Spectral properties of the Shroud of Turin

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Spectrophotometric results from the 1978 investigation of the Shroud of Turin are presented. The goals of the investigation were to characterize spectrally the body image in a region extending from the near UV to the near IR, to determine if the blood stains are actually blood, and to recommend storage parameters to prevent further degradation of the image. The bloodstained areas have the spectral characteristics of human hemoglobin. The image shows monotonically increasing (featureless) absorption with decreasing wavelength. The contrast is low: $R(550 \text{ nm}) = 0.85$ of that for the background linen. Simulated aging by air baking reproduced the color of the background linen. Simultaneously, an invisible deposit of perspiration plus skin oils became visible and displayed a reflection spectrum closely resembling that of the body image. Lightly scorched areas on the Shroud are also somewhat similar spectrally, suggesting that a similar resultant chemistry is possible for dissimilar causes. A likely cause for the body image is cellulose degradation stimulated locally by natural or applied substances transferred to the Shroud.

I. Introduction

The Shroud of Turin is an ~4.3- × 1.1-m relic known to be at least 600 years old. On the linen are faint full height frontal and dorsal images of a man. In addition, there are markings resembling blood stains and water stains.[1,2] The author was one of a group of investigators and assistants permitted to collect data between x-ray and mid-IR wavelengths in Oct. 1978. The purposes of the nondestructive measurements and subsequent analyses were to determine the mechanism for image recording, to determine if the blood stains are actually blood, and to characterize the stains for preservation purposes.

During its traceable history, the Shroud has been venerated by those believing its image to be that of Jesus of Nazareth and denounced by others as a forgery. A curious discovery was made concerning the imagery near the turn of the century. During routine photography by Pia[2] it was noted that the negative showed an image that is more natural in terms of physical appearance than the positive. Thus, it was concluded that the Shroud image itself can be described as a negative in the photographic sense. More recently[3] it has been suggested that the image density can at any point on the Shroud be related to the distance between that point

and a source (body). In other words, 3-D information is encoded in such a manner that a density scan across a body feature permits the contour of that feature (e.g., fingers, nose) to be reproduced. The minimum resolvable feature is 0.5 cm. It is also known that the image is spatially uniform in color and density despite its proximity to scorched and water doused areas. Much of the mystery associated with the Shroud is related to the mechanism for image imprinting, which is unknown, and the determination of whether the so-called blood stains are in fact human blood.

A previous (the only other study permitted) scientific investigation in 1969 included photography, textile comparisons, hematology, and visual microscopy. The 1978 investigation took advantage of the earlier study but employed an improved technological base for a more definitive set of measurements.

II. Experiments in Turin

Ultraviolet reflectance, fluorescence photography, and visible narrowband and wideband photography were done for image processing and analysis and are reported upon elsewhere.[4,5] The image contrast is low so filters were chosen to define spectrally the region of maximum contrast. One example from many of the filtered (blue) photographs is shown in Fig. 1. Ultraviolet and visible photoelectric spectral reflectometry is reported here; fluorescence is reported elsewhere.[6] Photomicrography is presented in another publication.[7] Infrared thermography in the 3–5- and 8–14-μm bands is reported in another paper.[8]

The observations eliminate the possibility that the body image is due to pigments or dyes applied to the linen.

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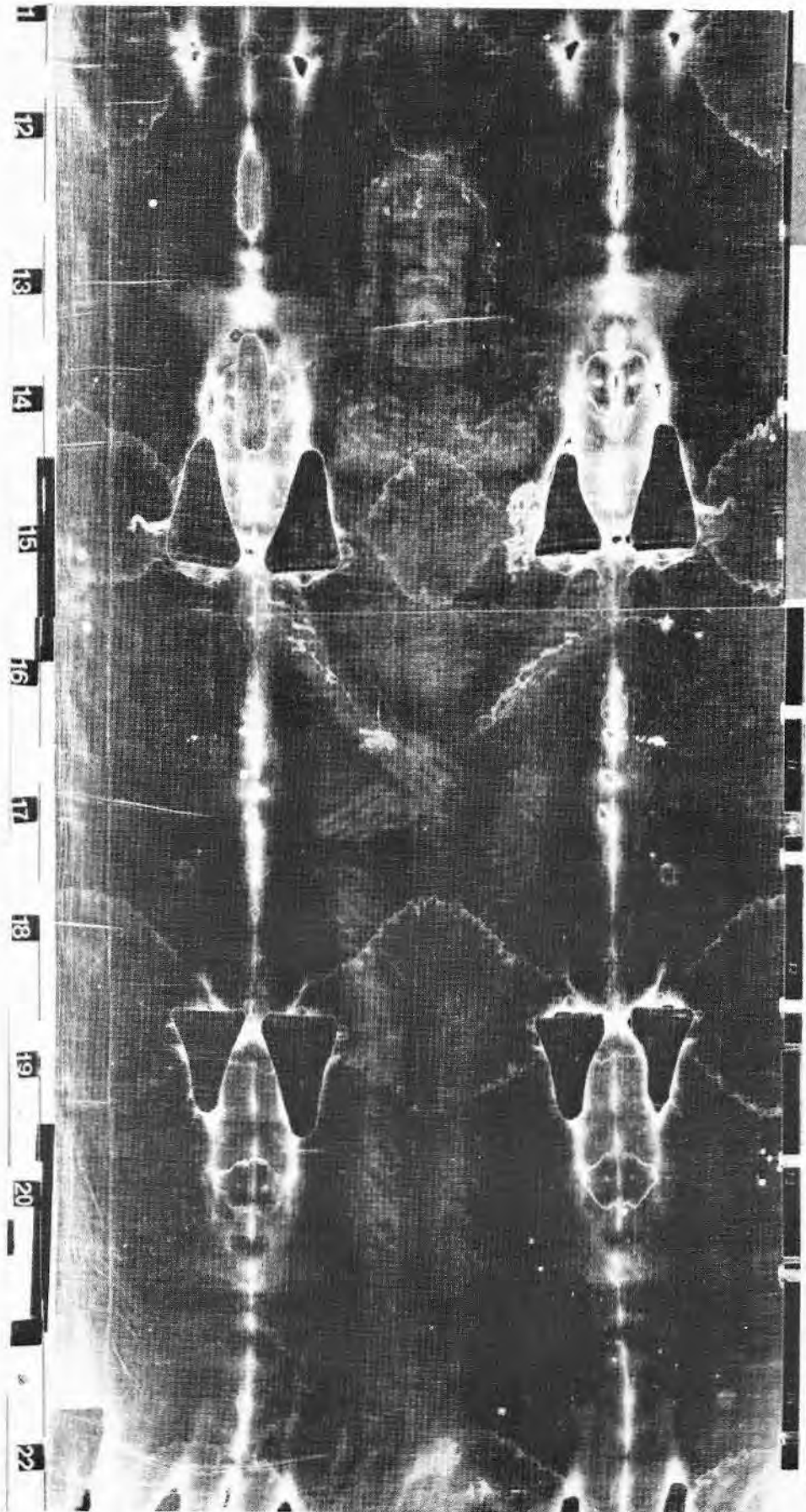
Fig. 1. Reversed image of a portion of the Shroud. Photo taken through 370–500-nm bandpass filter using xenon flashlamps. Maximum contrast is obtained at these short wavelengths between sepia/straw colored image and yellow tinted background linen. Skin as well as hair features have been recorded on the Shroud with about equal density. Scorch burns and water marks from 1532 fire are evident. Scourge and apparent blood stains agree with biblical literature descriptions (photo © V. Miller, Oct. 1978).
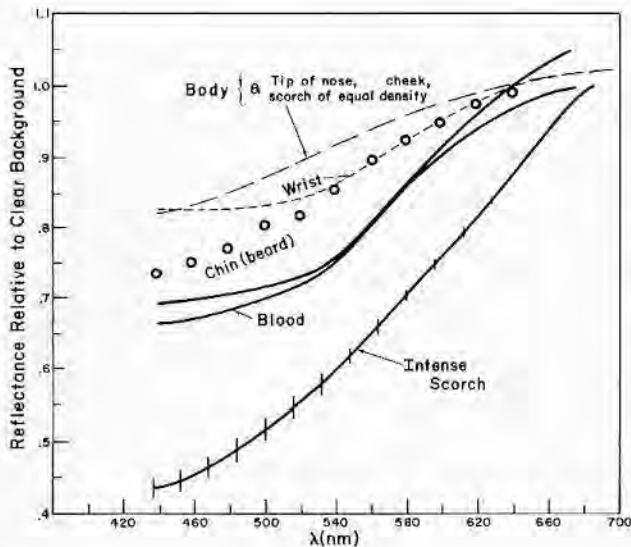
Fig. 2. Photoelectric spectroreflectometry of 1-cm diam areas of specific Shroud features made with a quick look spectrophotometer. Bandpass was 17 nm. Values are the result of ratioing to blank linen background to emphasize differences. Curves are normalized to ~1.0 at 700 nm.

All the stains are faint (except for dense scorches); i.e., the linen background contributes significantly to the faint scorch, the body, and even the blood images.

The blood curve (Fig. 2) has distinctive changes in slope compared with the other stains. This makes comparison with the spectral curve of human blood more straightforward.

IV. Detailed Spectrophotometry

The higher resolution (5-nm FWHM) continuous-wavelength scans of Gilbert and Gilbert[6] at Turin were used as base line data and compared with laboratory data consisting of total (diffuse plus specular) reflectance taken with spherical integrators on a Cary 14 spectrophotometer. The spectral resolution for the laboratory spectra was ≤ 4 nm between 500 and 600 nm and ~8 nm at each extreme. The background (no sample) signal of 0.02 was subtracted from each measurement. The noise on a measurement was ± 0.005 unit. The spectra taken by the two instruments at Turin agree within 5% of each other on an absolute scale. In spite of the different solid angles of view of the Gilbert spectrophotometer (~0.004 sr) and the laboratory spherical integrator (2π), the data are comparable because the diffusely scattered component is not wavelength dependent. This is treated in more detail below.

III. Quick Look Photoelectric Spectroreflectometry (440–700 nm)

A miniature battery-powered spectrometer was designed[9] for the expedition to Turin. It used a continuously variable interference filter wheel to resolve a 17-nm FWHM band and a silicon photodiode detector. A 1-cm diam field at 50-cm distance is viewed. Signals at 20-nm wavelength intervals were read out digitally with a liquid crystal digital voltage display; voltage is linearly proportional to radiance. A 500-W tungsten lamp illuminated the Shroud, and a MgO surface was used as a reference. Six samples of each type stain and clear background were measured, some repeatedly. The repeatability of a measurement was ~±1%.

Figure 2 presents reflectances relative to background and normalized to ~1.0 at 700 nm for body image areas, scorches from the year 1532 fire, and bloodstained areas. In general, all markings and also the clear linen absorb increasingly as the wavelength is decreased. The color index for each stain group is presented in Fig. 3, where color index = $R(680 \text{ nm})/R(440 \text{ nm})$ vs $R(550 \text{ nm})$. When plotted this way, color differences are emphasized, and groupings are evident. For example, dense scorches are redder and darker than any of the markings including blood. A representative light scorch and a body stain have nearly the same color. Visually the wrist and the chin (beard) appear to have the faint tint of the blood stains (the chin more so). This suggests that blood is present in these areas and indicates the sensitivity of such a parameter plot.
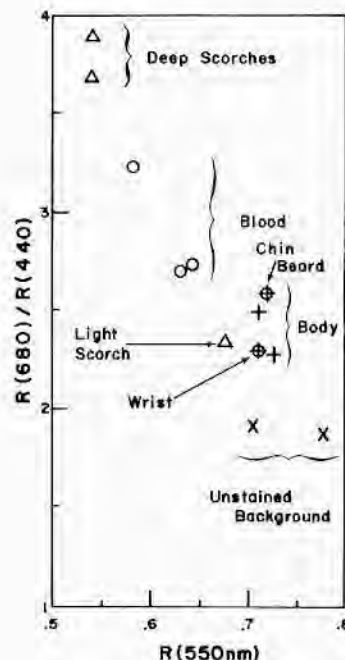

Fig. 3. Reflectance ratio of widely separated spectral points (440 and 680 nm) is plotted vs absolute reflectance at 550 nm. Grouping by stain type is evident. The darker the feature, the redder it is. Quick look spectrophotometer results.

A. Identification of Blood Stains

Figure 4 shows several blood reflectance spectra and one transmittance spectrum. The transmission curve shows greater band contrast than the reflection curve of the same sample, especially in the Soret 410-nm band. The influence of scatter from the background cloth on the spectral measurements is now discussed. If it is assumed that the Kubelka-Monk (K-M) theory for diffuse reflectance can be applied,[10] the remission function is $f(r) = k/S$, where k is the Beer-Lambert absorption coefficient, and S is the scattering coefficient. Then $\log f(r) = \log k - \log S$, where $\log k$ vs λ corresponds to the absorption spectrum, and $\log S$ is merely a displacement of the ordinate. For scattering dimensions $d \sim \lambda$, S is independent of λ.

The details on the linen fibrils are of dimension $> \lambda$, and the reflectance curve[6] shows a monotonic decrease with decreasing λ. Since this reflectance trend can be induced by heating linen in air without dimensional changes, the reflectance characteristic is believed due to an absorbing species. This large quasi-Lambertian scattered component can reduce the spectral contrast in an absorption band; this is demonstrated later. It can also be responsible for the variation in contrast of the image outline with viewing distance. As the observer's eye approaches within centimeters of the Shroud, the image becomes harder to distinguish. Restricting the angular subtense of view increases the image contrast by excluding some of the scattered component.

A discussion of absorption peak shifting in blood stained areas now follows. Considering the blood particles themselves as scatterers, they can be described as having $d > \lambda$ with k being a strong function of λ. For such particles,[10] the specular reflection coefficient is large and independent of λ and causes deviations from the K-M theory, in this case ~2%. The effect of the specular component is to lower the contrast in an absorption curve. However, in the neighborhood of a strong absorption band, S has dispersion similar to that of refractive index and thus can be λ-dependent. The result might be a shift in the band peak to shorter wavelengths when measured in reflectance. Other influences might also cause peak shifting and include the environment of the absorbing species (+ shift) and scatter (small + shift) along with the dispersion effects ($-\lambda$ shift). The resultant shift predicted[10] is +10 to +20 nm but is not observed in the transmission and reflection curves of the same blood smear on a glass slide in Fig. 4. Thus this phenomenon should not be a factor in the identification of any measurable absorption bands on the Shroud.

It is appropriate to make comparisons with samples that have areal coverage more closely reproducing that of the Shroud blood stains, as discussed above. Hence, the relative reflectances, i.e., ratioed to clear substrate (linen), are presented.

A comparison of laboratory data on whole blood smears with the curve for Shroud blood is given in Fig. 4. The laboratory data display, in addition to the Soret (400–420-nm) band, absorption bands in the 530-
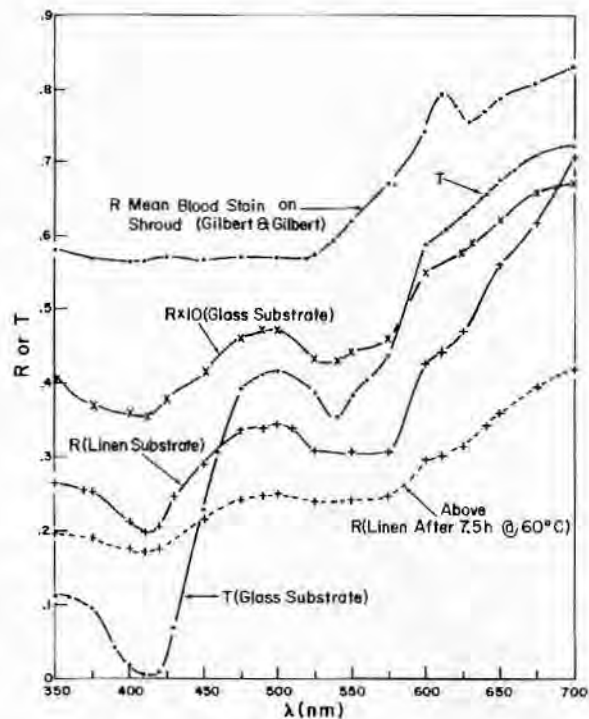

Fig. 4. Integrated reflectance and (one) transmittance curve for laboratory blood preparations, including Shroud blood reflectance values. Laboratory blood is 4 days old and in one case was artificially aged by baking. The large difference in contrast of Soret and α and β bands occurs when the same sample (on glass slide) is measured in reflection as compared to transmission. Baking also reduces contrasts of bands. Different average magnitudes of curves are due to a variety of exposed background cloth. Instrument bandpasses are 4 nm for the laboratory and 5 nm for Shroud measurements at 410 nm.

580-nm region (α and β) and a weak band at 625 nm. These are characteristic of the metal porphyrins of the heme proteins.[11] The loss in contrast of the Soret band when measured in reflectance is also demonstrated. The Shroud curve shows a pronounced band at 630 nm, a general band beginning near 525 nm, and no suggestion of a Soret band. The latter was probably obscured by the poor SNR of the measurement. There is, however, sufficient correlation in the spectrophotometry to decide that the material on the Shroud is blood. In fact, the absorption spectrum of a blood particle removed from the Shroud independently suggests that blood is present.[12] Furthermore, the resemblance to blood as seen in the photomicrography of these areas is strong.[7] The spectrum suggests denatured met-hemoglobin.

B. Spectra of Possible Image Recording Substances

The relative spectral reflectances of substances that might have once contacted the Shroud are shown in Figs. 5 and 6. These are presented relative to the reflectance of the linen substrate; the latter and Shroud background are on an absolute scale (referenced to $BaSO_4$ or MgO). The solid curves are data before baking; the dashed curves are data after a 5-h air bake
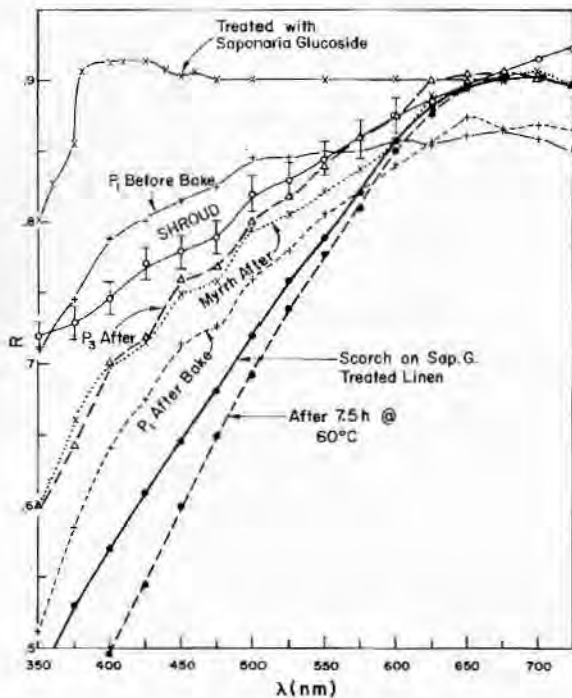
Fig. 5. Integrated reflectances (relative to their clear backgrounds) of Shroud image and a variety of materials that might be related to burial linens. Top curve is for linen treated with saponaria glucoside[13] and shows a fluorescent contribution <450 nm. Bottom curves are for scorch on this linen before and after baking. Other curves include perspiration and skin oil stains: P_1, heavy body grime; P_3, light perspiration; and myrrh. Scorch spectrum is included since a similarity between light scorches and body image was made. Note influence of baking (accelerated aging) at 150°C for 7.5 h.
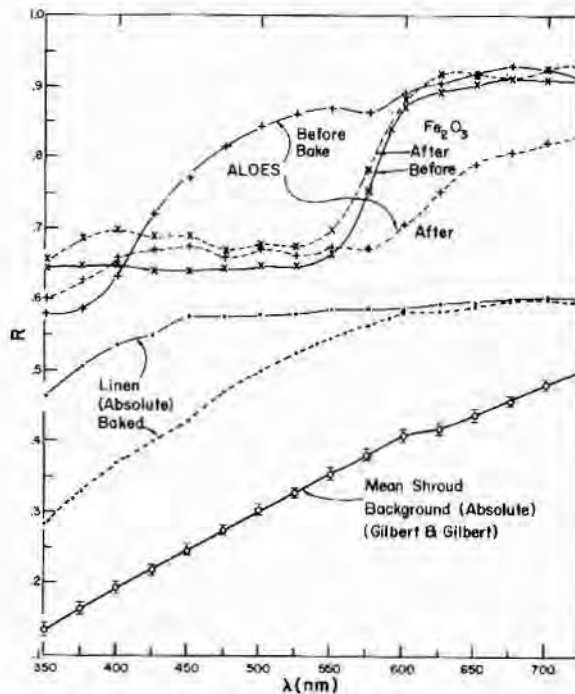

Fig. 6. Similar to Fig. 5 but includes curacao aloes, Fe_2O_3 smudges, and linen before and after 7.5-h bake at 150°C. Mean Shroud background spectrum is included for comparison with aged (baked = dashed curve) modern linen. The Fe_2O_3 *after* curve lies above the *before* because the linen darkens; Fe_2O_3 remains unchanged.
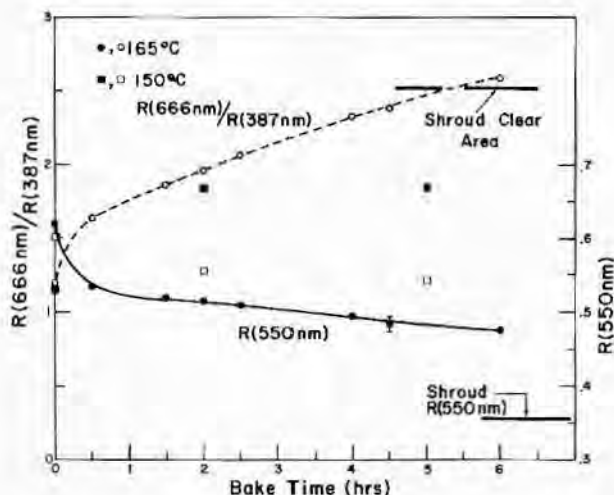

Fig. 7. Color and visual reflectance vs bake time for linen. This method of artificially aging linen was used to attempt to reach Shroud measured values. Color is approached after 5.5 h at 165°C, but reflectance of laboratory sample does not reach that for Shroud. Weave, composition, etc. for two linens are different, however, and this fact probably explains the reflectance difference.

at 150°C. As explained below, the bake simulates aging of the linen and produces a color close to that of the Shroud clean areas. This is demonstrated in Fig. 7. Presumably, the materials added undergo a similar time/heat exposure equivalence relationship. However, the clear background (substrate) reflectance $R(550$ nm$)$ is reduced to ~0.48 for the laboratory linen compared with 0.36 for the Shroud. Factors such as weave density, thread diameter, and composition and cleanliness influence the reflectance value. The effect of the air bake on linen is to accelerate cellulose bond breaking and dehydration, leaving a double carbon bond, which is responsible for the increasing absorption toward shorter wavelengths and may be the cause for the image coloration. The air bake is then assumed equivalent to the effect of a longer time at normal ambient temperatures,[14] i.e., a time/heat exposure equivalence is operating.

Comparing before- and after-bake spectra, the myrrh, aloes (curacao), and perspiration plus skin oils all darken; in addition, the myrrh and perspiration plus skin oils become redder, as shown in Figs. 5 and 6. The two perspiration-plus-skin oils samples are very different: P_1 (heavy) is a sample wiped from the back of the neck and was visually dirty before baking; P_3 is from a light contact with the forehead and was not visible before baking. After baking, their resultant spectral characteristics became similar. The significance of this

result is that, if the chemistry of the image imprinting process involved contact with natural skin substances (or myrrh), the pressure difference between the frontal and dorsal images of the body on the cloth would not register. In the case of the Shroud, no difference in image density is detectable between the frontal and dorsal images.

A further experiment was done using light coatings of olive oil on linen. Before baking these were invisible. After 1.5 h at 140°C, the spectral reflectance parallels those of aged P_3 and myrrh. After 3.5 h, it parallels that of aged P_1. Extending the bake time to 5 h causes <0.5% average deviation from the 3.5-h curve. These substances approximate the body image spectral characteristics (Fig. 5) closely.

The sample wet with tincture of myrrh and baked shows fibrils that are thoroughly stained. The aloes sample, however, contains small brown particles. There is no confirming evidence from visual microscopic or SEM examination of fibrils and particles removed from the Shroud that any of these substances exist as such today. Their original presence on or reaction with the linen in the context of serving as catalyzers or accelerators of darkening where contact was made is suggested.

An objection raised to the suggestion that contact with skin products or burial ointments contributed to the image formation is that these organic materials should be thermally unstable.[3] Thus the color or density of an image due to these materials would be altered with proximity to the burned areas. No such changes occur for the Shroud image areas.

To test for color stability, the stains for which the spectral properties were presented in Figs. 5 and 6 were scorched with a soldering iron. An olive oil stain was also included. The surface temperature of the iron was 250° ± 30°C. Two observations were made of the results. When the stains were lightly scorched, no discoloration aside from that of the linen material was detectable. When a stain was heavily scorched (dark brown) or ignited, no color or density change was seen beyond the expected ~2-mm wide brown-to-yellow transition zone indicative of the cellulose pyrolysis products.[13]

The darkening of these stains relative to the background linen due to baking apparently reaches a limiting value, beyond which more time or higher temperature does not increase the contrast or change the color.

C. Iron Concentration

The x-ray fluorescence experiment[15] found a large (50-μg/cm^2) concentration of iron in blood areas and less in clear and body image areas (~15 μg/cm^2). Fe_2O_3 has a spectrum resembling that of blood, and its presence is detectable optically. Using a series of Fe_2O_3 smudges whose areal concentration of Fe was determined,[16] an optical calibration was made.

In Fig. 8, the color ratio $R(666 \text{ nm})/R(387 \text{ nm})$ of linen smudged with Fe_2O_3 powder is related to the concentration of Fe via the relative (i.e., to clear background) spectral reflectance. The values measured for blood and body reflectances on the Shroud are also indicated (triangles and circles).[15] The upper curve shows the change in the red-to-blue reflectance ratio with green reflectance value for Fe_2O_3. The lower curve shows (right-hand scale) the Fe concentration vs green reflectance. From this curve, a concentration ~2 μg/cm^2 is optically detectable. The Shroud reflectance values follow a similar trend as the Fe_2O_3 reflectance curve but with a shallower curve and a displacement toward lower green reflectance values.

An example of the use of this diagram is as follows. For the finger measurement, $R(550)$ gives (from the lower curve) an Fe concentration ~4 μg/cm^2, and the color curve for Fe_2O_3 (upper curve) gives a color index = 1.44. The measured values on the Shroud are, respectively, ~13 μg/cm^2 and 1.17. Similarly, for the lance wound, $R(550) \rightarrow$ Fe concentration = 25 μg/cm^2 and color index 1.96. The measured values are 50–60 μg/cm^2 and 1.49, respectively. The concentration of Fe predicted is one-half to one-third of that measured in the Shroud areas; furthermore, the color of Fe_2O_3 is redder than any measured color on the Shroud. Therefore, the blood stains are not composed entirely of Fe_2O_3. Similarly, Fe_2O_3 is not responsible for the image since the concentration of Fe_2O_3 particles predicted for the body image areas would be detectable. Figure 4 shows that neither the curve for Shroud stains nor that for known bloodstains is identical to the Fe_2O_3 curve (Fig. 6).

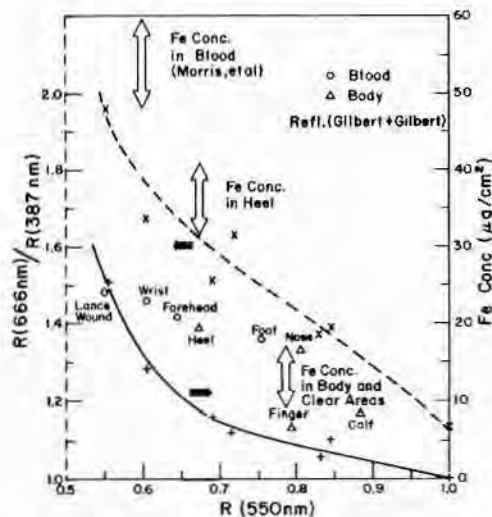A further observation from Fig. 8 is that there is a greater variation in color among the body points than

Fig. 8. Combined presentation of color (right-hand curve) and Fe concentration (left-hand curve) vs reflectance at 550 nm for Fe_2O_3 smudges, including some blood and body points from Shroud Fe concentration measurements. Circles and triangles are color measurements. Trends for Shroud results parallel those for laboratory calibration, but optical results predict less Fe than was measured by x-ray fluorescence on the Shroud.
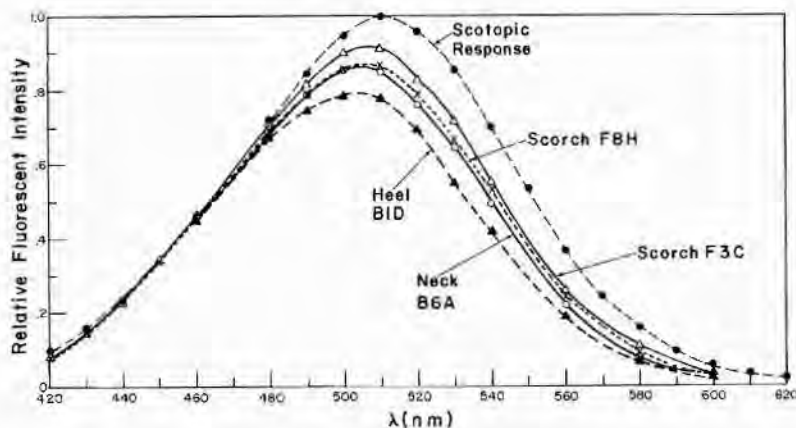
Fig. 9. Fluorescent color difference between Shroud features is examined, and visual descriptions of colors are explained when the photoelectric measurements of Gilbert and Gilbert are convolved with scotopic curve of the eye. Designations refer to locations.[6]

among the blood points. The reflectance values at 550 nm for body points (0.7–0.9) are close to corresponding values on the Fe concentration curve. Fe_2O_3 is not believed to be the colorant for the body image because it visually is too red, and its reflectance curve is different from that of the body image (Figs. 6 and 7).

The time/temperature exposure used reproduces the color of the Shroud; however, the 150°C temperature is high enough to cause degeneration of the heme proteins into products not expected for ancient human blood.[12] To eliminate this possibility, whole blood was baked at 60°C for 7.5 h instead of the previous aging temperature. The $R(666$ nm$)/R(387$ nm$)$ and $R(550$ nm$)$ values obtained are 2.1 and 0.41, respectively, off the upper left corner of Fig. 8, but consistent with the x-ray Fe concentration determination and the optical result.

V. Additional Studies

A. UV Fluorescence Observations and Spectroscopy

Observation of the details was made visually by the author and measured photoelectrically by Gilbert and Gilbert[6] as the Shroud was illuminated by the 366-nm line of a Hg discharge tube. In addition, fluorescent photography with wideband excitation was done. The excitation band for the fluorescence photography included (HM pts) 335–375-nm wavelengths. A blocking filter on the camera admitted only wavelengths >410 nm. The background linen fluoresced a faint yellow-green tint, while the image and blood stains were nonfluorescent. Lightly scorched regions fluoresced brownish red; water-stained areas had tints ranging from green to yellow as the gradient across the visual boundary was traversed. The light outline for blood in the lance wound area fluoresced noticeably.[17] The only other fluorescent markings were candle wax spots of unknown age. These were brighter than any other marking and fluoresced greenish yellow in color.

When the photoelectric data are convolved with the scotopic response curve and normalized (Fig. 9), it becomes obvious that the background linen itself is responsible for the measured[6] response on the blood and image areas, since there is an identical wavelength characteristic. This agrees with the visual description. The curve for scorches having visual reflectance corre-

sponding to that of image areas shows only a subtle weighting toward the orange region relative to the curves for body image, although the color difference is obvious to the eye and in the fluorescence photography.[5] The explanation might be that the eye has an excellent ability to distinguish between color differences when compared side by side. The larger band of UV wavelengths used in the fluorescence photography might be responsible for the stimulation and recording of a larger range of colors.

The laboratory stains discussed in Sec. IV.B, both scorched and unscorched, were examined for visual fluorescence when irradiated with the 366-nm Hg line. The basic linen blue-white fluorescence changed to faint yellow-green with baking. Neither myrrh nor aloes stains fluoresced. The perspiration-plus-skin oils stain fluoresced slightly brighter yellow than the linen but not nearly as bright as the lightly scorched clear linen. The olive oil stain fluoresced a very faint reddish gray color. There was no color or brightness difference between the scorched and unscorched (adjacent) areas of these stains.

Interestingly, the similar appearance between body image and scorch in natural lighting (see also the photomicrography[7]) has led to the speculation of a common causative agent (e.g., contact with a hot solid). In truth, the result may be the only similarity, i.e., coloration due to the disruption of carbon chains and partial dehydration. The fluorescence in the scorched areas is apparently due to the furfural pyrolysis products.[13]

B. Multispectral Photography

Visual descriptions and color photos made before the 1978 expedition indicated a sepia colored image on a yellowing linen background. Under the microscope the image bearing fibrils look straw colored. To enhance the image contrast with respect to the background as much as possible was one goal of the photography. A set of 10–20-μm wide filters was used with emphasis toward the blue end of the spectrum where maximum contrast was predicted and later verified. A three-color subtractive set of filters, consisting of $R(585 \rightarrow 750$ nm$)$, $G(500$–575 nm$)$, and $B(370$–500 nm$)$, was also used. In addition, the liquid filter used to isolate the 335–375-nm band (HM pts) for fluorescence excitation was also used

for reflective photography. Maximum contrast was obtained through the 386-nm narrowband and the B and UV filters; an example of a B-band photo is shown in Fig. 1. There was very low contrast for filters at λs > 550 nm. The choice of wavelengths used for the color index ratios (e.g., Figs. 5 and 8) was made because narrowband photography was done at the same effective wavelengths. Using digital subtractive and ratioing techniques, these scanned photographs can be processed to produce spatial maps locating areas of similar color.

VI. Conclusions

The results of the spectral data analysis for the blood stained areas on the Shroud are consistent with their interpretation in terms of human hemoglobin. The large amount of background scatter and the chemical state of the blood serve to dilute the contrast of typical blood absorption bands. To an optical detection limit of <5 $\mu g/cm^2$, Fe_2O_3 is not a contributor to the color (density) of the image areas. The color of the linen can be reproduced in the laboratory on modern linen through the technique of air baking according to a time/heat exposure equivalence relationship. Using the accelerated aging technique, natural perspiration plus skin oils, olive oil, and myrrh form visible stains that have spectral properties remarkably similar to those of the Shroud image areas. This suggests that contact with a human body plus the passage of time played a significant role in the later appearance of an image imprint of that body. Faintly scorched linen displays a greater dissimilarity from the Shroud image in reflection properties than these stains do. Perhaps the chemical changes to the linen that result in a visible image are identical in the above cases.

It has been established that organic materials, or more appropriately perhaps the products of their reactions with linen, are stable to the temperatures associated with proximate scorches. This observation is in agreement with the uniformity of body image color over the Shroud.

The decrease in image contrast with decreasing observation distance is partially the result of the increased contribution of scattered light into the cone of vision. No fluorescence was observed from body image or bloodstains; the linen itself is fluorescent. Light scorches fluoresce a faint reddish brown. Fluorescence observations of simulated body image stains are in accord with Shroud data.

While the difference between image and faint scorch was discernible as a color difference, the photoelectric measurements showed only a small excess return from the scorches. This may have been due to the narrower excitation band of wavelengths for the photoelectric measurements or to inadequate SNR. Multispectral photography using narrowband filters revealed that the greatest contrast between body image and background occurs at the shortest wavelengths. More blue light is absorbed by the body image than by the background linen.

To ensure future preservation of the already low contrast image, some guidelines resulting from this work are suggested. Storage should be in an inert gas atmosphere (N_2) with a nonzero relative humidity (e.g., $\sim 30\%$). The temperature should not exceed 25°C, and exposure to solar UV should be avoided. Both temperature and humidity should be constant. The physical handling (such as rolling) should be minimized to reduce the loss of blood particles due to abrasion and flexing of the weave.

Future spectroscopy should be aimed toward the resolution and identification of organic absorption bands in the 250–5000-nm region and should be done at a SNR $>200:1$. Fluorescence spectroscopy should utilize wideband excitation, including wavelengths <300 nm, and a greater SNR and larger collection optics. For both studies, more areas must be sampled. Further followup laboratory simulation studies are needed.

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