As one crosses a waterstain boundary one finds the background iron value on the outside of the stain to be a slight elevation of this value in the margin itself, and a slightly depressed value for the iron on the inside of the stain. This is consistent with the chromatographic model proposed to explain the presence of iron oxide particles in the waterstain margins. If one follows the iron content from the tip of the nose in the facial image across the cheek and into the background cloth it again shows a uniform value along this path, although the image intensity varies by about an order of magnitude over this same path. Therefore to attribute the image intensity variation to any form of iron, let alone iron oxide, would constitute a violation of the Beer-Lambert law. Again this study fails to support the contention that the Shroud is an iron oxide painting.

Ultraviolet and visible reflectance studies were carried out on the Shroud and also some fluorescence spectroscopy.<sup>38, 39</sup> In general these results complemented the observations seen in the fluorescence photography study. The visible reflectance spectra and the red-green-blue characteristics of the body images were a closer match to the lightly scorched areas (an oxidized cellulose area) than to controls of linen with an iron oxide coating. The near UV spectra showed a broad band assignable to those observed for conjugated carbonyl absorption. This is in agreement with the body image chromophore being a dehydrated oxidized form of cellulose and not being an artist's applied iron oxide painting.

An infrared reflectance examination of the Shroud accompanied the thermographic study.<sup>27</sup> Although the spectra taken were of low resolution, the peak ratios of the carbonyl region to that of the hydroxyl region showed clear evidence of an increasing state of oxidation in going from the background cloth to body image to scorch to the burned areas. The typical amide absorptions associated

with proteins could be evidenced in the blood mark spectra, but not in those of the body images. These results were confirmed and extended in a more recent high resolution microspectrophotometric FTIR investigation of fibers and particles extracted from the STURP sticky tape samples.<sup>8, 40</sup> Each type of fiber now showed a distinctive absorption pattern. A conjugated carbonyl absorption pattern was clearly seen in the body image samples, but no evidence for protein amide bands which, however, were clearly seen in the serum coated fibers and blood particles. These results are again in accordance with the previous conclusions drawn above and do not support the contention that the body images on the Shroud of Turin are simply paintings.

### **Image Formation Mechanisms**

From the foregoing, it is clear that the Shroud is not a painting. It is of interest to note that the same conclusion has been drawn on the basis of artistic criteria.<sup>41</sup> In claiming the discovery of a mechanism, one must show that all the body image criteria, e.g., non-contact, one-fiber-deep body image, areal density image, conjugated carbonyl chromophore, VP-8 characteristic, etc., are met. It is not enough to simply get a brown colored image. One must also account for the blood images and their criteria, e.g., contact image, composed of clot exudate chemical species from traumatic wounds, not in stereoregister with the body images, on the cloth first and not overlaying the body image, showing clot retraction rings, etc. It does not suffice to say that the blood wounds are painted on after with whole blood. On the basis of these criteria many of the recently proposed formation mechanisms have been analyzed and rejected.<sup>30, 33, 42</sup> Several recent proposed mechanisms have involved some type of radiation released during an assumed miraculous dematerialization of the body and also assuming this radiation corrupted the radiocarbon date. Unfortunately, this assumption requires one to suspend belief in some of the basic laws of physics, e.g., mass-energy conservation. The atomic explosion accompanying such an event would certainly destroy the cloth. It is also unlikely that any of these ionizing radiation models will produce a one-fiber-deep image with a proper VP-8 characteristic, as has already been exemplified by an experimental study of an X-ray model which did meet several of the required criteria.<sup>42</sup> Such particle radiations would also eventually convert some of the calcium present to scandium and some of the iron present to either cobalt or nickel and these elements are not detected, again arguing against these types of proposed mechanisms. It has been noted that a coronal discharge model also meets many of the required criteria, but more experimental study is required before this can be accepted as a possible explanation for the formation of the body images.<sup>33</sup>

### **Provenance and Age of the Shroud**

The cloth now known as the Shroud of Turin has had a known history from the time of the de Charny display.<sup>1-6</sup> While its prior history is a matter of conjecture, a reasonable theory tracing its existence back to the time of the crucifixion has been proposed and is well supported by a great deal of varied historic, artistic (iconographic), and other circumstantial evidence.<sup>4</sup> A pollen analysis of tape samples

from the Shroud has now definitively established its provenance as the immediate vicinity of Jerusalem.<sup>43</sup> Needless to say, this whole argument for authenticity remains polemical.

To try to resolve this polemic, a radiocarbon dating examination was authorized and carried out in 1988.<sup>44</sup> As this examination assigned a 14th century date to the Shroud, it only exacerbated the polemics. Unfortunately the protocol recommended by a convened panel of experts<sup>45, 46</sup> for the taking of proper cloth samples for this dating analysis was not followed. Only a single sample was taken and from a most unsuitable location, i.e., from the edge of a bounded waterstained scorched area where evident repairs have been made. Therefore while this dating study can claim good precision for its reported date, it cannot assign any accuracy to the date as it is not clearly established that the location sampled is typical of the rest of the cloth. To check this point, fibers from the radiocarbon sample were included in the microspectrophotometric FTIR study cited above<sup>40</sup> for comparison with other Shroud fiber types. The radiocarbon samples show a distinctly different spectrum and therefore it can be inferred that their composition is not typical of the rest of the cloth.<sup>8, 40</sup> Why this is so is not entirely clear, but it does establish the fact that the accuracy of the radiocarbon date can be questioned on the basis of direct experimental evidence.<sup>8</sup>

Recent image studies of the dorsal head wound blood marks on the Shroud show a very high congruence with a similar complex blood mark pattern on the Sudarium of Oviedo, another claimed relic of Christ's passion.<sup>8, 47</sup> Since this is a complex pattern, the agreement is not coincidental. Further, since these are both established marks of real blood derived materials, both cloths must have been imprinted at the same point in historical time. As the cloth of Oviedo can be historically traced firmly to Spain in the 7th century,<sup>47</sup> this provides direct experimental evidence that the radiocarbon date is indeed inaccurate.<sup>8, 47</sup>

Many theories and explanations have been advanced to attempt to resolve these dating discrepancies. Experimental evidence that the fire of 1532 could have produced kinetic isotope changes in the cellulose structure at the sampling site and thus corrupting the observed date has been reported.<sup>48</sup> A theoretical analysis of a simple proposed chemical kinetic mechanism to explain these results has also been carried out and shows the observed kinetic behavior quite well, including the observation that the isotope exchange ratio goes through a maximum.<sup>49</sup> This analysis also shows that the time at which this maximum will appear is a function of the volume of the experimental container.

The differential expression for the rate limiting step required for such a maximum to appear is of the form  $k c(a)c(b)$ , where  $k$  is the step rate constant for the bimolecular collision of the species  $a, b$  involved in the step reaction and  $c$  is their concentration. However, to solve the set of simultaneous differential equations for such a mechanism, one must also invoke conservation of mass, which is given in terms of the number of moles,  $n$ , and not concentration,  $n/V$ , where  $V$  is the volume of the system. Thus the rate expression becomes  $k(\text{obs})n(a)n(b)$ , where  $k(\text{obs}) = k(1/V^2)$ . However, as the rate itself is of the form  $dc/dt$ , the overall observed dependence on volume will be  $1/V$ . Thus one investigator using an experimental apparatus of the same size as that used in the original study

has reproduced the original data,<sup>50</sup> while two other investigators<sup>51, 52</sup> employing much smaller volumes have failed to reproduce the data (their system going through its maximum in seconds instead of hours and therefore unobserved).

While this model might resolve a portion of the date discrepancy, it is unlikely to resolve all of it. Clearly there are problems in the use of some of the procedures used in going from the experimentally observed date to the corrected date.<sup>48</sup> Needless to say, this has become polemical and will require some well directed experiments to resolve, as many do not seem to appreciate the differences that kinetic isotope vs. equilibrium isotope effects<sup>53</sup> will make in actively growing biological systems.

### **Conservation Issues**

Nothing lasts forever and this includes the Shroud of Turin. There is already evidence of degradative processes taking place, as for example in the observed abrasion of the blood marks. The various conservation and preservation issues and their possible resolution have been analyzed and reported in some detail. As the need for action is paramount and pressing, a Conservation Commission has been appointed and a program to actively carry out their recommendations has been initiated. For example, the Shroud is no longer kept rolled up, but kept flat to reduce mechanical damage, etc. To continue to further this work, more data acquired by further testing on the Shroud itself is required.<sup>54</sup>

### **Recommendations for Further Testing**

A biological assay for the microflora and microfauna actually resident on the cloth is imperative. Information leading to a better understanding of the chemical structures found on the cloth is also imperative. Since the last examination, improved portable spectroscopic instruments with high resolution and improved signal to noise ratios are now available. Using fiber optic probes fluorescence,<sup>37</sup> UV-visible, and FTIR spectra can be taken at designated points of interest. If these studies are complemented by some of the newer imaging techniques using filters,<sup>55</sup> spectral imaging,<sup>56</sup> etc., it should not be necessary, to remove any further fiber samples for off-site testing. Surface pH measurements should also be carried out. However, further radiodating should not be carried out until we really understand why the present study failed.

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