

Studies on the radiocarbon sample from the shroud of turin

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Abstract

In 1988, radiocarbon laboratories at Arizona, Cambridge, and Zurich determined the age of a sample from the Shroud of Turin. They reported that the date of the cloth's production lay between A.D. 1260 and 1390 with 95% confidence. This came as a surprise in view of the technology used to produce the cloth, its chemical composition, and the lack of vanillin in its lignin. The results prompted questions about the validity of the sample.

Preliminary estimates of the kinetics constants for the loss of vanillin from lignin indicate a much older age for the cloth than the radiocarbon analyses. The radiocarbon sampling area is uniquely coated with a yellow–brown plant gum containing dye lakes. Pyrolysis–mass–spectrometry results from the sample area coupled with microscopic and microchemical observations prove that the radiocarbon sample was not part of the original cloth of the Shroud of Turin. The radiocarbon date was thus not valid for determining the true age of the shroud.

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1. Introduction

The Shroud of Turin is a large piece of linen that shows the faint image of a man on its surface. Many people believe it is the burial cloth of Jesus, making it extremely controversial. Radiocarbon ages were determined in 1988 [1], which should have settled controversies as to the age of the linen. The 1988 radiocarbon age determinations were the best that could have been obtained. Sample preparation methods were compared and confirmed, and the measurements were made with the best available instruments. Damon et al. reported [1] that “The age of the shroud is obtained as A.D. 1260–1390, with at least 95% confidence.” However, that date does not agree with observations on the linen-production technology nor the chemistry of fibers obtained directly from the main part of the cloth in 1978 [2,3]. The 1988 sampling operation was described in [1]: “The shroud was separated from the backing cloth along its bottom left-hand edge and a strip (~10 mm × 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.” 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. However, the operation was done in secrecy, and no chemical investigations were made at the time to characterize the sample.

2. Samples

Professor Gilbert Raes of the Ghent Institute of Textile Technology cut the 1973 sample [4] mentioned by Damon et al. [1]. Raes found that one part of his sample contained cotton, but the part on the other side of a seam did not. He reported that the cotton was an ancient Near Eastern variety, *Gossypium herbaceum*, on the basis of the distance between reversals in the tape-shaped fibers (about eight per centimeter). I received 14 yarn segments from the Raes sample from Prof. Luigi Gonella (Department of Physics, Turin Polytechnic University) on 14 October 1979. I photographed

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the samples as received and archived them separately in numbered vials. Some of the samples were destroyed in chemical tests between 1979 and 1982, but most of the segments have been preserved.

As part of the shroud of turin research project (STURP), I took 32 adhesive-tape samples from all areas of the shroud and associated textiles in 1978 [2]. Ronald Youngquist of the Minnesota Mining and Manufacturing Corporation produced the tape specifically for the project; an amorphous, inert, pure-hydrocarbon adhesive that would not contaminate the shroud or the samples. It enabled direct chemical testing on recovered linen fibers and particulates, and the adhesive could be removed by washing with xylene. I applied the tapes to the surface of the shroud with a pressure-measuring applicator to enable semi-quantitative comparisons among samples.

The shroud was badly damaged in a church fire in A.D. 1532. Nuns patched burn holes and stitched the shroud to a reinforcing cloth that is now known as the Holland cloth. I also sampled it in 1978. The Holland cloth provides an authentic, documented sample of linen as it was produced in Europe between 1532 and 1534.

On 12 December 2003, I received samples of both warp and weft threads that Prof. Luigi Gonella had taken from the radiocarbon sample before it was distributed for dating. Gonella reported that he excised the threads from the center of the radiocarbon sample.

3. Alternate methods for linen age estimation

STURP was not allowed to take radiocarbon samples in 1978; therefore, it was useful to devise independent methods for age determination to test the validity of the published date [1]. The most obvious aging change is the deepening sepia color of linen. Absolute spectral reflectance measurements were made on the shroud and many museum samples of linen by Gilbert and Gilbert [5]. No simple relationship between color and age could be derived, because bleaching methods have changed through the centuries.

The crystalline structure of flax fibers acts like a dosimeter: it collects radiation defects over time. Unfortunately, background radiation varies greatly with storage conditions and latitude. Radon collects in many old buildings and tombs, and alpha-particles cause short, intensely birefringent ionization tracks. Electromagnetic radiation (ultraviolet, X-ray, and gamma-ray) causes a diffuse background birefringence that varies with location and linen-production methods. Neutrons produce recoil protons in the interior of fibers, and energetic protons produce long ion tracks that occasionally branch. Radiation-based age estimation is very subjective; however, defect populations indicate that the shroud's linen has been absorbing several kinds of radiation for a very long time.

The lignin at growth nodes on the shroud's flax fibers (Fig. 1) did not give the usual chemical spot test for lignin (i.e., the phloroglucinol/HCl test for vanillin). The Holland cloth and other medieval linens gave a clear test. This sug-

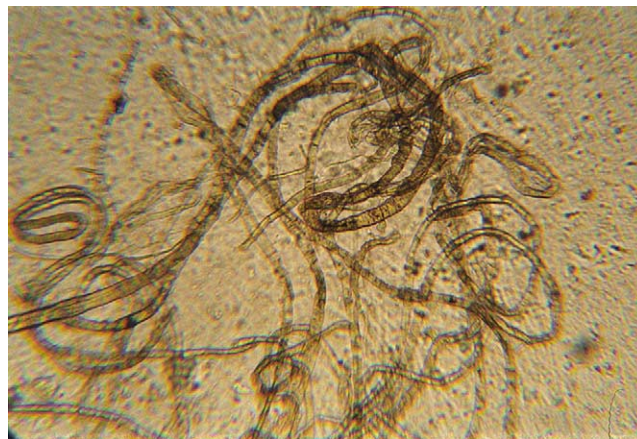


Fig. 1. Colored image fibers from the back of the ankle (400 \times) that are still embedded in the sampling tape's adhesive. Dark lignin deposits are easily visible at the growth nodes. The deposits do not give the spot test for lignin.

gested that the rate of loss of vanillin from lignin could offer a method for estimating the age of the shroud. The phloroglucinol–hydrochloric-acid reagent detects vanillin (4-hydroxy-2-methoxybenzaldehyde) with good sensitivity. The lignin on shroud samples and on samples from the Dead Sea scrolls does not give the test. If the detection limit for the test is assumed to be constant, aged samples of lignin can be compared by observing the times and temperatures that give the last observable color reactions. Stanley T. Kosiewicz of Los Alamos aged samples that contained lignin at 40, 70, and 100 °C for up to 24 months. Comparison of detection limits among the samples showed the rate of vanillin loss is very low. A suitable chemical-age predictive model therefore could be produced.

Rates of all kinds of chemical reactions are modeled with the Arrhenius expression

$$\frac{d\alpha}{dt} = kf(\alpha)Ze^{-E/RT} \quad (1)$$

where α is the fraction reacted at any time t ; k is the rate constant, s^{-1} ; Z is the Arrhenius frequency factor, s^{-1} ; E is the Arrhenius activation energy, $J\ mol^{-1}$; R is the gas constant, $8.314\ J\ K^{-1}\ mol^{-1}$; and T is the absolute temperature in kelvins. $f(\alpha)$ is the depletion factor; and it depends on the physical state of the reactant, the type of reaction, and/or the number of molecules involved in the reaction. Analysis of the time/temperature/detection-limit data gave the following Arrhenius predictive model for the rate of vanillin loss from lignin.

$$k = 3.7 \times 10^{11} e \exp\left(-\frac{123800}{8.314T}\right) \quad (2)$$

After the rate constant has been calculated at a specific temperature, the amount of time required for vanillin to be depleted by a first-order reaction at that temperature can be calculated from

$$-\ln(1 - \alpha) = kt \quad (3)$$



Fig. 2. Fibers from the surface of a radiocarbon warp segment, dry at 100 \times .

The major problem in estimating the age of the shroud is the fact that the rate law is exponential; i.e., the maximum diurnal temperature is much more important than is the lowest storage temperature. However, some reasonable storage temperatures can be considered to give a range of predicted ages. If the shroud had been stored at a constant 25 $^{\circ}\text{C}$, it would have taken about 1319 years to lose a conservative 95% of its vanillin. At 23 $^{\circ}\text{C}$, it would have taken about 1845 years. At 20 $^{\circ}\text{C}$, it would take about 3095 years.

If the shroud had been produced between A.D. 1260 and 1390, as indicated by the radiocarbon analyses, lignin should be easy to detect. A linen produced in A.D. 1260 would have retained about 37% of its vanillin in 1978. The Raes threads, the Holland cloth, and all other medieval linens gave the test for vanillin wherever lignin could be observed on growth nodes. The disappearance of all traces of vanillin from the lignin in the shroud indicates a much older age than the radiocarbon laboratories reported.

The fire of 1532 could not have greatly affected the vanillin content of lignin in all parts of the shroud equally. The thermal conductivity of linen is very low, $2.1 \times 10^{-4} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ }^{\circ}\text{C}^{-1}$; therefore, the unscorched parts of the folded cloth could not have become very hot. The temperature gradient through the cloth in the reliquary should have been very steep, and the cloth's center would not have heated at all in the time available. The rapid change in color from black to white at the margins of the scorches illustrates this fact.

Any heating at the time of the fire would decrease the amount of vanillin in the lignin as a function of the temperature and time heated; however, different amounts of vanillin would have been lost in different areas. No samples from any location on the shroud gave the vanillin test.

Because the shroud and other very old linens do not give the vanillin test, the cloth must be quite old. It is thus very unlikely that the linen was produced during medieval times.

All threads from the Raes sample and the yarn segments from the radiocarbon sample show colored encrustations (or coatings) on their surfaces (Figs. 2 and 3). The coating ma-

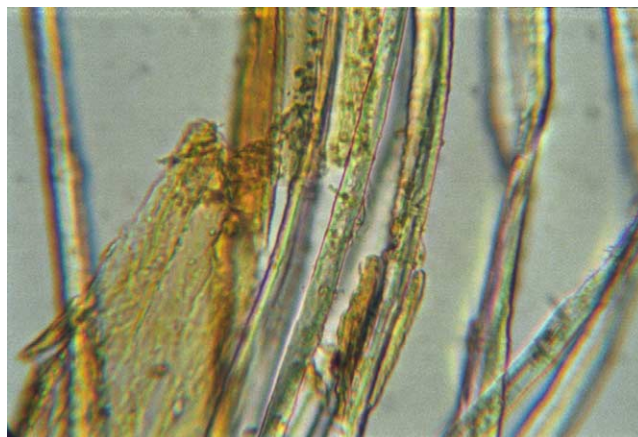


Fig. 3. Warp fibers from the radiocarbon sample, 800 \times in water. The gum is swelling, becoming more transparent, and detaching from the fibers.

terial is not removed by nonpolar solvents, but it swells and dissolves in water. There was absolutely no coating with these characteristics on either the Holland cloth or the main part of the shroud. When Raes and radiocarbon-sample threads were teased open at both ends with a dissecting needle, the cores appeared to be colorless, suggesting the color and its vehicle were added by wiping a viscous liquid on the outside of the yarn. A marked difference between inside and outside fibers is characteristic of both the Raes and radiocarbon samples. The yellow–brown coating on the outside of the radiocarbon warp sample is so heavy that it looks black by transmitted light (Fig. 2). Chemical tests on both the radiocarbon and Raes samples show their coatings to consist of a plant gum containing alizarin dye present in two forms. Some is dissolved in the gum, giving it a yellow color. A variable amount is complexed with hydrous aluminum oxide [$\text{AlO}(\text{OH})$] to form red lakes (Fig. 3). The lakes are gelatinous and usually very small. A good microscope is required to observe them, and the gum vehicle for the dye/mordant system on the Raes and radiocarbon samples makes it difficult to observe the lakes. The gum cannot be removed without damaging the lakes, but it can be made invisible by matching its index of refraction in a 1.515 index oil. With the gum invisible or swelled slightly in water, it is easy to see the lakes suspended in the gum and stuck to the fibers. Fig. 3 shows (upper left) colloidal red dye lakes suspended in the gum. To the right of that, some discrete lakes can be seen adhering to the surface of a cotton fiber. Several areas of yellow-dyed gum can be seen. Four cotton fibers and two flax fibers appear in the view. The radiocarbon sample contains both a gum/dye/mordant coating and cotton fibers. The main part of the shroud does not contain these materials.

Alizarin and purpurin are extracted from Madder root and first appeared in Italy about A.D. 1291 [6]. Alizarin has long been used as an acid–base indicator in chemical analysis. It is yellow below pH 5.6, red above pH 7.2, and purple above pH 11.0. The colored coating shows all of these changes as

a function of pH. HCl (6N) brings the lakes into solution and turns bright yellow. Alum has been a common mordant for millennia. The red lakes are diagnostic for Madder root dyes and alum. The solubility characteristics of the red lakes indicate $\text{AlO}(\text{OH})$. The coating was insoluble at pH 8.0 but dissolves at both lower and higher pH. The red dye/mordant lakes dissolved in 2N NaOH to give a purple solution. The presence of aluminum in the coating material is consistent with the results of Adler, Selzer, and DeBlase [7], who performed X-ray elemental analyses on different shroud materials, including fibers from radiocarbon-sample warp threads. They reported concentrations of aluminum on the radiocarbon sample 20-times those on shroud fibers. Mordants other than $\text{AlO}(\text{OH})$ produce different colors with Madder root dye. Calcium compounds produce blue colors, and a few blue lakes can be seen on some gum-coated fibers. They are removed with 6N HCl. The color suggests alizarin on crystals of calcite or aragonite in the threads.

The presence of alizarin dye and red lakes in the Raes and radiocarbon samples indicates that the color has been manipulated. Specifically, the color and distribution of the coating implies that repairs were made at an unknown time with foreign linen dyed to match the older original material. Such repairs were suggested by Benford and Marino [8,9]. The consequence of this conclusion is that the radiocarbon sample was not representative of the original cloth.

The gum coating was quickly hydrolyzed by either concentrated HCl or 2N NaOH. That fact and its solubility in water suggest that it is probably a polysaccharide and not a denatured protein. Hydrolysis at a moderate rate in 6N HCl suggests that it is probably a pentosan, composed of five-carbon sugar units. Pentosan plant gums form a reversible, bright-yellow color with aqueous iodine. The color completely disappears after the solution evaporates, proving that the color is not a result of iodination reactions or iodine-catalyzed dehydrations. Both Raes and radiocarbon samples give this reaction.

One of the analytical methods used during the STURP studies was pyrolysis mass spectrometry. The Midwest Center for Mass Spectrometry (MCMS) at the University of Nebraska, Lincoln, made dozens of scans on different samples in 1981. The chemical-ionization system used was the most sensitive MS at the time, sufficiently sensitive to detect parts-per-billion traces of oligomers from the polyethylene bag that Gonella had used to wrap the Raes threads. The instrument at MCMS is equipped with a pulsed source that has a time resolution of 100 ns, and it produces a series of mass spectra as the sample heats up. However, it was impossible to quote an accurate, absolute sample temperature when single microfibrils were being analyzed, only relative sample temperatures could be compared. Seven different samples underwent multiple analyses at MCMS. Results were corrected with instrument blanks. Perfluorokerosene was used as an internal calibrant, its spectrum was subtracted by the instrument's computer. Total ion currents (TIC) were measured.

Some of the samples came from areas of apparent blood flows, some from scorched areas, one (“the Zina thread”) was a complete yarn segment that had been withdrawn from the heel image area, one came from a pure image area, one came from a water stain in an image area, and several were modern reproductions of ancient linen technology. Mrs. Kate Edgerton (deceased), made the reproductions from raw flax according to historic accounts of ancient technology. To obtain replicate data, some of the pyrolysis/ms analyses had to be run on single 10–15- μm -diameter fibers that were 5–6 mm long. Compared with fibers extracted from the sampling tapes, there was ample material from the Raes sample, which should be representative of the entire Raes/radiocarbon sampling area.

At the time the samples were analyzed, the goal of STURP was to test whether the image had been painted. The results of the pyrolysis/ms analyses proved to be consistent with an array of independent observations and data [2], showing that the image was not the result of an applied material. With that conclusion established, the dozens of pyrolysis/ms data sets can now be reanalyzed to compare samples from the radiocarbon area with samples from the main cloth.

Cellulose pyrolyzes to produce hydroxymethylfurfural (mass 126), which begins to deformylate in a series reaction to produce furfural (mass 96). Furfural is always a minor product of cellulose decomposition. Linen fibers from the main part of the shroud did not show significant product evolution until relatively high temperatures (probably about 260 °C), but the products contained both expected fragments (Fig. 4). Pentosans do not produce hydroxymethylfurfural. They also pyrolyze much faster at lower temperatures than cellulose. When the first pyrolysis products appeared during heating, the Raes fibers showed a signal for furfural at mass 96 (Fig. 5). There was no signal at mass 126. These results prove that the gum coating on the Raes and radiocarbon samples is a pentosan. None can be detected on any fibers from the main part of the shroud.

Incidentally, the pyrolysis/ms spectra of samples from apparent blood spots showed hydroxyproline peaks at mass 131, a pyrolysis product of animal proteins.

The fact that vanillin can not be detected in the lignin on shroud fibers, Dead Sea scrolls linen, and other very old linens indicates that the shroud is quite old. A determination of the kinetics of vanillin loss suggests that the shroud is between 1300- and 3000-years old. Even allowing for errors in the measurements and assumptions about storage conditions, the cloth is unlikely to be as young as 840 years.

A gum/dye/mordant coating is easy to observe on Raes and radiocarbon yarns. No other part of the shroud shows such a coating. The early thermal evolution of furfural during pyrolysis/ms analyses, the relatively easy water solubility, the yellow color formed with iodine, and the easy hydrolysis suggest gum Arabic. Gum Arabic is obtained from *Acacia senegal* and is composed of pentose-sugar units. Its presence

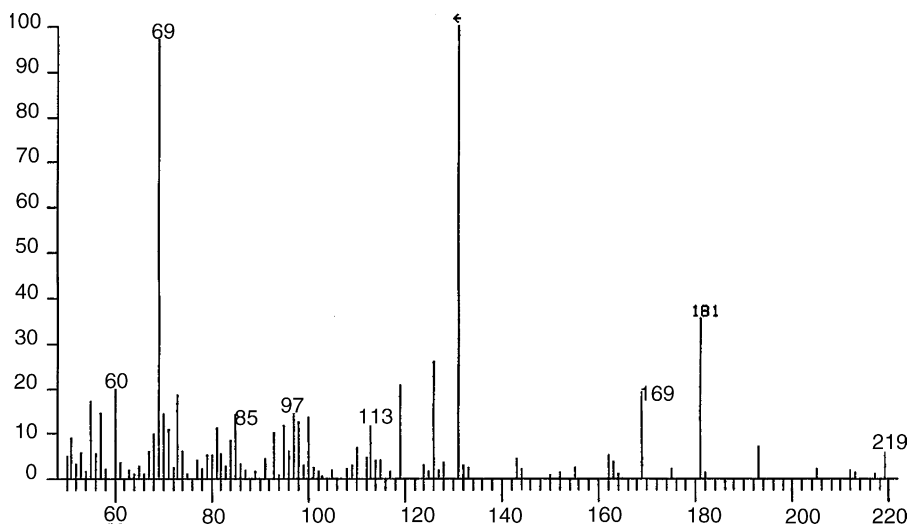


Fig. 4. A mass spectrum obtained from the pyrolysis of a shroud-image fiber. The sample did not produce a significant amount of furfural (mass 96) until it reached higher temperatures; i.e., it did not contain a significant amount of pentose sugars or pentosans. The ordinate shows the relative ion intensity for each product at that temperature, and the abscissa shows the mass of the ion.

as a major component in the coatings on the Raes and radiocarbon samples is not a surprise, because it has long been a common vehicle in tempera paints. The radiocarbon sample had been dyed. Dyeing was probably done intentionally on pristine replacement material to match the color of the older, sepia-colored cloth. The gum is probably the same age as the Raes and radiocarbon yarn and should have no effect on the age determination. In any case, this water-soluble, easily-hydrolyzed gum would have been removed completely by the cleaning procedures used on the dated samples [1].

The dye found on the radiocarbon sample was not used in Europe before about A.D. 1291 and was not common

until more than 100 years later [6]. The combined evidence from chemical kinetics, analytical chemistry, cotton content, and pyrolysis/ms proves that the material from the radiocarbon area of the shroud is significantly different from that of the main cloth. The radiocarbon sample was thus not part of the original cloth and is invalid for determining the age of the shroud. Because the storage conditions through the centuries are unknown, a more accurate age determination will require new radiocarbon analyses with several fully characterized and carefully prepared samples.

A significant amount of charred cellulose was removed during a restoration of the shroud in 2002 [10]. Material

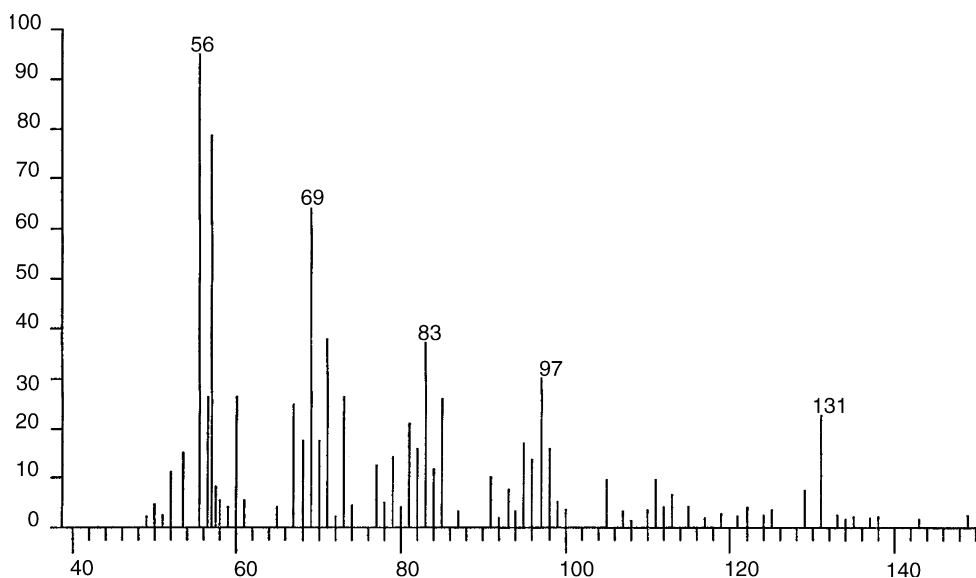


Fig. 5. A mass spectrum from the low-temperature pyrolysis of fibers from a Raes sample. As shown by the signal at mass 96 and the absence of a signal at mass 126, the sample contained a significant amount of pentosan. The ordinate shows the relative ion intensity for each product at that temperature, and the abscissa shows the mass of the ion.

from different scorch locations across the shroud was saved in separate containers. The elemental carbon could be completely cleaned in concentrated nitric acid, thus removing all traces of foreign fibers, sebum from repeated handling, and adsorbed thymol from an unfortunate procedure to sterilize the shroud's reliquary in 1988. In addition, the separate samples would give a "cluster" of dates, always a desirable procedure in archaeology. A new radiocarbon analysis should be done on the charred material retained from the 2002 restoration.

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