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Portable unit permits UV/vis study of "Shroud"

A newly-designed portable spectrophotometer was used to examine the Shroud of Turin. The tests indicate the nature of many of the stains, but numerous questions remain.

In October 1978, a group of U.S. scientists, which included the first author, was permitted to make measurements on the relic known as the Shroud of Turin. That event was the culmination of efforts by the team, known officially as the Shroud of Turin Research Project Inc. (STURP), to obtain permission for the nondestructive examination.

The examination coincided with the completion of the one-month-long public exhibition—the first in 45 years—commemorating the 400th anniversary of the Shroud's safekeeping in Turin, Italy.

Our ambitious schedule of experiments ranged from x-ray fluorescence and radiography to infrared spectroscopy. Also included were UV/visible reflectance and fluorescence spectroscopy, microscopy, tape sampling, and multispectral photography (1, 2). The time allotted before return of the Shroud to its nitrogen-purged safe was five days and nights.

For the determination of the spectral characteristics of some of the marks on the cloth, the authors designed and constructed a portable photoelectric instrument. This device uses a silicon photodiode and a CVF wheel, and it has a digital readout (4). The resolution was 17 nm. Thus, we were able to measure points every 20 nm between 420 and 700 nm.

In a similar unit, Marty and Roger Gilbert of Oriel Corp. assembled a fluorimeter/photometer with a readout between 250 and 750 nm, with 5 nm resolution (5). The simplicity of design and the portability permit use of this instrument, for example, in field measurements of *in vivo* plant reflectances, in soil and other earth resources applications, in biological, chemical, and photographic labs, and in classrooms.

Using this small spectrophotometer, we obtained spectral reflectance ratios for the Shroud features. In an attempt to explain the cause for the body image, we then used these data (4) in conjunction with the continuous, higher-resolution measurements of Gilbert and Gilbert (5) as data points for laboratory simulations of the Shroud body image. In this work, we used spherical integrators and a Cary 14 spectrophotometer to obtain total (diffuse plus specular) reflectances from the various areas of interest.

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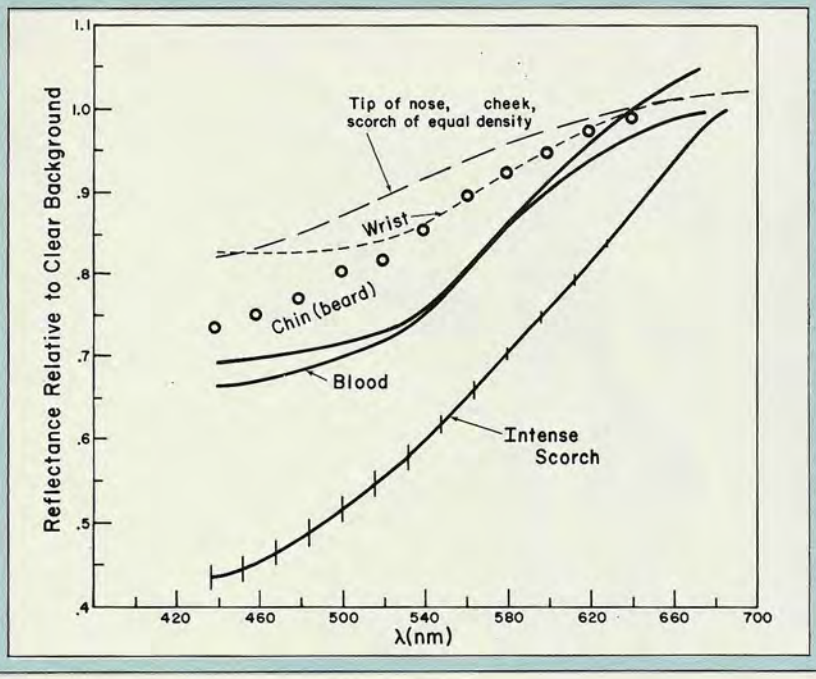
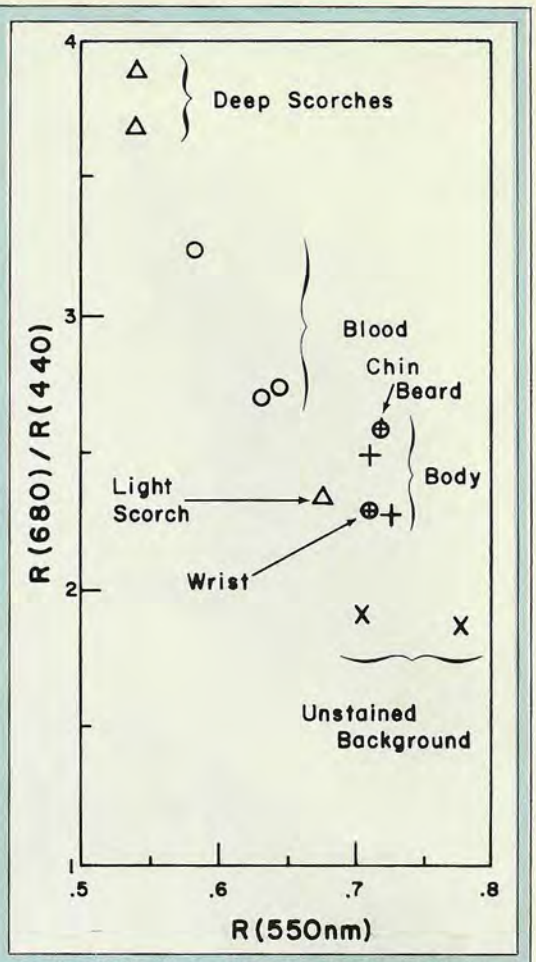
Shroud detail reflectance (below) taken with miniature spectrophotometer, all ratioed to clear background areas.





Spectral reflectance (R) ratios for Shroud features were used in lab simulations.

Aged linen—The first task was to simulate aged linen. Since all of the Shroud markings were underdense, we ratioed all of the spectra of the features against the Shroud background area measurements. Thus, the measurements contained the spectra for the linen background.

We found that baking modern linen in air at temperatures below the pyrolysis temperature of cellulose (~210 C) for several hours would artificially age the linen. The color of the Shroud background could be reproduced by baking at 150 C for about four hours.

In fact, we noted that there is an inverse relationship between time and temperature. The yellowing attained by the Shroud at ambient temperatures, resulting from the passage of many years, could be simulated by a short-duration bake.

Denatured blood—Next, we attempted to simulate aged blood by the same technique. In this case, however, the whole blood applied to the linen could not be raised to temperatures higher than 60 C without the possibility of decomposition. On completion of these tests, the match of laboratory blood with the Gilberts' spectra for Shroud "blood" was quite good.

Using microspectrophotometry of a blood fleck pulled from the Shroud by tape, John Heller and Alan Adler (6) have ob-

tained a positive identification for denatured acid methemoglobin.

Body image—In attempting to reproduce spectrally the body image, we started with expected skin substances such as perspiration and oils—and also with myrrh and olive oil, two materials possibly present in burial ointments. On subjecting these compounds to the same accelerated aging procedure, we found that stains developed—and the stains closely resembled the body image coloration.

On the Shroud, the darkened fibrils making up the body image are colored. There are no foreign colorants visible. We then compared the spectral characteristics of the aged perspiration plus skin oils, myrrh stains, olive oil, and the Shroud image—obtaining a fairly good match.

Microscopist Walter McCrone has suggested that an artist's pigment containing Fe_2O_3 is responsible for the body image. He bases this conclusion on the presence of submicrometer iron oxide particles seen on the thread fibrils at magnifications of several hundred times.

Yet photomicroscopy of image areas at 20X show no colored particles (7). Our tests indicate that a concentration as small as 2 $\mu g/cm^2$ is detectable optically. And the reflectance spectrum of Fe_2O_3 is so different from that of the body image that we cannot support Dr. McCrone's conclusions.

The body image spectrum, being a monotonically decreasing function with decreasing wavelength, has no resemblance to inorganic pigments or to organic pigments capable of surviving the fire of 1532 without change. It is unchanged in color or density, even where the image approaches scorched areas.

Cause of the image—What then is the cause for the body image? Other observers have noted that in visible light the faintly scorched areas resemble the body image areas. On the other hand, spectrophotometrically, they are slightly redder.

Our team also found that under UV excitation the scorches emitted reddish fluorescence. But the body image does not fluoresce; instead, it absorbs the background fluorescence of the linen. Thus, the image appears black.

The artificial yellowing experiments gave a clue to the cause for the presence of the body image. Cellulose yellows through the loss of water, and through the breaking of the interatomic bonds that make up the molecule. The new structure, containing C=C or C=O bonds absorbs blue light more

Photometer in a shoe box

The shoe-box-size portable spectrophotometer is battery-powered by three 9-V cells. It uses readily available parts: a continuously-variable filter (CVF) wheel (OCLI VC180-017), a liquid-crystal display (Intersil ICL 7106 EV/KIT), a silicon diode (*e.g.*, EGG uv100, 1.25 nm active dia), an FET operational amplifier (LF355), and standard lenses.

For use in measuring spectral reflectances in the detail of the Shroud of Turin, we chose fixed object distance, size, and spectral resolution. A 1-cm dia area at 50-cm distance was imaged by a 100-mm *f*.1. lens onto a 3-mm dia field stop placed just before the CVF wheel.

This stop, together with the CVF dispersion, determined the spectral bandwidth (17 nm). The element was re-imaged at one-third magnification to fill the photodiode. The photodiode was removable to permit insertion of a low-power eyepiece for viewing the object field.

In Turin, the illuminator was a 500-W tungsten lamp. We calibrated a vernier dial (National Radio SCN) and used it to rotate the CVF through its cycle.

The electronics consist of a current-mode preamplifier, sensitivity and offset circuitry, and the digital readout module. The preamp is made up of the LF355 op amp, a 10^8-ohm feedback resistor, and a bandwidth-limiting capacitor. In addition to the simplicity, this configuration offers several advantages in comparison to the voltage-amplification mode preamp.

Good low-frequency-noise and offset-drift performance are required to keep the least significant digit of the digital readout from flickering. In this configuration, virtually all of the photocurrent flows through the feedback resistor. Therefore, the op-amp negative terminal remains at or near ground (keeping the voltage across the photodiode at zero). As a result, the impedance of the photodiode is prevented from contributing low-frequency noise.

The primary noise (Johnson) source is the feedback resistor. This noise increases as $\sqrt{R1}$, while the amp gain is proportional to R1. Thus, the signal-to-noise ratio increases when a large R1 is used.

Voltage drifts and temperature offsets are low because the offset voltage appears at the output terminal with no gain factor. The feedback capacitor, C1, limits the high-frequency bandwidth to 10 Hz.

The readout unit is powered by a separate battery because the low side of the input is not ground-referenced, and a differential input is not provided. Battery life for the photometer is greater than 100 hr; the stabilization time is less than two min.

If the user has access to a monochromator, he or she will find that wavelength calibration is relatively easy. If a monochromator is not available, the mercury-vapor 435.8- and the 546.1-nm lines and the sodium 589-nm line could be used.

It is convenient that each 5-deg rotation of the CVF wheel corresponds linearly to a wavelength change of 100 nm. Because of this relationship, only a few points are needed to establish the scale.

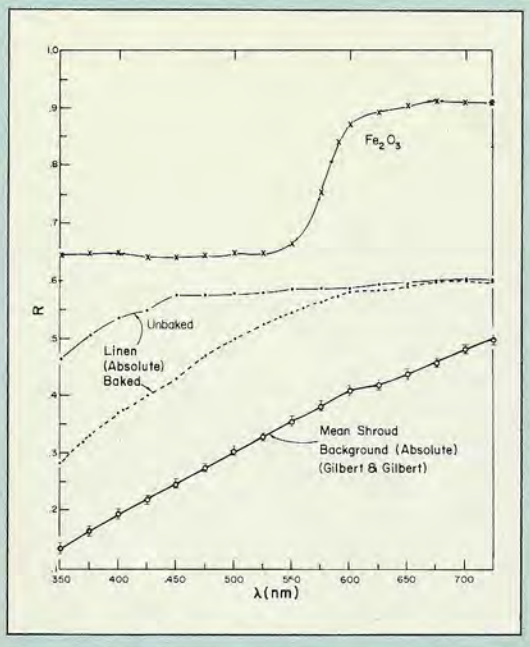
If the photodiode is not over-illuminated, photometric linearity is excellent. Thus, neutral-density filters can be used to check the linearity.

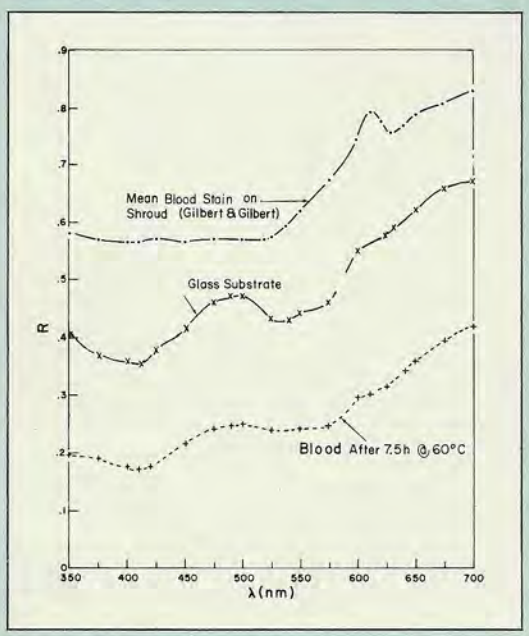
The photographic grey scale can be used for calibration of wavelengths between 450 and 650 nm. A blue-color correcting filter (Wrattan 80A or equivalent) is cemented to the detector to help in balancing the excessive red response.

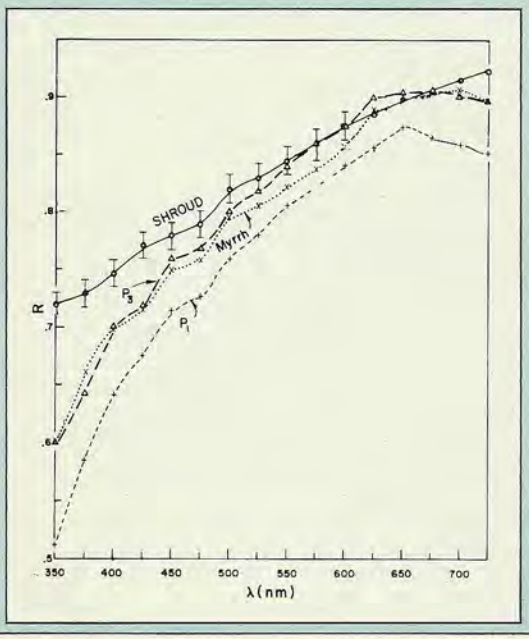
The user can make absolute reflectance measurements by standardizing against a white standard such as MgO or $BaSO_4$. In Turin, we used a freshly-smoked surface of MgO. Repeatability during several hours was better than 1%.

The optics and the detector have virtually no polarization sensitivity. Therefore, the inclusion of a polarizer allows the instrument to be used as a photo-polarimeter.

The instrument is susceptible only to excessive mechanical shock. And pointing the instrument at the sun will damage the detector by overheating.







strongly than it does red. Thus, it appears reddish by reflection.

The literature on cellulose chemistry and on textile processing indicates that cellulose undergoes degradation in the presence of heat or light. The addition of foreign substances that absorb the heat or light energy catalyzes or advances the rate of discoloration.

For these reasons, we have hypothesized that natural skin substances or applied burial ointments were transferred to the Shroud by contact with the body. These materials acted as the catalysts necessary to accelerate the degradation of the cellulose at those points where contact was made.

With the passage of time, an image formed. The original substances have disappeared, either through washing or by being consumed in the reaction. We are left with an image that is made of nothing else but locally darkened cellulose.

Image transfer—We might know the composition of the image, but we still are trying to discover the mechanism for the image transfer. The high-resolution details present in the scourges, in particular, on Vern Miller's UV fluorescence photos suggest direct contact between cloth and body.

On the other hand, Drs. E.J. Jumper and J.P. Jackson have reconstructed-contour information from density-gradient scans. These data suggest that the form of the body is recorded undistorted. The direct-contact corollary to our hypothesis meets with difficulty here because body features of large slope would be distorted by total contact; deep features normally would not be contacted by a stiff linen cloth.

A suggested alternative mechanism of transfer across space by radiation or by molecular diffusion would not give the detail seen on the body features. Thus, the exact mechanism still is being sought.

We have established these points:

☐ There are no paints or pigments on the Shroud.

☐ The blood marks appear to be human blood.

☐ The body image is a result of degraded cellulose—nothing more.

Does any of this discount the possibility that the Shroud could be authentic? The answer is no. In our opinion, there is no way to prove who the man of the Shroud might have been. That case could rest only on circumstantial evidence. ☐

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Artificially aged linen shows a reflectance spectrum similar to that of portions of the Shroud that contain no image (upper left). Similarly, the spectrum of aged blood shows a good match for the "blood" stains on the Shroud (center left). Comparison of the reflectance of aged myrrh, two different perspiration and skin-oil mixtures (P_1, P_3) and the Shroud image show similarities (lower left).

THE AUTHORS

Samuel F. Pellicori is an optical physicist at Santa Barbara Research Center, Santa Barbara, CA. A graduate of Univ. of Arizona and a member of STURP, he participated in the multispectral photography, the photomicroscopy, the reflectance spectrophotometry, and the UV fluorescence experiments in Turin.

Richard A. Chandros is a technical staff member at SBRC. He designed, built, and tested the electronics for the portable instrument. Both engineers have worked on various NASA space programs.