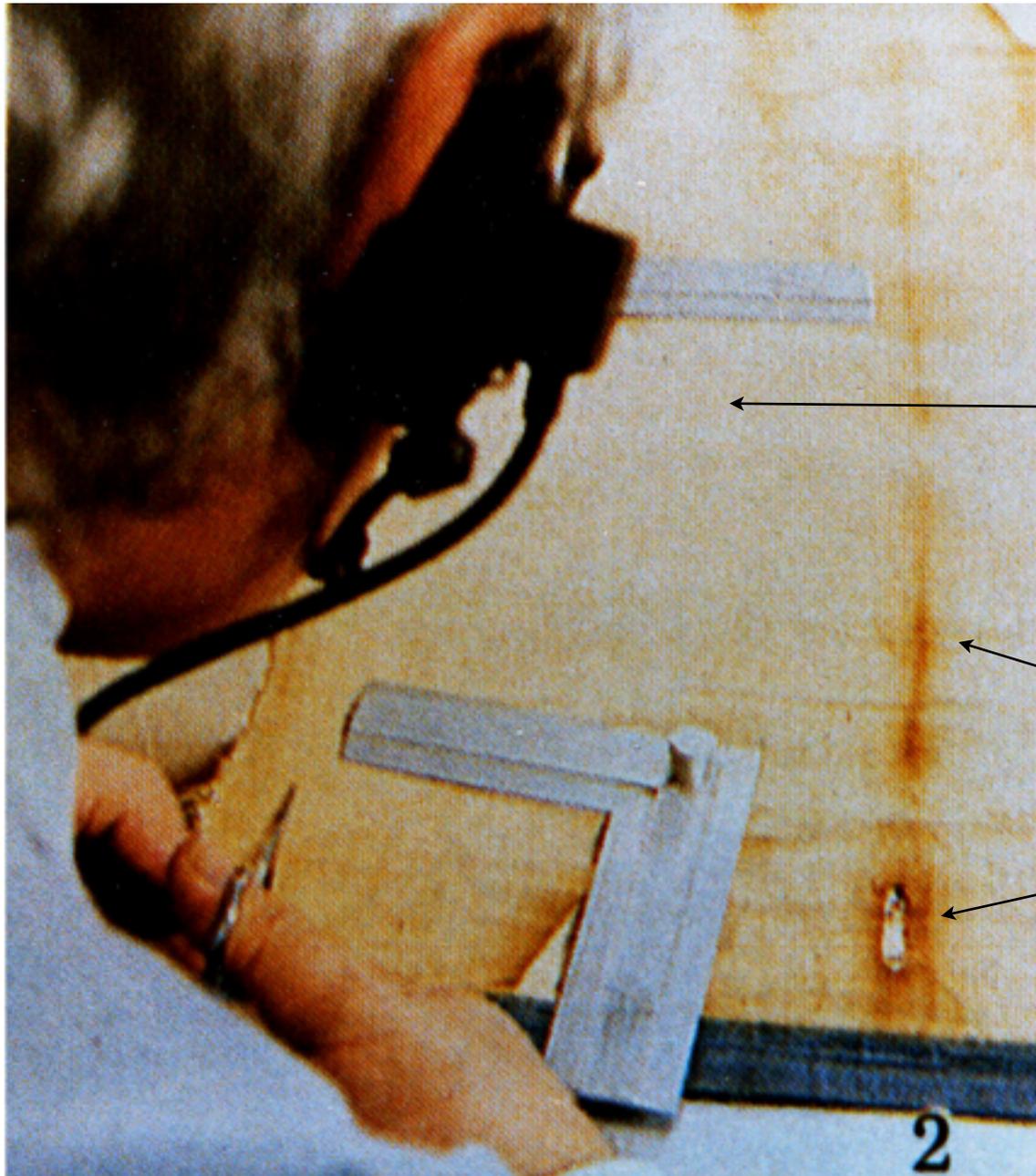


The presence of dye in the 1988 radiocarbon date samples of the Shroud of Turin.¹

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December 8th 2015.



This paper argues that the radiocarbon date samples of the Shroud of Turin, dated by laboratories in Oxford, Arizona and Zurich in 1988 were contaminated by dye, mordant, plant gum and cotton. These were not removed by the pre-cleaning of the samples which invalidates the radiocarbon date results.

The image to the left labelled with the figure 2 shows Professor Giovanni Riggi di Numana cutting the sample from the Shroud of Turin.² It is part of a set of three photographs documenting the removal (see below).² There are several different colours which appear on the Shroud in the photograph left. The top arrow points to the natural colour of the Shroud undamaged by either the fire of 1532 or the water used to extinguish the flames. The area being cut by Professor Riggi is not the colour seen at the top arrow.

The arrows below highlight the colour of Shroud damage caused by fire and carbonated douse water.

Circular carbonated water stain

Fire charring





This image with the figure 3² precedes the previous one and shows the process to decide how much was cut from the Shroud. The area of the Shroud about to be cut is a dark colour.

The area marked A is the backing cloth to the Shroud, known as the Holland cloth, which was stitched to the Shroud after the fire damage of 1532. The original corner of the Shroud has been cut away but the missing corner was not removed because of fire damage. The fire burnt straight though layers of cloth in the two lines down the centre of the Shroud. If it had burnt the corners, all four corners would be missing. On the Shroud only two corners are missing.

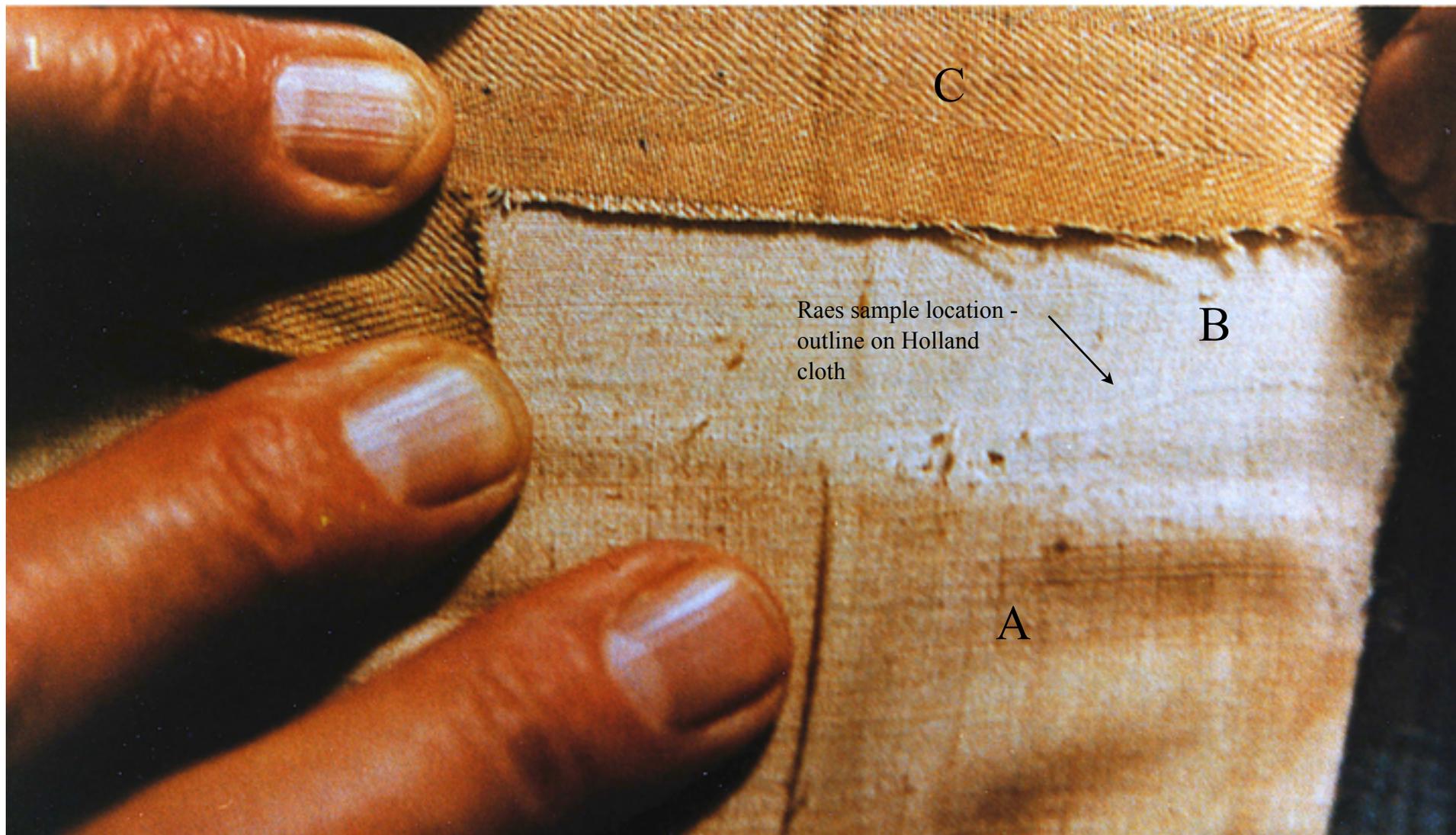
A is quite dark in colour but the colour is not as dense or as consistent as in the Shroud area to be cut. The area at B is also the Holland cloth but it is light in colour. B was under an piece of the Shroud known as the Raes sample. In 1973 Gilbert Raes was given the sample (see image below³) for analysis.

So the Holland cloth at A and B shows two different colours. The colour at A is not aging because it matches the colour of the Shroud about to be cut and the Shroud in this area is not consistent with the natural colour of the aging cloth in image 2. It could be dirt which has accumulated on the cloth, perhaps from the soil covered hands of priests. Or it could be artificial: a dye of some sort.

Raes sample

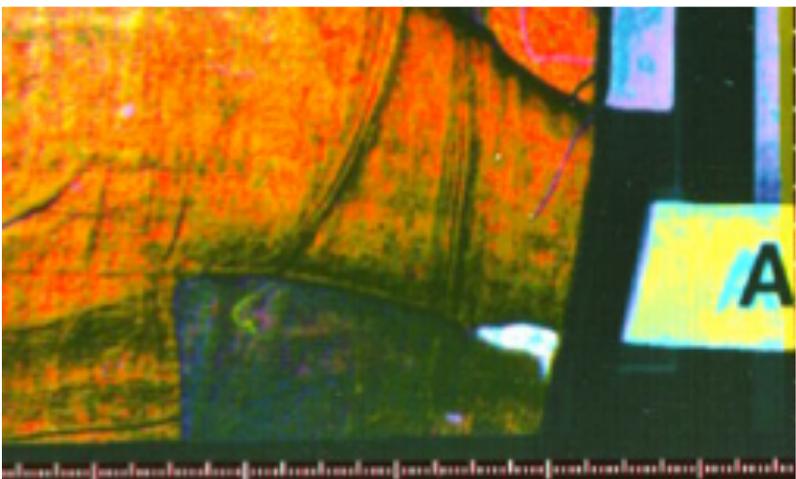


At first glance dye expert Teresinha Roberts MA⁴ suggested the colour could be from one the following: iron oxide substances such as ochres (like earth colours from soil); blood; tannin or dyes such as madder root and weld.



The third image above labelled with the figure 1² shows a detail of the area cut for radiocarbon dating. B is the natural colour of cotton. The area at A on the Holland cloth has absorbed colour: it is not the same colour as the area at B, even though it is the same cloth. The close up of the colour again indicates iron oxide substances (ochres/earth), blood, tannin or dyes such as madder root and weld. The Shroud C is the colour of A, not the colour of natural cotton B which suggests the Shroud has absorbed one of the possible colour change agents.

In the Raes area the Holland cloth shows the mark of the position of the Raes sample. This photograph confirms photograph 3 and demonstrates the natural colour of the Holland cloth under the Raes sample. It is likely the natural colour of the Holland cloth was chosen in 1532 -1534 because it was a good colour match for the Shroud itself not the areas of the Shroud damaged by fire or carbonated douse water [image 2]. The colour change at A and C are both out of place.



The Raes sample shown above³ measured 4 cm by 1.3 cm and can be seen above and in situ below on the C14 corner image. In both the 1988 Quad mosaic image⁵ and the 1978 Barrie Schwartz⁶ image of the Shroud, the Holland cloth underneath the Raes area is pale. The cloth in that area has not apparently absorbed the colour change substance. There is a density of colour in the fabric taken for radiocarbon date in Barrie Schwartz's image and an unusual dark green in the corner of the Quad Mosaic. Fibres from the Raes sample were meticulously examined by the chemist Raymond Rogers, and their chemical composition is better understood than the adjacent radiocarbon date sample. Rogers did not report evidence of iron oxide/ochres (earth colours) or blood. Neither does he mention tannin, although tannin may be a factor in the discoveries he made.



Rogers published various articles on the Raes sample area. His unpublished notes entitled Summary of Raes Observations were created on October 1st 2001, and they detail his Raes threads findings (25 bullet points including some mentions of dyeing). His complete notes are reproduced in Appendix I ⁷ and include the following:

- 2) All Raes threads show "frosty" surface. They are coated with an amorphous, colored (brown-yellow) material. Some colored material is seen in linen medulla. No encrustation on Shroud fibrils, except for blood areas.
- 3) The frosty coating softens and swells in water. Its color but not the crust is eliminated by 6N HCl, and the encrustation is eliminated by con HCl. The encrustation is not simply a mordant. Hydrous aluminum oxide, the mordant for red alizarin dye, is soluble in 6N HCl.
- 11) All of the Raes samples show colored amorphous encrustations on the outside of the yarn. There is much less to none on the inside of the yarn.
- 12) Some blue lakes can be seen on Raes #14, and they probably appear on other samples. The color and appearance indicate traces of alizarin on crystals of calcite in the cloth. This agrees with the observation of a bright yellow color in HCl (after solution of the mordants). It also agrees with observations of high calcium by XRF.
- 13) Bright red lakes can be seen on Raes #14. They are probably alizarin/purpurin (Madder root dye) on a hydrous aluminum oxide mordant.
- 18) When I teased Raes #14 open at one end, the centre of the thread appeared to be clear, nearly completely colorless. The outside of the thread showed the deepest encrustation of any of the samples, except one end of Raes 1 (the spliced thread). This observation suggests that the colour and its vehicle were added by wiping them on the threads which were used in the presumed reweaving. The object must have been to match colours.



The images show Raes #14 before and after treatment with 6N HCl.⁸

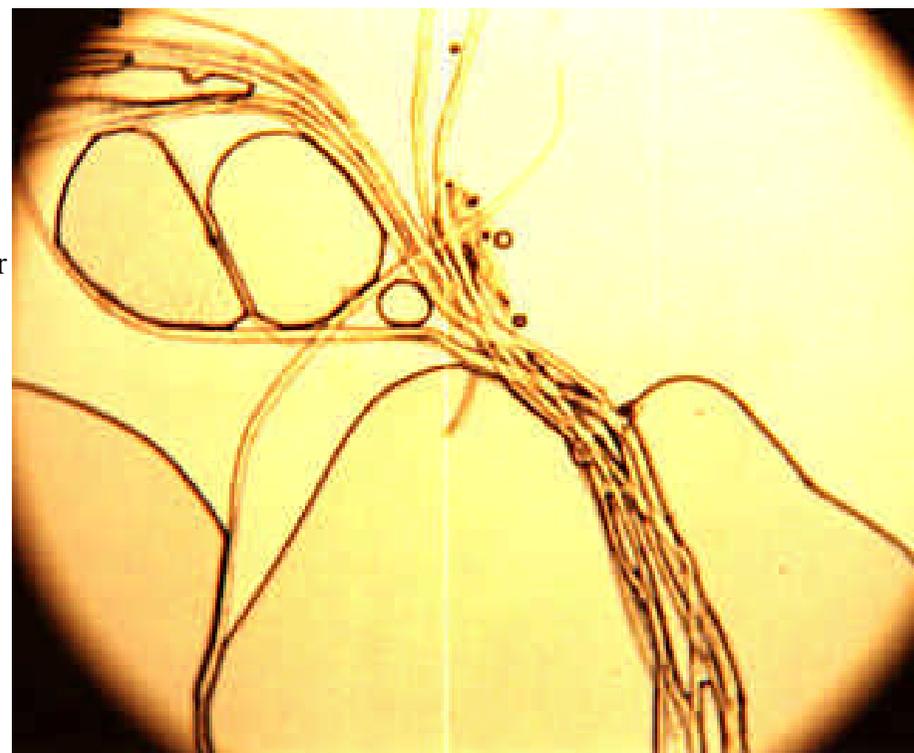


Figure 12: Heavily encrusted fibers from the outside of Raes #14 (400X) mounted in water 13: The same fibers shown in figure 12 mounted in 6N HCl. Notice the bright yellow color

Rogers continued by analysing cotton fibres found in the Raes sample.⁷

- 17) The colored encrustation does not seem to stick to linen as well as cotton. Some linen fibers appear to be nearly clean, but the cotton fibrils can be heavily encrusted in the same thread sample. This suggests that the cotton was added to the Raes threads to make dyeing possible. The cotton in the threads would have made color matching easier. Linen is difficult to dye or stain.
- 19) After treating the frosty fibers in concentrated HCl, the color and frosty crust are completely removed. Fibers of #14 are clear and clean. Some polysaccharides are easily and quickly hydrolyzed in con. HCl. This suggests a plant gum that is largely composed of pentose-sugar units.
- 21) The "frosty" coating is almost certainly a plant gum. The most probable gum is gum Arabic, an acacia gum that is mostly pentose units, because it is relatively easily soluble in water. Agar, gum tragacanth, and flax-seed gum are less popular for textile work. Gum Arabic, agar-agar, and gum tragacanth all turn bright yellow in iodine water. Identification of specific gums is a major task.
- 24) One dye used must have been alizarin (Madder root). Madder has been used with mordants to produce a beautiful red color for thousands of years.

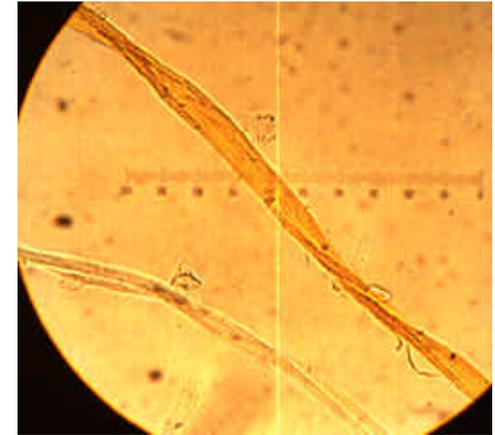
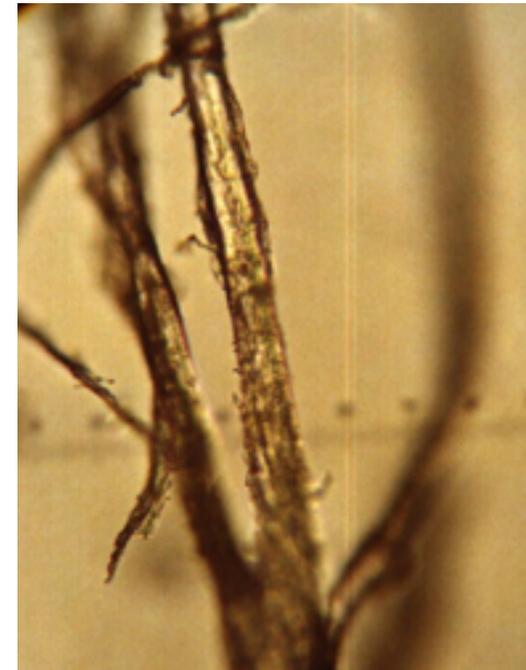


Figure 11: Two cotton fibers (X400) from a Raes thread, one nearly colorless from inside and one encrusted and red from outside.

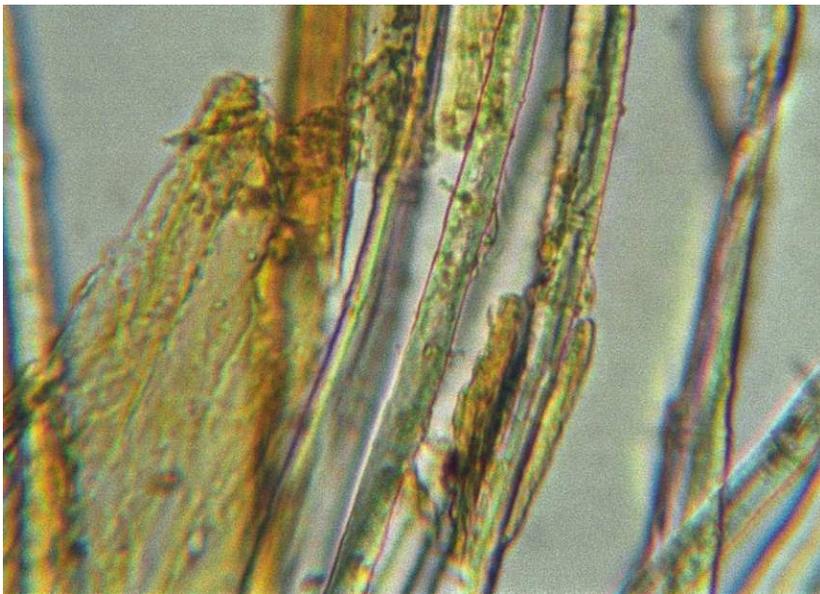
Gum Arabic is a polysaccharide ‘composed of pentose-sugar units.’⁷ It is a natural gum made from the sap of two species of acacia tree: *Senegalia (Acacia) senegal* and *Vachellia (Acacia) seyal*. Gum tragacanth has similar characteristics but comes Middle Eastern legumes of the genus *Astragalus* (common name ‘goat’s thorn’). Rogers wrote that the gum was relatively easily soluble in water. In an email he expanded this⁹:

"R-14-dry" shows some fibers mounted dry. The coating that Garza-Valdes thought was a "bioplastic polymer" is clearly visible. It looks red-brown when dry and magnified. It is not a bioplastic polymer.

"R-14 wet-2" shows several fibers mounted in water. (see Raes #14 in water above left). The coating wets quickly and begins to swell within a few minutes, and it will mostly dissolve (see image left¹⁰). When the water evaporates, a colorless, easily seen film of the gum is deposited around the fiber."



A detail of R-14-dry.¹¹



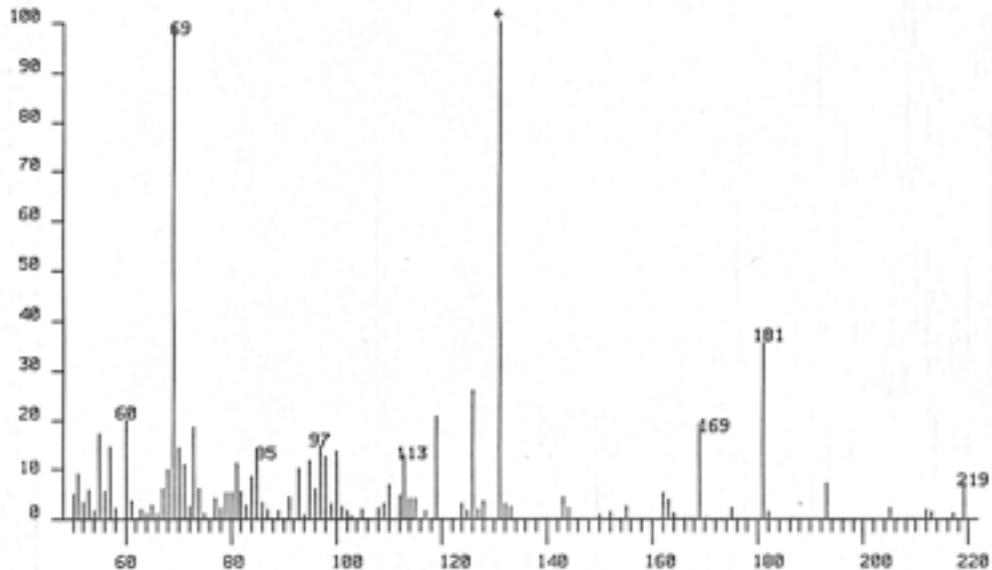


Figure 1: Mass spectrum obtained from a low-temperature pyrolysis of Shroud image sample 1EB (from the back of the ankle).

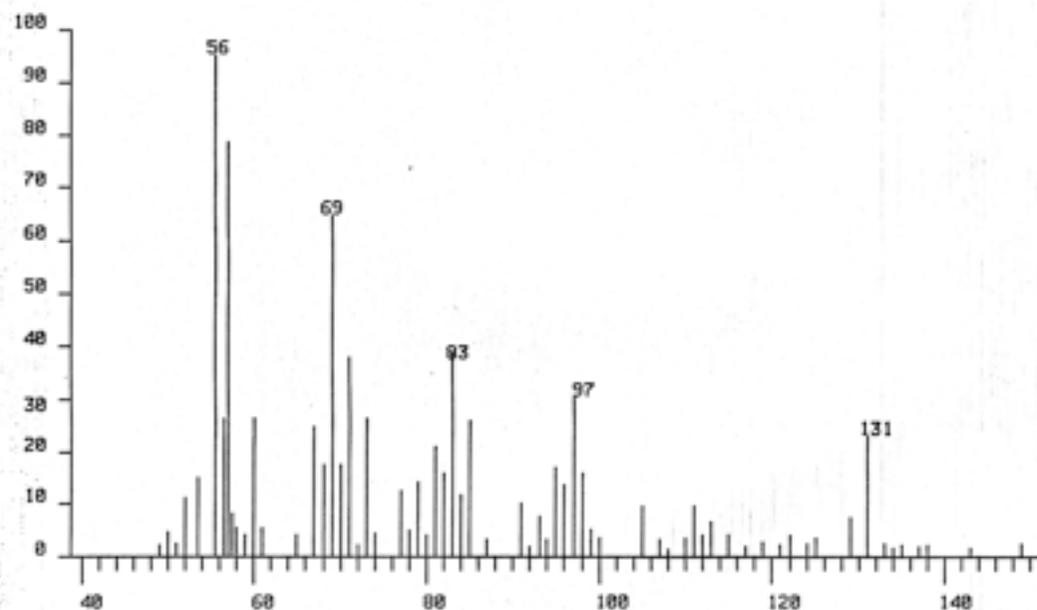


Figure 2: Mass spectrum of the low-temperature pyrolysis of fibers from Raes sample #3.

Pyrolysis-mass spectroscopy

Dating archaeological textiles which have been dyed is a science that is rapidly developing: ‘Our knowledge of the dyestuffs used in archaeological textiles has increased very considerably during the last two decades because of the advent of powerful analytical techniques.’¹¹ Bruno Barbaris highlighted the usefulness of ‘methodologies like High-performance liquid chromatography mass spectroscopy (HPLC-MS), High- performance liquid chromatography infrared (HPLC-IR) or Gas chromatography.’ (GC-MS).¹²

Rogers did not use the first two techniques but he did use a form of GC-MS (pyrolysis-mass spectroscopy) on a Shroud image sample and compared it to fibres from a Raes sample¹³:

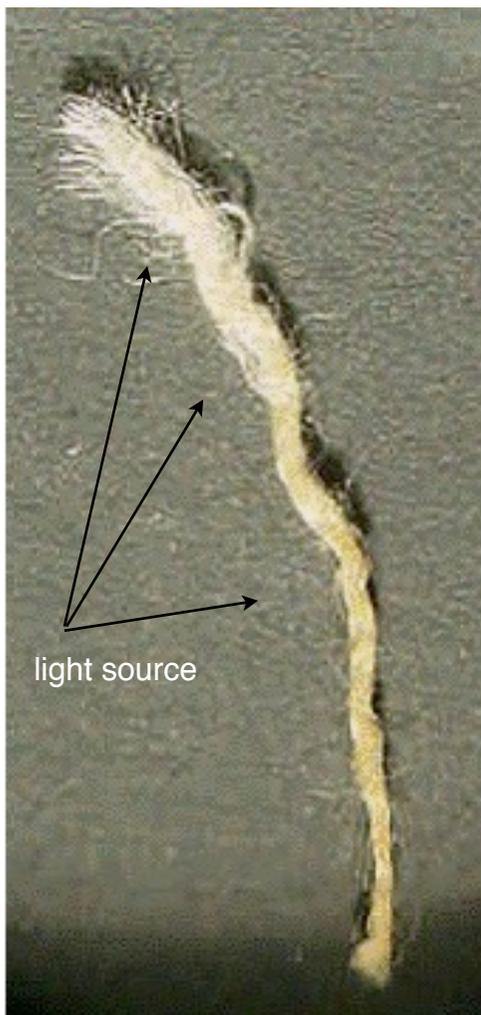
‘The spectrum obtained for the Raes sample (cut in 1973 from the area adjoining the radiocarbon sample of 1988) shows absolutely no m/e 126 signal: the cellulose of the sample had not yet started to pyrolyze. There is, however, a significant m/e 96 signal: furfural was being produced at this temperature. This proves that the sample contained some pentose-sugar units. This is unique among all of the Shroud samples: no other area showed this pentose signal.’

Rogers concluded ‘the pyrolysis/MS data confirm the identification of a gum coating on the Raes threads’

Further evidence of dye or encrustations.

Mordant

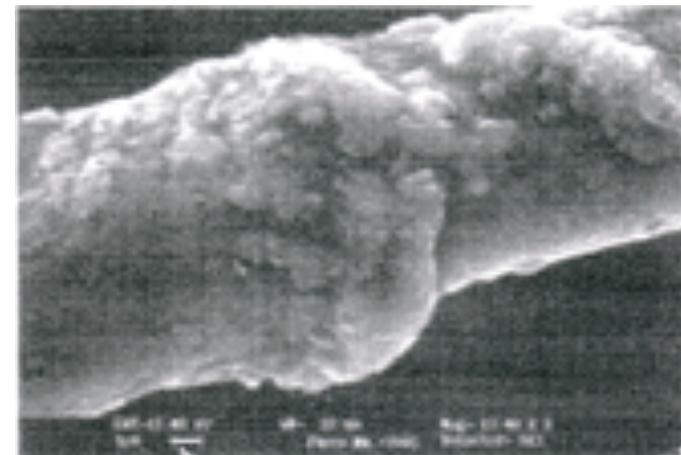
Rogers discovered the use of madder root dye mixed with a gum. In a published work he confirms that and wrote of the use of a mordant¹⁴: 'Al Adler had found large amounts of aluminum in yarn segments from the radiocarbon sample, up to 2%, by energy-dispersive x-ray analysis. I found that the radiocarbon sample was uniquely coated with a plant gum (probably gum Arabic), a hydrous aluminum oxide mordant (the aluminum found by Adler), and Madder root dye (alizarin and purpurin). Nothing similar exists on any other part of the Shroud.



Splice

The image left is of thread #1³ taken from the Raes sample. It is the spliced thread¹⁵ with a large cotton component and a terpene crust.¹⁶ Gums such as acacia and tragacanth are terpenes.

One end of the yarn is apparently a different colour to the other. There is some shadow underneath the yarn suggesting the light source came from above, in the direction of the arrow. The area at the bottom is in shadow, (probably from the person taking the photograph) but neither of these light and shadow effects completely explains the difference in colour of fibre from one end to the other.

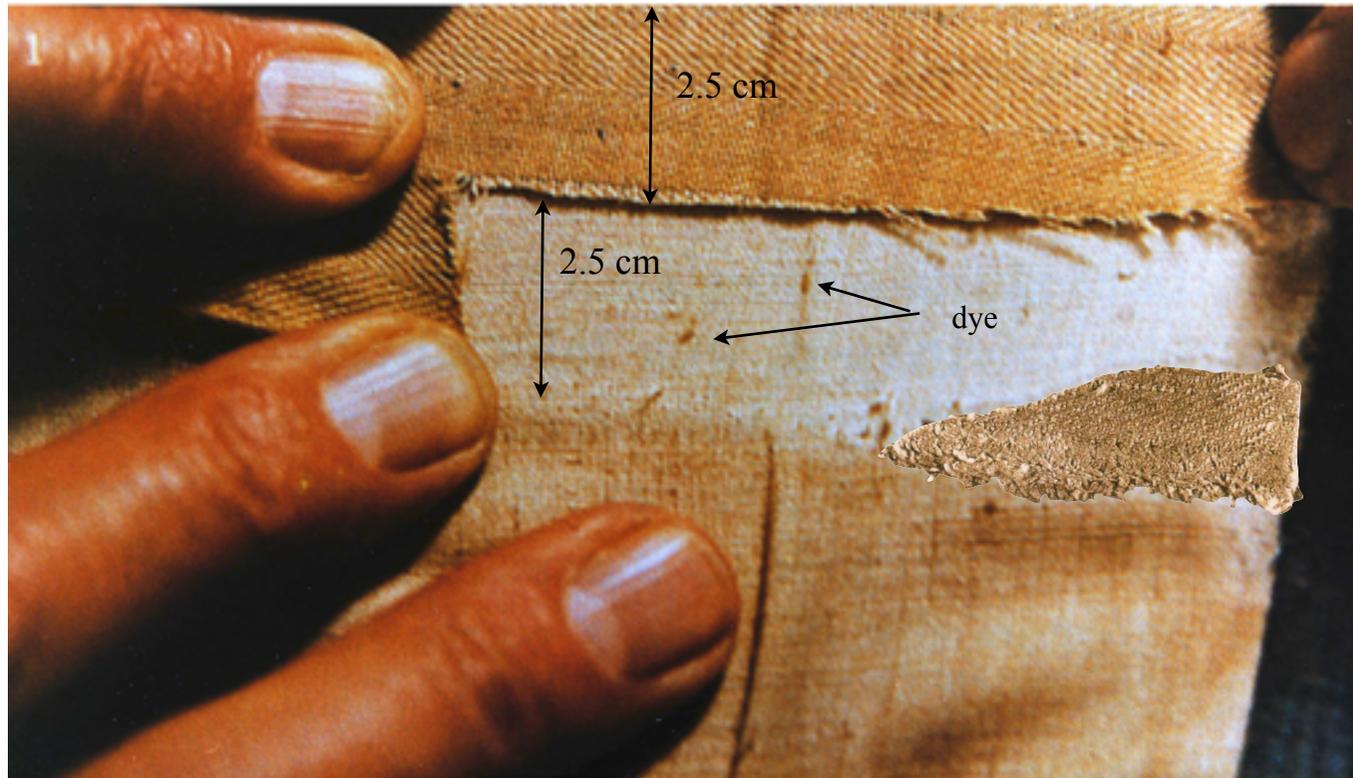


Encrustation

The image above right shows the microscopic encrustations on the Shroud of Turin taken from vacuumed samples: (G. Fanti, I. Calliari, C. Canovaro).¹⁷

In the light of the encrustations found on the Raes sample there is a possibility that this image shows the same contributing factor.

Rogers wrote 'Because the radiocarbon sample was cut from immediately above the Raes sample, it would be hard to believe that it was devoid of the plant gum. The ultraviolet photographs do not show any sharp demarcation between Raes and radiocarbon samples, and the two areas share at least some warp yarns.'¹⁸



In fact the dye had gone beyond the Raes sample into the body of the cloth which was removed for C14 dating. The picture taken in 1988 demonstrates that the dye substance must have covered the whole sample area. The area cut measured 8.4 cm by 2.5 cm and the matching colour extends beyond the cut area by at least 2.5 cm. Also there is a slight pattern of dye on the Holland cloth underneath the Oxford, Arizona and Zurich sample areas. It includes small, more dense deposits of colour. It is not as clean as the area of the Holland cloth above the Raes sample.

Chemical analysis of radiocarbon rather than Raes fibres also suggests contaminants. From A. Adler, R. Selzer and F. DeBlase:¹⁹

"The administrators of the radiodate sampling, L Gonella and G. Riggi, kindly provided three threads from the radiocarbon sample for our study. Two were warp threads from the outer and inner edges of the trimmed sample and the third was a weft thread from the middle of this sample. Five fibers were taken from each of these samples for comparison with those collected from the sticky tapes. Interestingly, under microscopic investigation, these samples resembled exaggerated versions of the water stained specimens. They were non-fluorescent, unevenly colored from dark yellow to splotchy brown, roughly surfaced (even showing patchy encrustations in spots and showed a very strong and variably multicolored birefringence pattern. Considerable microdebris was also evident."

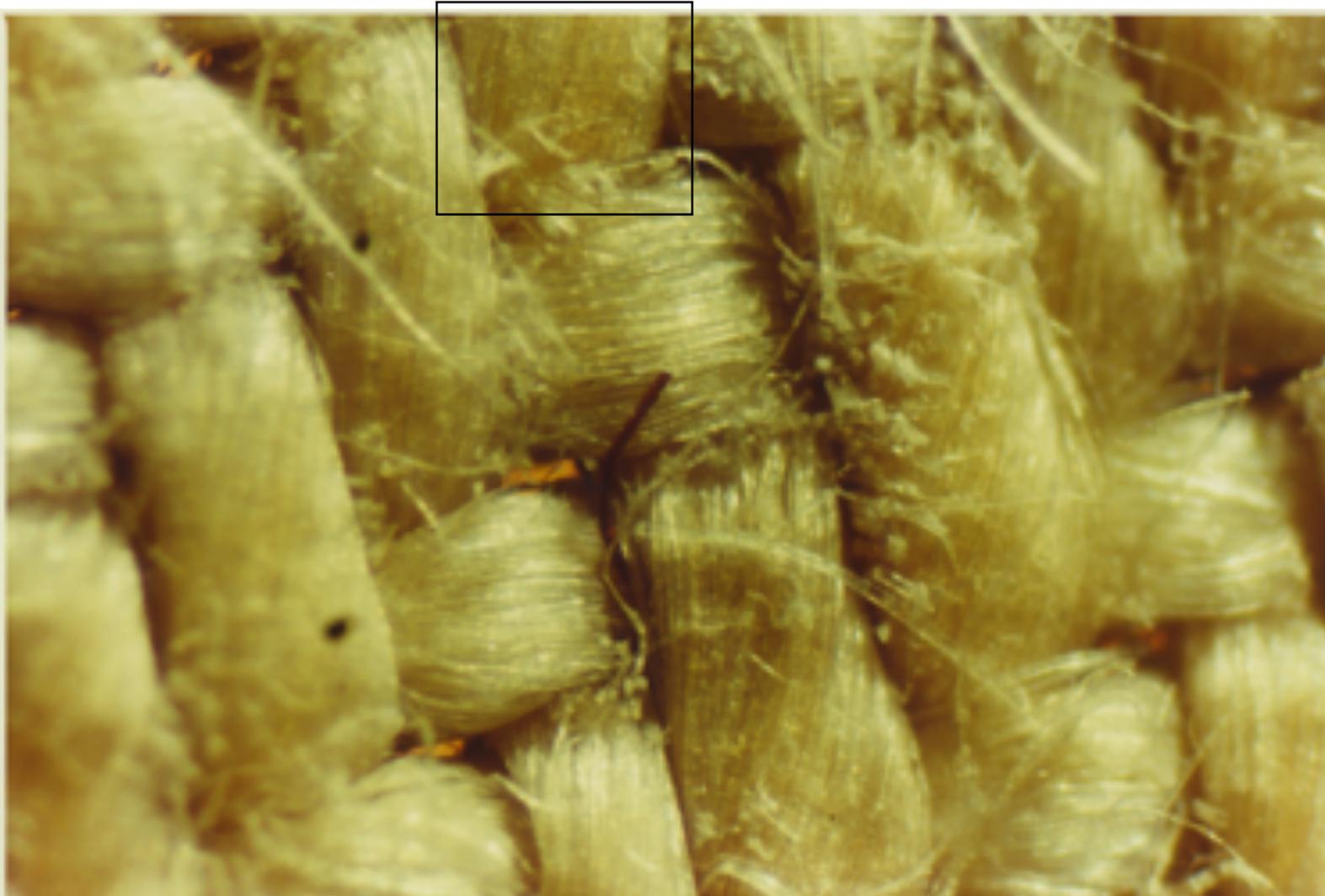
There is very little data about the samples tested by Oxford, Zurich and Arizona: no chemical analysis has been published and most of the photographic evidence is not sufficiently detailed. However, further evidence of encrustation is visible in the Oxford photographs.²⁰ Below is a comparison of the three samples tested at higher magnification (the Shroud, Thebes and Nubia). There is a density of encrustation coating Shroud sample p2574_9 which is not present on the other two samples. The “frosty”⁷ contaminant is also not present on the Mark Evans image of the Shroud.²¹ As ‘the "frosty" coating is almost certainly a plant gum in the Raes sample’⁷ it is likely to be a plant gum in the Oxford sample.



Oxford photograph p2574_9

Oxford photograph p2574_9 enlarged shows more detail of the extent of the encrustations. The loose fibres are more visibly coated than those still bound, but even the bound fibres show evidence of mottling, such as the yarn in the marked box. Rogers wrote the following about the Raes sample: '*All Raes threads show "frosty" surface. They are coated with an amorphous, colored (brown-yellow) material*' (my italics). Potentially *all* the radiocarbon date threads are coated with the substance.

Equally, if these encrustations are the same plant based gum resin mixed with dye that Rogers found on the Raes sample then they will probably be present in the Zurich and Arizona samples also: the colour of fabric is fairly consistent across the whole cut area (image 3 below).



The date of the application of dye and gum.

The Shroud was extensively repaired between 1532 and 1534 following the fire and douse water damage and it is likely this was the time the dye was applied. However, the Shroud was also repaired in the 17th and 19th centuries, when dye could have been used.

The processes of dyeing fabric explained by Teresinha Roberts

a) manufacture of madder root dye.

Madder root dye is extracted from the roots of the common madder plant *Rubia tinctorum* (see image right)²² and contains two organic dyes: alizarin and purpurin. The washed and dried roots are soaked in water for up to a month to extract the colour. Then they are simmered for an hour, often with calcium carbonate added to the water to increase the colour. The liquid is strained and the water allowed to evaporate to produce the dye. Weld (*Reseda luteola*) is mixed with madder to create yellow/brown.



b) the use of mordants

Natural dye does not adhere easily to linen so a mordant is required. The mordant is a binder between the molecules of dye and the molecules of the fibres of the cellulose. For madder root dye alum (potassium aluminium sulfate) and soda ash are the mordant of choice. They combine to create a clear, non staining liquid. The first application of mordant is soaked into the cloth and left for a day. This is washed out and a second mordant of tannin is applied, which can stain the fabric slightly yellow. After this second day the tannin is washed out and the final application of alum and soda ash is soaked into the cloth for the final day. Once the final application is washed out the fabric is ready to receive the dye. In terms of the Shroud this means alum, soda ash and tannin molecules were bonded to the fibres: probably explaining 'large amounts of aluminum in yarn segments from the radiocarbon sample, up to 2%'¹⁴

c) preparation of the dye for application and the use of gums.

A limited amount of dye could have been soaked into the corner in which case there would be no need for a gum. This method of application would also have left a visible line on the cloth. Given the presence in the Raes sample of gum, and the lack of a line, it is highly probable that dye was carefully painted onto the Shroud.

The preferred gum for careful controlled painting is gum tragacanth. It allows a dye to be applied without bleed or wicking (wicking is the ability of a fabric to brush off the liquid and not absorb the dye). It allows the artist very good control of the dye. Unlike acacia, gum tragacanth does not stick to itself. Gum tragacanth also creates a stiffness in the fabric, which is visible in image 3 (right) showing the Shroud carbon date corner before it was cut. The dye mixed with gum is painted onto the fabric containing the mordent and after it has dried the colour is set.

Rogers mentioned gum tragacanth, although he did not mention its preference in painting linen: Gum Arabic, agar-agar, and gum tragacanth all turn bright yellow in iodine water. Identification of specific gums is a major task.⁷



How indelible is the dye?

The purpose of dyeing fabric is to irrevocably bond the dye substance to the fibres of the material being dyed; the mordant acts as a bond between the molecules of cellulose and dye. The mordant and dye applied to the Shroud will have completely changed the chemical and molecular composition of the Shroud, adding additional carbon to the cloth. Dye by itself does not cause the encrustations seen in the Raes sample and probably the Oxford photographs; they were caused by plant gum.

The pre-cleaning of the Shroud in 1988.

Unless the pre-cleaning processes for radiocarbon dating removed the dye, the mordant and the gum, the results cannot be considered reliable. Rogers' experiments with fibres from the Raes sample showed that the dye was eliminated with 6N HCl and the gum with concentrated HCl. The processes from Arizona, Oxford and Zurich are reproduced below and none of the laboratories used sufficient concentration of HCl to remove the dye or the gum.²³

'The Arizona group split each sample into four subsamples. One pair of subsamples from each textile was treated with dilute HCL, dilute NaOH and again in acid, with rinsing in between (method a). The second pair of subsamples was treated with a commercial detergent (1.5% SDS), distilled water, 0.1% HCL and another detergent (1.5% triton X-100); they were then submitted to a Soxhlet extraction with ethanol for 60 min and washed with distilled water at 70° C in an ultrasonic bath (method b).

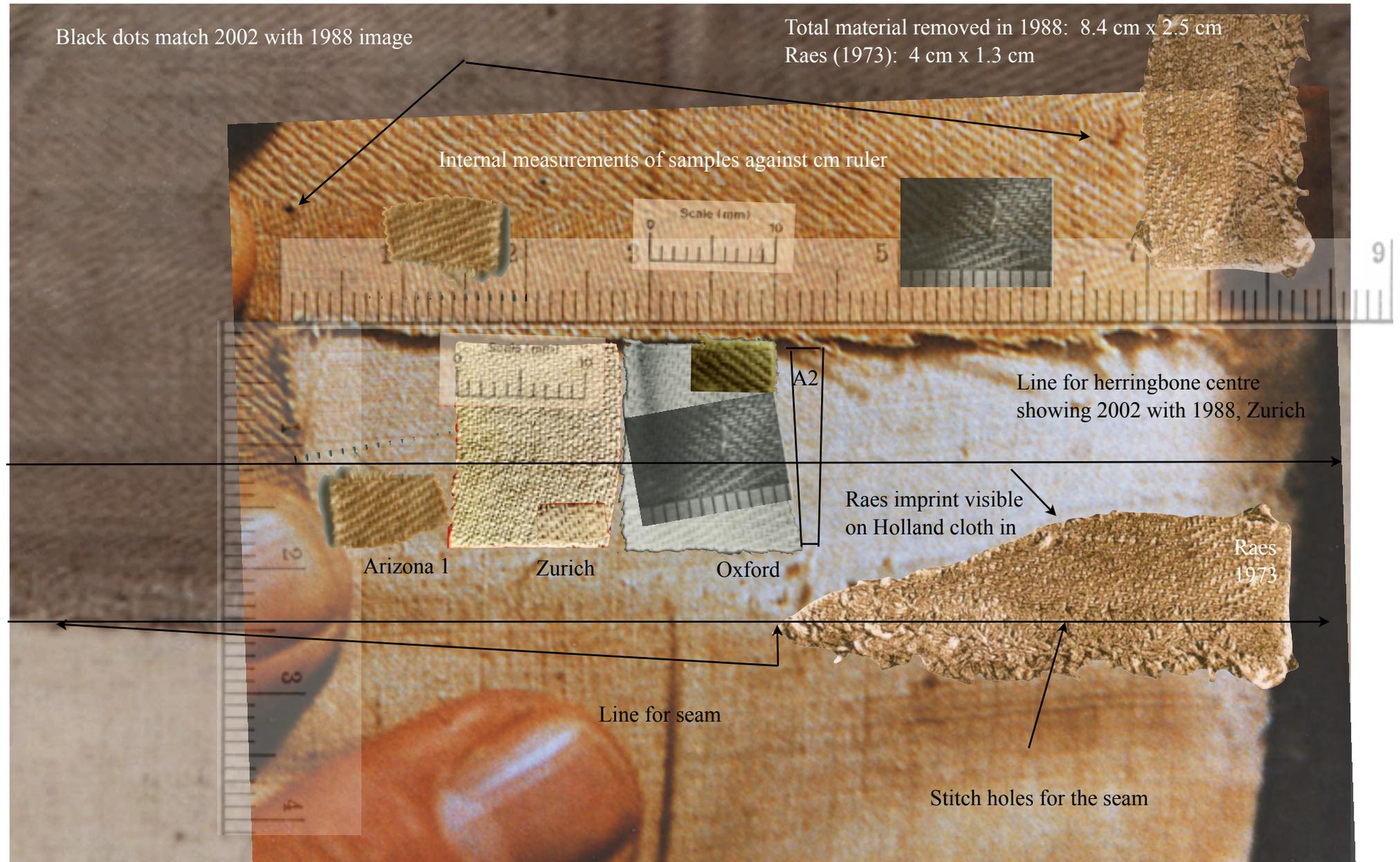
The Oxford group divided the precleaned sample into three. Each subsample was treated with 1M HCL (80° C for 2h), 1M NaOH (80° C for 2 h) and again in acid, with rinsing in between. Two of the three samples were then bleached in NaOCL (2.5% at pH-3 for 30 min).

The Zurich group first split each ultrasonically cleaned sample in half, with the treatment of the second set of samples being deferred until the radiocarbon measurements on the first set had been completed. The first set of samples was further subdivided into three portions. One-third received no further treatment, one-third was submitted to a weak treatment with 0.5% HCL (room temperature), 0.25% NaOH (room temperature) and again in acid, with rinsing in between. The final third was given a strong treatment, using the same procedure except that hot (80° C) 5% HCL and 2.5% NaOH were used. After the first set of measurements revealed no evidence of contamination, the second set was split into two portions, to which the weak and strong chemical treatments were applied.'

The following summary was written by Rogers²⁴:

- (1) Image areas (all of them listed in "Midwest Center") and normal linen are not coated with a significant amount of pentosan. The gum is unique to the Raes (and probably the radiocarbon) area.
- (2) The gum used to carry the dye and mordant used to stain the Raes/radiocarbon sampling areas is a pentosan plant gum.
- (3) Because the radiocarbon sample was cut from immediately above the Raes sample, it would be hard to believe that it was devoid of the plant gum. The ultraviolet photographs do not show any sharp demarcation between Raes and radiocarbon samples, and the two areas share at least some warp yarns.
- (4) If the Raes/radiocarbon sample was stained with a well-known coloring composition (an no other part of the Shroud is), the radiocarbon sample can not be valid for dating the time at which the cloth was produced.

Is the photograph from 1988 reliable? The 1988 photograph matches exactly with the 2002 Durante image.²⁵ It corresponds with the Oxford²⁰, Arizona²⁶ and Zurich²⁷ samples and with the Raes sample⁴. The colour of the samples are all different because they were photographed with different exposures in different light, but the weave pattern stays the same, particularly the centre of the herringbone unit (Appendix 1I for detail of the image below). While the colours change from one photograph to another the same colour of dye shown in two areas of the *same* photograph is indisputable. The radiocarbon date sample was dyed and 16th century (or later) dye products were dated together with the Shroud fibres.



Why was the Shroud dyed in this corner?

As there is strong evidence for dye in the radiocarbon date material it is worth exploring reasons for the presence of dye. This can only be speculative as there is no definitive explanation.

The most obvious answer is that additional cotton material was added to the corner and dyed to cover up the colour difference. There is significant textile evidence of the use of invisible reweave presented by Sue Benford and Joe Marino.²⁸ Donna Campbell reported that the Oxford photographs may direct research toward ‘the effects of mends on the sample.’²⁹ Therefore cotton was added to the corner and then the whole area was painted with dye to make a continual colour. Secondly, the linen needed dyeing for a different reason and cotton was added to the corner to make that dyeing and colour matching easier. Rogers alluded to that:

- 17) The colored encrustation does not seem to stick to linen as well as cotton. Some linen fibres appear to be nearly clean, and the cotton fibrils can be heavily encrusted in the same thread sample. This suggests that cotton was added to the Raes threads to make dyeing possible. The cotton in the threads would have made color matching easier. Linen is difficult to dye or stain.⁷

Thirdly the purpose of the dye and the additional cotton was to make the corner look like a different part of the Shroud: ‘the object must have been to match colours.’⁷ The cut area has a similar colour to the fire and water damage immediately to its right although the corner was not damaged by fire in 1532. If the corner was removed because of bacterial damage following the use of douse water and the linen was bleached to kill the organisms damaging the Shroud then dyeing the area was a very effective cover up. Fourth, a combination of all three of the above.

Conclusion

The colours seen in the photographs of Professor Giovanni Riggi di Numana, including the artificial colours in the images labelled 1 and 3²; the discoveries of dye and gum on the Raes sample,⁷ the spectroscopy confirming gum,¹³ the presence of ‘up to 2% aluminium,’¹⁴ the fibres of cotton, the splice and encrustations,^{15,16,17} the presence of visible ‘frosting’ on the Oxford photographs²⁰ point to the use of dye, mordant and gum in the radiocarbon date area of the Shroud. These agents were not removed before the Shroud was dated.

The dye was probably madder root, mixed with weld in a gum tragacanth or gum arabic solution painted onto an alum, soda ash and tannin mordant. Soaking the corner of the Shroud in a solution of alum and soda ash for 48 hours and tannin for 24 hours, followed by the application of dye and gum is significant for radiocarbon dating. It is difficult to know where to begin to calculate the impact of those processes on the results of 1988.

Consequently, as Rogers wrote: ‘the radiocarbon sample can not be valid for dating the time at which the cloth was produced.’²⁴

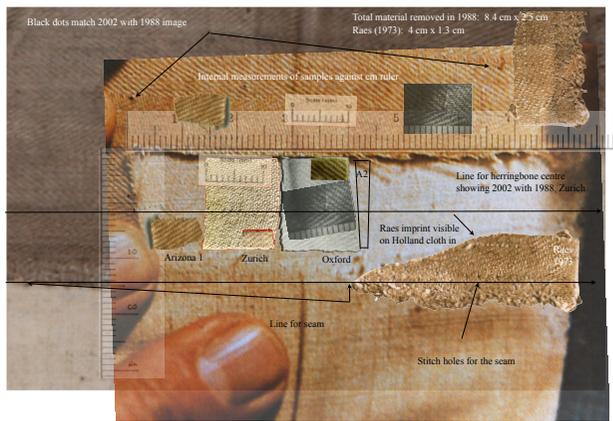


Appendix I: Summary of Raes observations.doc.
Raymond N. Rogers: 1st October 2001.

- 1) Only one small spot of starch identified on Raes threads with iodine. Fibers test light blue with I₂ after soaking in con. HCl to remove gum. Shroud fibers were red in I₂ when did iodine-azide test (high-molecular-weight starch).
- 2) All Raes threads show "frosty" surface. They are coated with an amorphous, colored (brown-yellow) material. Some colored material is seen in linen medulla. No encrustation on Shroud fibrils, except for blood areas.
- 3) The frosty coating softens and swells in water. Its color but not the crust is eliminated by 6N HCl, and the encrustation is eliminated by con HCl. The encrustation is not simply a mordant. Hydrous aluminum oxide, the mordant for red alizarin dye, is soluble in 6N HCl.
- 4) There is no fluorescence in the Raes threads, 20 BC Dead Sea linen sample, or Shroud fibrils. Modern white linen shows a bright, blue-white fluorescence (brighteners). UV-fluorescence photograph from 1978 shows dark area along seam in Raes/¹⁴C area. Shroud background shows 435-nanometer fluorescence peak.
- 5) The cotton fibers on the surface of the Holland cloth and inside the Raes threads are all what Raes identified as *Gossypium herbaceum*, the ancient Near Eastern variety (show 1.2-mm reversal spacing).
- 6) There is only a slight traces of herbaceum cotton on Shroud samples. There are traces of modern cotton on some tapes. There is one lavender modern-cotton fiber on the 1EB tape.
- 7) There is a great variation among the fibers on Shroud tape samples from different areas of the cloth in the amounts of lignin seen at the linen growth nodes. Some joints are heavily encrusted with lignin. No Raes fibers show heavy lignin.
- 8) Raes threads, fibers from the Holland cloth, and modern linen have much less lignin at growth joints, and the amounts are quite consistent throughout a sample.
- 9) Linen made by the ancient technology shows heavy encrustations of lignin at growth joints.
- 10) Image areas show large numbers of yellow fibers, in agreement with reports by Skirius at the McCrone Institute.
- 11) All of the Raes samples show colored amorphous encrustations on the outside of the yarn. There is much less to none on the inside of the yarn.
- 12) Some blue lakes can be seen on Raes #14, and they probably appear on other samples. The color and appearance indicate traces of alizarin on crystals of calcite in the cloth. This agrees with the observation of a bright yellow color in HCl (after solution of the mordants). It also agrees with observations of high calcium by XRF.
- 13) Bright red lakes can be seen on Raes #14. They are probably alizarin/purpurin (Madder root dye) on a hydrous aluminum oxide mordant.
- 14) Raes #14 shows the largest amount of yellow-brown encrustation of any of the samples observed. The encrustation is not removed by non-polar organic solvents.
- 15) Scorching damage can easily be observed in the medulla of tape sample 11B, the scorch control sample. There is no similar scorching in the medullas in Shroud fibers. The yellow of image fibers was not caused by scorching of the cellulose.
- 16) Iodine on unwashed #14 gives very few blue flecks. There is very little starch in or under the gummy coating. There does not appear to be any dextrin either (amyloextrin is blue, erythroextrin is red, and achroodextrin is colorless). However, I get a bright red color with iodine on Raes fibers that have been cleaned in con. HCl. There probably had been a purified starch ("soluble starch") on the Raes yarn before the coating was applied. This might indicate use of a commercial, wheel-spun yarn in the Raes area. The red color we saw on linen shroud fibers with iodine-azide may indicate a residue of the highest-molecular-weight fraction of starch on the shroud. It would have been the last fraction removed by washing with *Saponaria*.
- 17) The colored encrustation does not seem to stick to linen as well as cotton. Some linen fibers appear to be nearly clean, but the cotton fibrils can be heavily encrusted in the same thread sample. This suggests that the cotton was added to the Raes threads to make dyeing possible. The cotton in the threads would have made color matching easier. Linen is difficult to dye or stain. The commercially-produced Holland cloth may have contained cotton for the same reason.

- 18) When I teased Raes #14 open at one end, the center of the thread appeared to be clear, nearly completely colorless. The outside of that thread showed the heaviest encrustation and deepest color of any of the samples, except one end of Raes #1 (the spliced thread). This observation suggests that the color and its vehicle were added by wiping them on the outside of threads that were to be used in the presumed reweaving. The object must have been to match colors.
- 19) After treating the frosty fibers in concentrated HCl, the color and frosty crust are completely removed. Fibers of #14 are clear and clean. Some polysaccharides are easily and quickly hydrolyzed in con. HCl. This suggests a plant gum that is largely composed of pentose-sugar units.
- 20) Raes #14, after cleaning with HCl, gives a light-blue color with iodine. Apparently there had been starch on the yarn before the stain was put on. Starch is harder to hydrolyze than are gums.
- 21) Iodine on unwashed Raes threads gives a bright-yellow coating that is highly visible. Plant gums show this characteristic. Solutes in a liquid phase that is in contact with another, immiscible phase distribute themselves between the phases according to fixed "distribution coefficients." For example, iodine distributes between an aqueous layer and chloroform to show an intense violet color in the chloroform. It shows the yellow to brown color in alcohols and other solvents that contain hydroxyl group. Sugars all contain hydroxyl groups. The "frosty" coating is almost certainly a plant gum. The most probable gum is gum Arabic, an acacia gum that is mostly pentose units, because it is relatively easily soluble in water. Agar, gum tragacanth, and flax-seed gum are less popular for textile work. Gum Arabic, agar-agar, and gum tragacanth all turn bright yellow in iodine water. Identification of specific gums is a major task.
- 22) After drying the yellow gum in iodine solution, it is colorless. The iodine has vaporized completely. It did not react with the substrate. This is important, because it shows that the yellow did not involve iodination or iodine-catalyzed dehydration or condensation. It was pure solution.
- 23) The yellow colors of gums in iodine are amorphous. This helps confirm the fact that there was no chemical reaction, and the gum coating is amorphous..
- 24) No dye stain remains after treatment with iodine in water and washing with pure water. One dye used must have been alizarin (Madder root). Madder has been used with mordants to produce a beautiful red color for thousands of years. Other mordants produce different colors, including blues with calcium compounds. A mixture of mordants with alizarin could produce any shade of yellow or brown that was desired.
- 25) After encrusted fibers on a microscope slide have been wetted with water and allowed to dry, it is easy to observe the gum that dissolved and migrated away from the fibers. I could observe a significant amount of *herbaceum* cotton on the Holland tapes, but there was absolutely no encrustation. There is no encrustation on image fibers. The encrustation is unique to the Raes samples.

Appendix II



herringbone unit centre

The image above comprises:

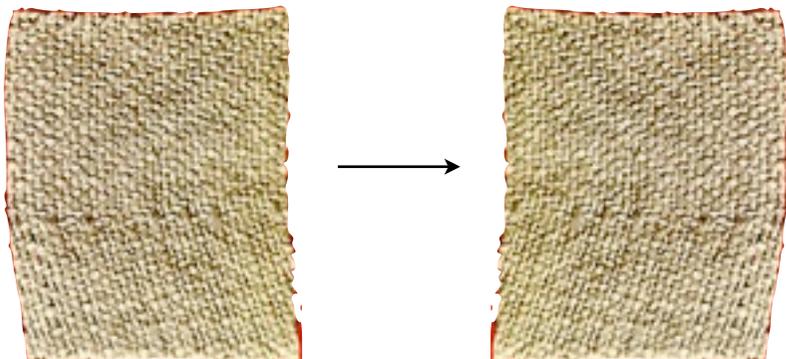
The Durante image showing the cut measuring 8.38 cm x 2.5 cm

The shape of the cut and the black marks match the 1988 Riggi image 1.

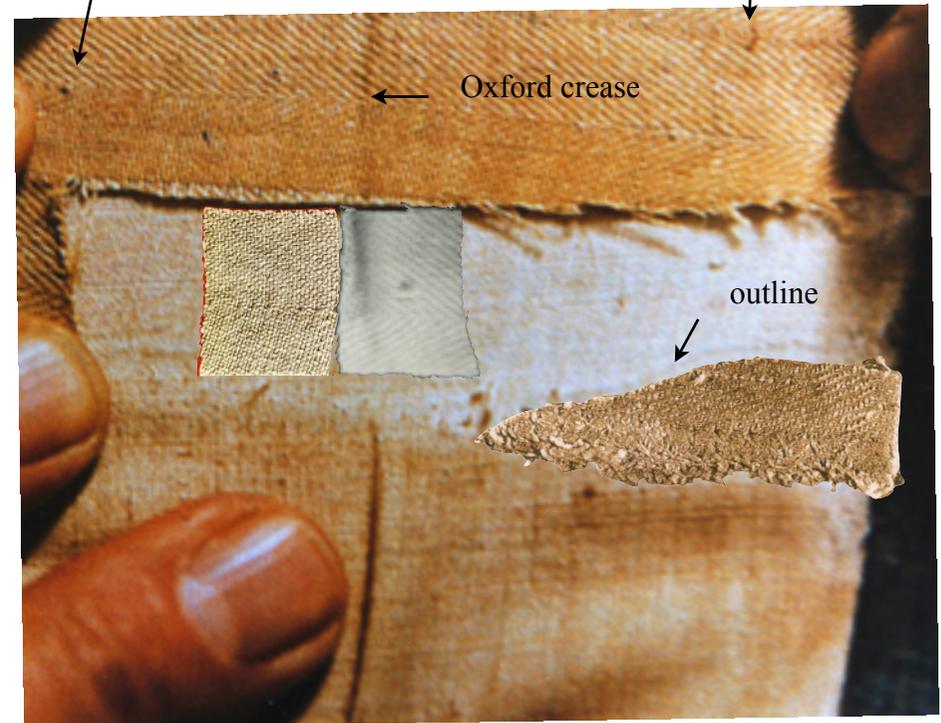
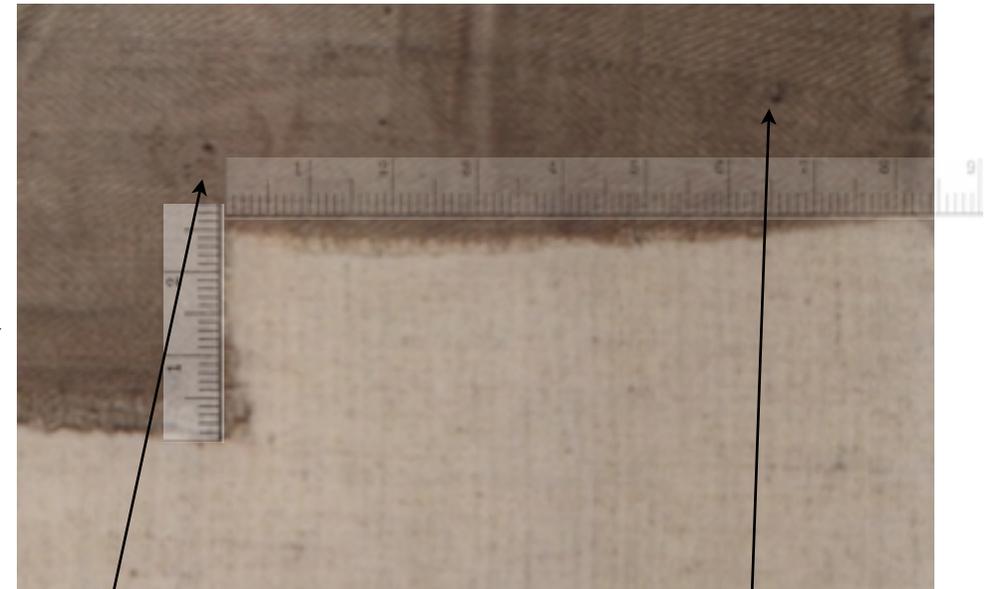
The Raes sample fits the outline provided

Oxford has to match both the crease and the centre of the herringbone unit

The Zurich image is flipped because it is an image of the reverse of the Shroud



herringbone unit centre



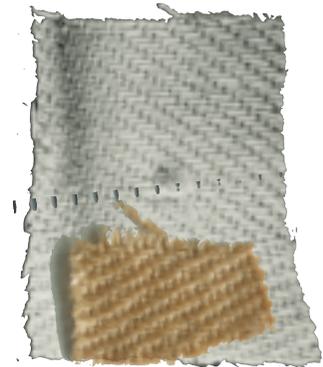
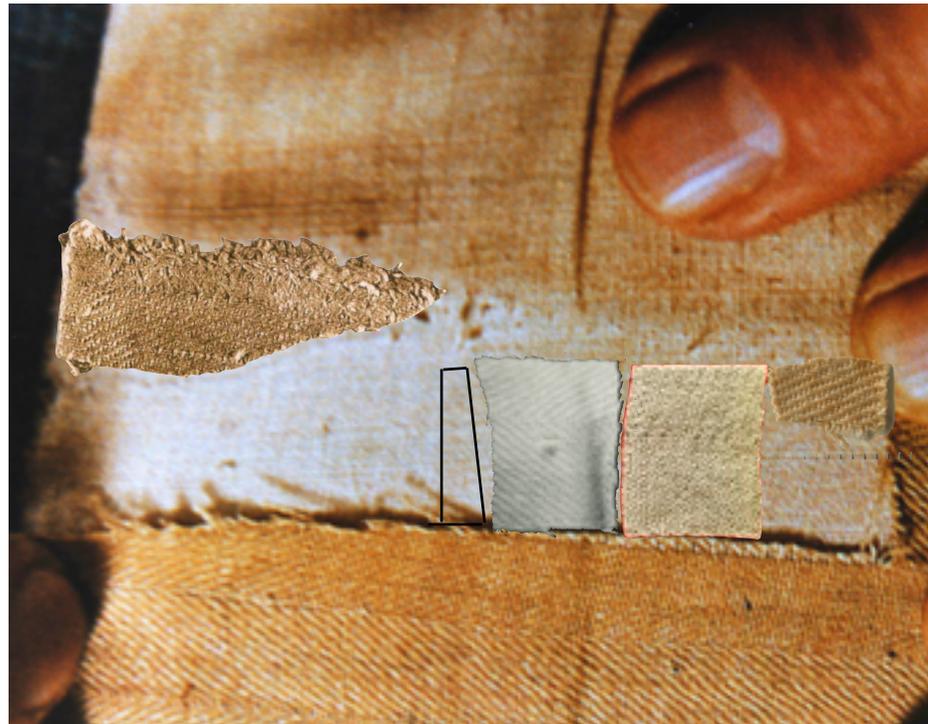
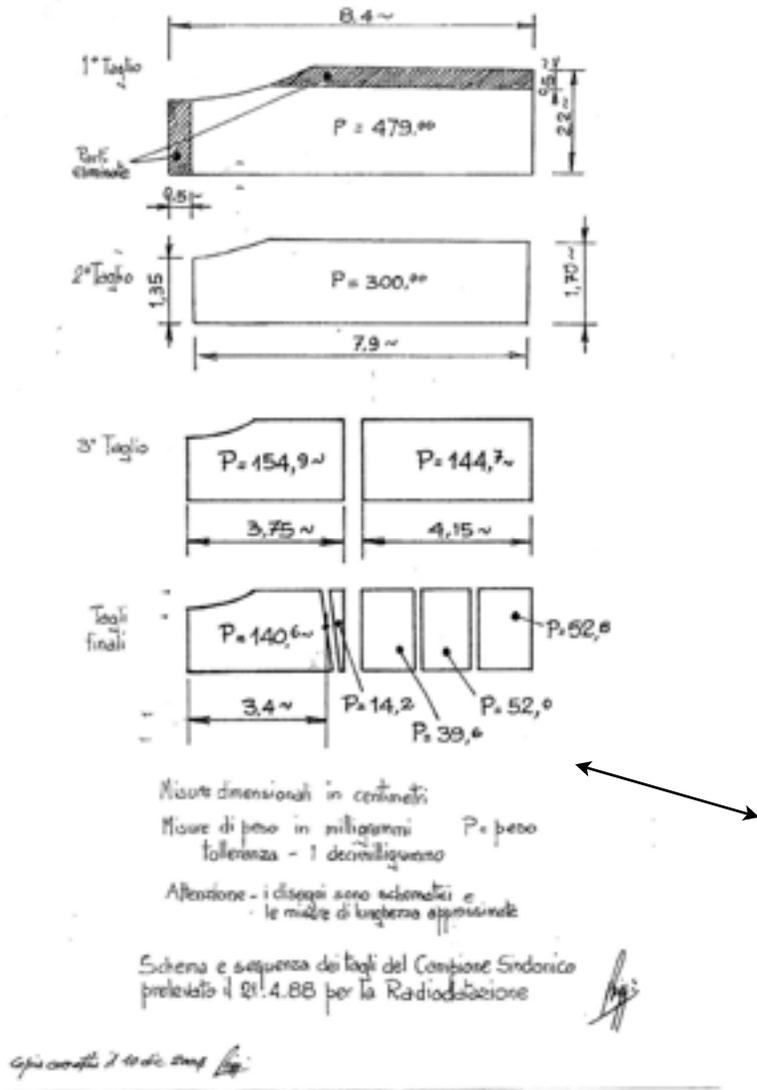
The Riggi diagram (left)³⁰ created by Professor Riggi to document the removal of the C14 material was the original model for suggesting the position of samples. The image below has deviated from the diagram:

The total cut (using the Durante 2002 image) was 2.5 not 2.2 cm. This could be caused by stretch of the fabric.

Reading from left to right Riggi draws Raes; retained sample, Arizona 2 (14.2); Arizona 1 (39.6); Oxford (52.0); Zurich (52.8). However Oxford was 52.0 not 39.6 and needs to be in the Arizona 1 position to accommodate the crease (see image below).

The position of Zurich (52.8) and Arizona 1 (39.6) has been switched. The triangle for Arizona 2 (14.2) has been flipped so it fits the missing area on Oxford. The position from left to right following the diagram below is Raes; retained sample; Arizona 2 (14.2); Oxford (52.0); Zurich (52.8); Arizona (39.6).

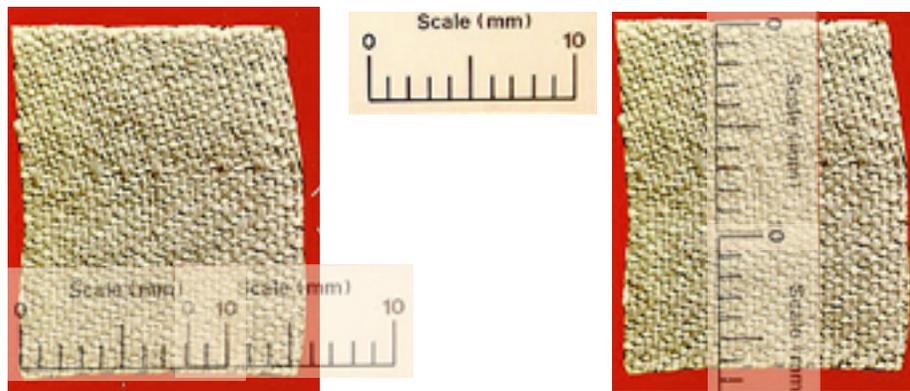
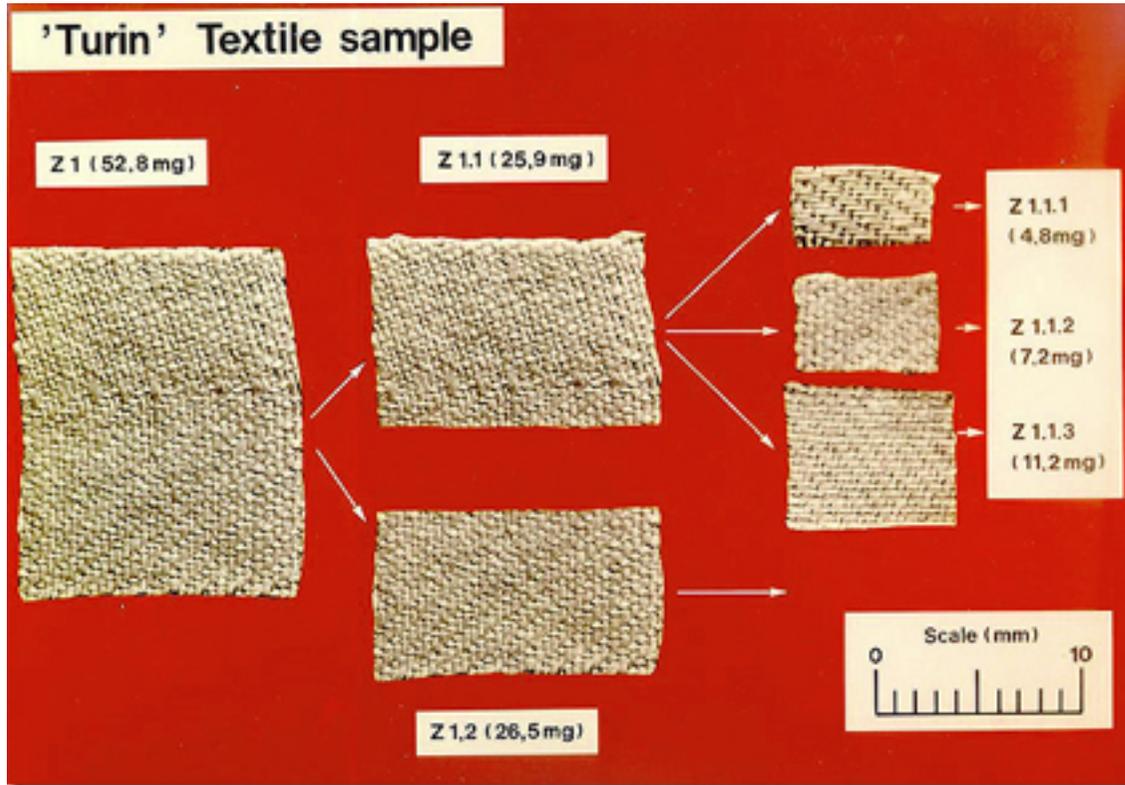
Arizona 1 has been superimposed onto Oxford to match the weave and work out the position above or below the herringbone unit line (see below right)



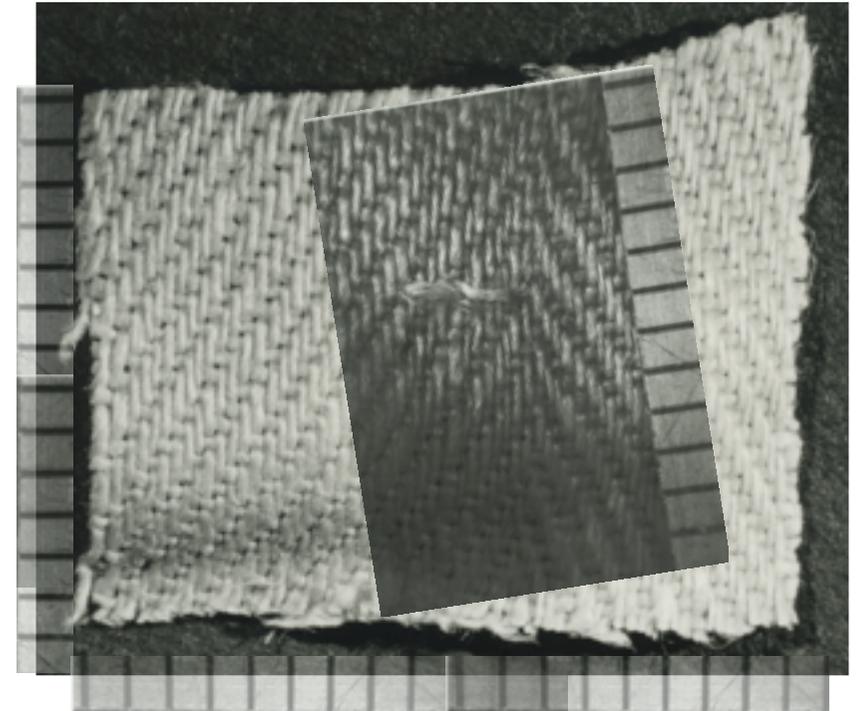
Measuring Zurich, Oxford and Arizona

Extra images containing scale and weave patterns can help work out measurements from Oxford¹⁴ Zurich²⁰ and Arizona.¹⁹ These are (see measurements below): Zurich 1.65 cm x 1.35 cm (2.23 cm² by 52.8mg); Oxford 1.70 cm x 1.25 cm (2.13 cm² by 52.0mg). This gives a unit weight of 23.7 mg per cm² for Zurich and 24.5 mg per cm² for Oxford. The discrepancy may possibly be accounted for by the irregular shape of Oxford. Comparing Arizona 1 weight and length with Zurich would give 1.65 cm by 1.00 cm (1.65 cm² x 39.6mg which gives a unit weight of 24.0 mg per cm²). The fragment of Arizona 1¹⁸ measures around 1.0 cm x 0.65 cm, so it may be the width of the Arizona cut. Arizona 2 is too difficult to measure if it curves like the Oxford sample.

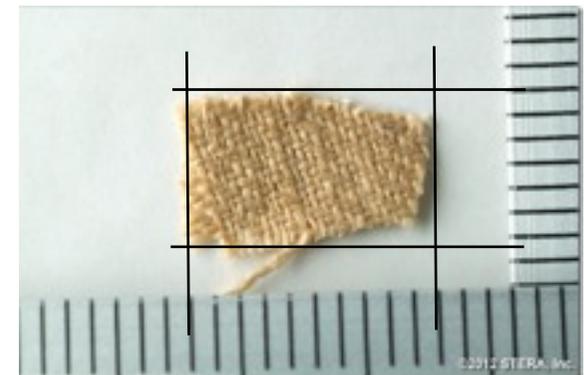
The size of Zurich: superimposing the measure onto the sample



The size of Oxford - matching the weave of p2574_8 with p2574_6.



The size of Arizona From Barrie Schwartz's image (reverse).¹⁸



Footnotes

1. This paper came out of an online conversation with Joe Marino and Paul Maloney, with additional input from Bill Meacham, Professor Emanuela Marinelli and Barrie Schwartz. I am deeply indebted to them for sharing their knowledge, wisdom and advice. Also a thank you to Donna Campbell. When I showed her Barrie's Arizona images in 2014 she said that the Shroud fibres looked "too orange." It was that thought that allowed me to understand some of the problems of colour in Figure 1 (page 3) after Joe sent the image. Revised with contributions from bloggers at Dan Parter's Shroud Blog: <http://shroudstory.com>
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This paper is dedicated to the memory of the great Shroud experts on whose shoulders it stands: Ray Rogers, Sue Benford, Al Adler, Professor Giovanni Riggi di Numana, Vernon Miller

December 8th 2015 The Feast day of the Immaculate Conception.