Non-Destructive Age Measurements of Material from the Shroud of Turin

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Abstract

In 1988, samples taken from a single corner of the Shroud were carbon dated to 1260-1390 AD with a 95% confidence. This conclusion did however contradict a substantial body of relative dating evidence which indicated that the Shroud was much older than this result would suggest, which led to widespread concern that the radiocarbon test had failed to accurately determine its true age. Although many scientists would wish to repeat that test, the Church authorities have so far refused to allow any further samples of material to be removed from the Shroud. Scientists studying the Shroud have therefore been limited to using just a few minute fragments of Shroud material that were removed during examinations during the 1970s and in 1988.

This restriction has undoubtedly hampered Shroud research but it hasn't completely stopped its progress. Indeed, during the last ten years, scientists have found new, non-destructive ways of measuring the age of linen fabric, which are based upon the fact that the structure of cellulose molecular chains changes slowly over time. They have shown that there is a clear correlation between the age of linen and measurements made using various spectroscopic and mechanical techniques. The results obtained from using these techniques to determine the age of some of the material previously removed from the Shroud are consistent with it having a first century origin.

1. Introduction

The Shroud of Turin is one of the most mysterious and potentially significant items in human possession. It is made of linen thread spun from flax plant fibres and woven into a 3-to-1 herringbone weave and contains full-size front and dorsal (back) images of a man who was crucified exactly as Jesus was crucified according to the New Testament. Based on these images, ancient tradition has long claimed that the Shroud of Turin is Jesus' burial cloth. There are also scorch marks and burn holes on the fabric which were caused in 1532 when the chapel where it was kept in Chambery, France was destroyed by fire. The Shroud was rescued from the fire and doused with water, leaving water stains that are also still visible.

The Shroud is kept in the *Cattedrale di San Giovanni Battista* (Cathedral of St. John the Baptist) in Turin, Italy, where it has been since 1578. Before that it had been in various locations in France, with records tracing a continuous history of the cloth to a public exposition in 1355 in Lirey, France. Earlier historical documents record the existence of a burial cloth of Jesus containing a full body image 'not made by human hands' in sixth century Anatolia in Turkey, which was eventually taken to Constantinople, the capital of the Byzantine empire. There is evidence that this cloth influenced how Byzantine artists depicted Jesus from the sixth century onwards and there are many icons, coins and other artefacts dating from the sixth to the twelfth century which bear portrayals of Jesus that are strikingly similar to the image seen on the Shroud.

One example is a coin minted in the reign of Byzantine Emperor John I in the period 969 to 976 AD. The engraver who produced the die for this bronze follis coin has highlighted some distinctive and extraordinary features that indicate that he must have studied the Shroud facial image, including a distinctive ‘cross-shape’ incorporating the eyebrows, forehead and nose, an injury to the cheek and two parallel strands of hair on the left side (fig 1). The only plausible explanation for the engraver having chosen to depict the face of Jesus with these irregular features is that he had copied them from an image that he had believed to be a true representation of the face of Jesus Christ.

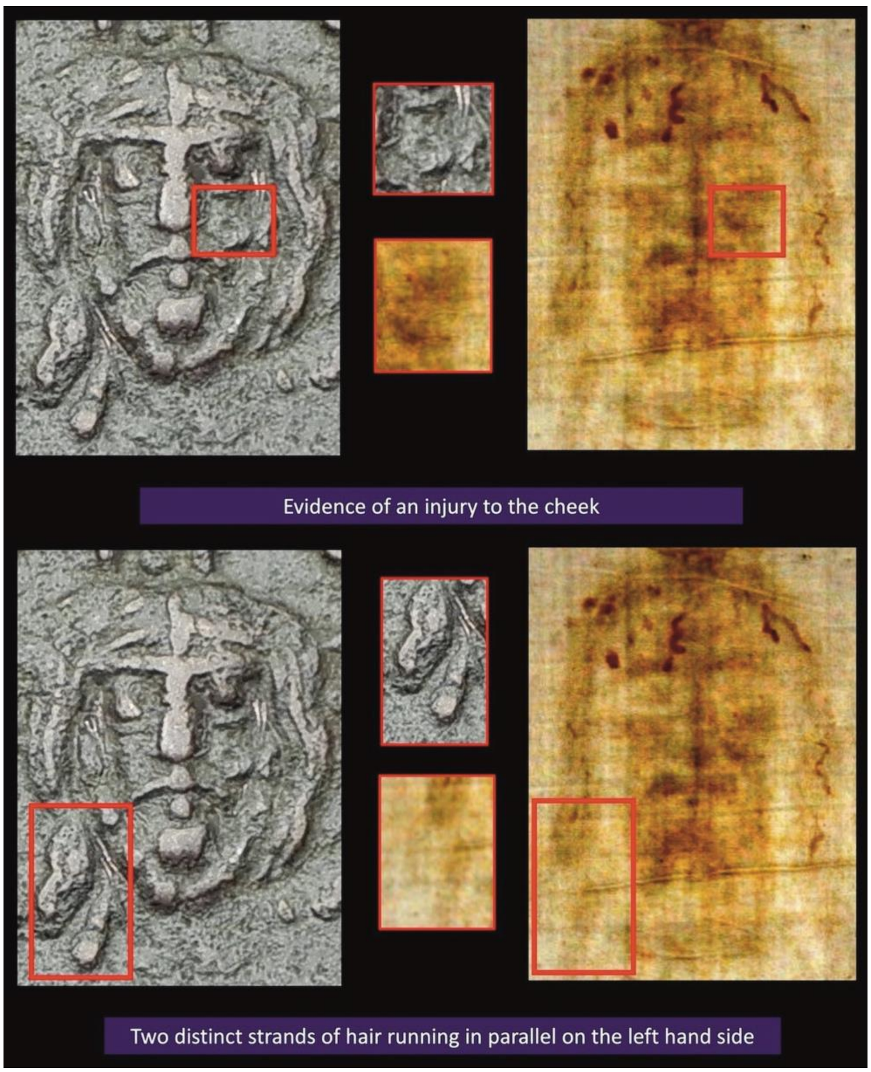

Figure 1. A comparison of features visible on a bronze follis from the reign of John I (969 to 976 AD) with equivalent features that can be found on the Shroud facial image. © Justin Robinson.

This coin along with many other similar examples of portrayals that have clearly been inspired by the Shroud, provide a series of 'date-stamped' snapshots that mark the Shroud's presence at various points throughout history.

2. New Absolute Dating Methods.

The radiocarbon dating method is founded on the fact that a small proportion of the carbon atoms present in organic materials, such as the flax fibres used to make linen fabric, are carbon-14 atoms. Unlike the other naturally occurring carbon isotopes (C^{12} and C^{13}) which are stable, C^{14} is a radioactive isotope which decays at a known rate. It's possible to determine the ratio of C^{14} to C^{12} that was originally present when the flax was harvested and so by comparing this with the measured ratio of these isotopes currently present in an ancient cloth, it is possible to calculate the age of the fabric.

An alternative method of directly measuring the age of linen fabric is only possible if there are other measurable flax attributes that change slowly as the age increases and where the relationship between the property being measured and sample age can be defined and calibrated. One of the main constituents of flax is cellulose, which is a complex molecule found in the cell walls of plants and which helps to give plants their strength and structure. It is also known to degrade slowly over time.

The action of photosynthesis in living plants combines water and carbon dioxide to form energy-rich molecules such as glucose. Some of this glucose is used to create cellulose molecules, which are formed by thousands of these glucose molecules being joined together to form a long chain, releasing a molecule of water as each glucose molecule is added to the end of the chain (Fig. 2).

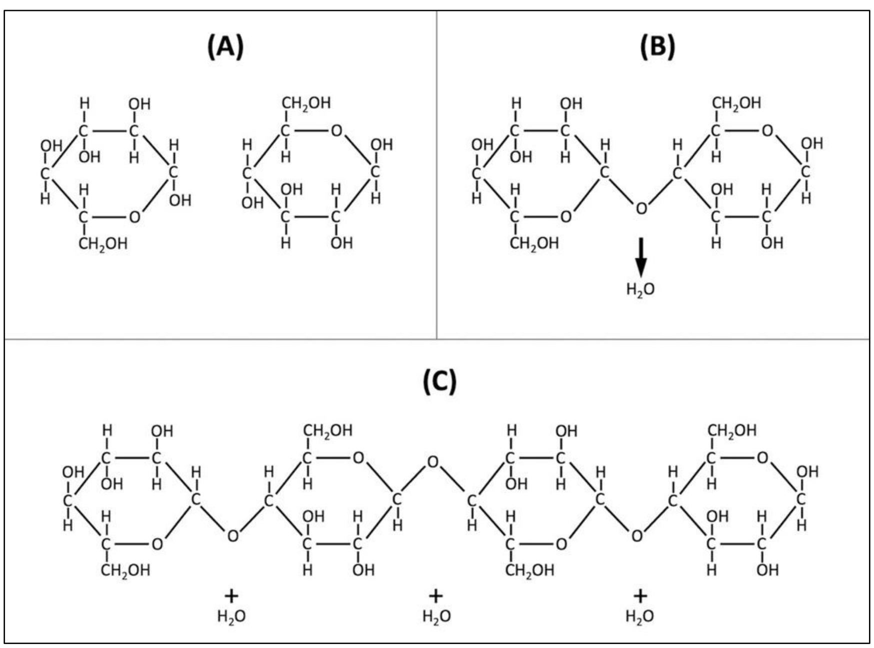

Figure 2. How glucose is transformed into cellulose. (A) shows two glucose molecules with the right hand molecule flipped vertically. (B) shows the two molecules joined together through photosynthesis to form the first link in a cellulose chain, releasing a molecule of water in the process. (C) shows a cellulose chain of four molecules; cellulose molecules typically consist of thousands of such glucose links.

These bonds gradually break over time and so the length of the cellulose chains present in flax fibres used to make linen gradually decreases with increasing fabric age.

Another age-dependent characteristic of cellulose arises from the oxygen and hydrogen (OH) groups that are present in every glucose 'link' in a cellulose molecule chain. These groups have an electrostatic attraction to each other and so corresponding glucose links in each cellulose chain are weakly connected by this force of attraction between their respective OH groups. This results in a tendency for cellulose molecules to line up alongside each other, creating an ordered structure of parallel chains which chemists refer to as having a crystalline form. Where the molecular chains are disordered, the cellulose is referred to as having an amorphous form (Fig. 3). The crystalline cellulose gradually degrades with increasing age due to the parallel molecular chains become increasingly disordered, causing the structure of flax fibres to become progressively amorphous with age.

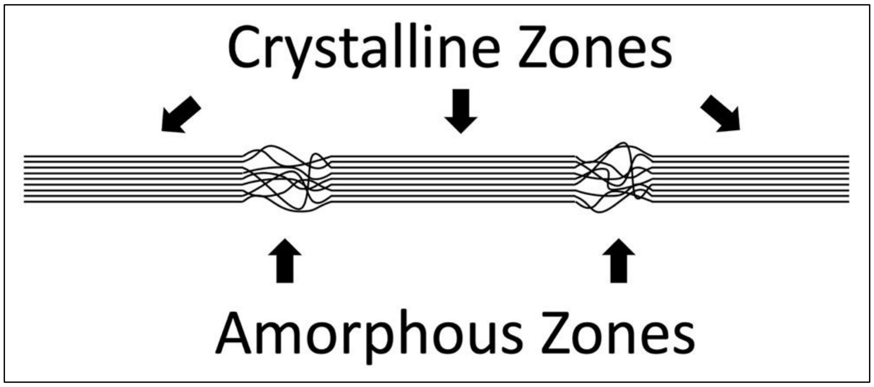

Figure 3. Representation of how hydrogen bonds can produce an ordered, crystalline arrangement of parallel cellulose chains. There is an amorphous, unstructured arrangement in areas where these bonds have not taken effect. Crystalline zones degrade over time, increasing the amount of amorphous cellulose.

These two age-related characteristics of degraded cellulose, which affect both the spectroscopic and mechanical properties of flax, provided a sound basis for the new techniques that were developed to measure the age of ancient linen fabrics.

3. Dating linen using Infrared and Raman Spectroscopy

An infrared spectrometer analyzes materials by directing infrared radiation over a range of frequencies through a sample and measuring the absorptions made by the various molecular bonds. Each molecular bond has its own natural vibrational frequency and these typically correspond with frequencies found in the infrared region of the electromagnetic spectrum. When a molecular bond is exposed to infrared radiation with a frequency which matches the bond's natural vibrational frequency, it absorbs some of that radiation. The transmitted radiation is then detected and analysed using Fourier Transform Infrared Spectroscopy (FT-IR) which produces a spectrum shown as a plot of transmittance intensity against wavenumber, which indicates the wave cycles in a given distance (infrared wavenumbers typically range from approximately 10 to 14,000 cycles per centimetre). The transmitted spectrum contains a series of dips which indicate the frequencies which have been absorbed (fig. 4) and since no two organic compounds produce the same spectrum, this method is useful for identifying the molecules present in an unknown sample. However, it is also possible to detect age-related cellulose degradation using infrared spectroscopy as this deterioration produces changes in the intensity of the dips seen in the cellulose spectrum.

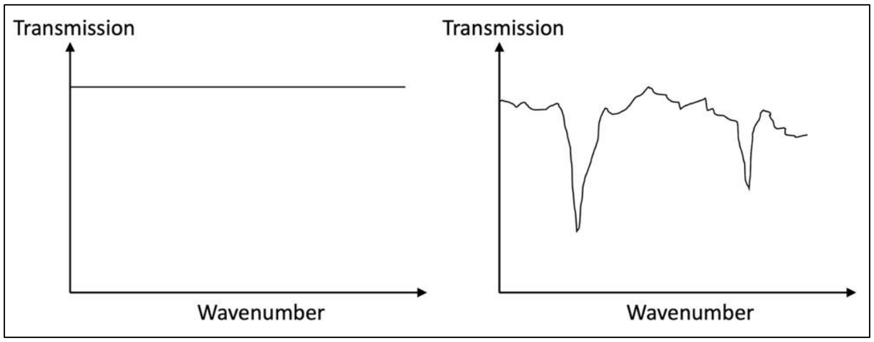

Figure 4. The left chart depicts the infrared spectrum produced by the radiation source, with equal intensity across all frequencies. The right chart shows a typical infrared spectroscopy spectrum with dips of varying intensity caused by molecular bonds absorbing specific frequencies of radiation.

In Raman spectroscopy, the sample to be examined is exposed to a single frequency laser beam, with a frequency in the range between ultraviolet and infrared, corresponding to wavelengths between 266 and 1064 nanometres. The resulting spectrum can then be analysed to determine the sample's chemical structure. When photons from the laser source strike molecular bonds present in the sample, they cause an increase in the rate of vibration. Since visible light and ultraviolet radiation have a higher frequency than infrared radiation, these photons have much more energy and cause the vibrational frequency of a bond to surge above its natural energy states to a virtual energy level. The bond immediately returns to one of its natural vibrational energy states, emitting a photon in the process with a frequency that corresponds to the drop in energy.

Most of the bonds return to their original vibrational state and so the emitted photons have the same frequency as the source radiation, which results in what is known as Rayleigh scattering. However, some return to higher vibrational state and emit photons with less energy and a lower frequency than the source radiation, while others return to a lower vibrational state, emitting photons with more energy and a higher frequency. This is known as Raman scattering (fig. 5).

Each molecule has its own Raman spectrum or 'fingerprint', which can be used to identify the chemical composition of a sample of material. However, the spectrum produced by cellulose also shows differences caused by age-related degradation and so like FT-IR, this is another spectroscopic method which could potentially be used to measure the age of linen fabric.

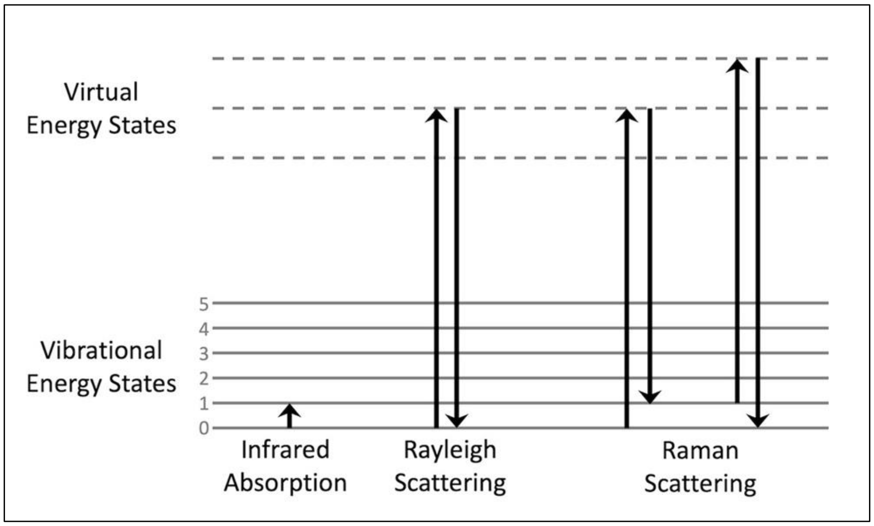

Figure 5. While infrared radiation can cause the frequency of a molecular bond to jump to a higher vibrational energy state, photons of visible light and ultraviolet radiation have sufficient energy to cause a jump to levels beyond the bond's natural energy levels. Raman scattering occurs when the there is a difference between the start and end vibrational energy state, with the frequency of the emitted photons differing from the source radiation by an amount corresponding to the difference in energy between these two states.

The recognition that these two techniques could provide the basis of new techniques for measuring the age of linen fabric led to a collaboration between four Italian scientists who began to explore their potential use for this purpose. The team, which comprised Giulio Fanti and Roberto Basso from the University of Padua, Anna Tinti from Bologna University and Pietro Baraldi from the University of Modena and Reggio Emilia, showed that there were clear correlations between the age of linen samples and features found in their respective FT-IR and Raman spectra [1].

They obtained several samples of new and ancient flax textiles of known age for use in their research. These were examined for any evidence of excessive contamination or damage that could distort the measurements and about 30% of these samples were eliminated from this screening process, leaving thirteen which were deemed to be suitable. Three of these were samples of modern linen fabric but the rest dated progressively older, with the most ancient being from a flax mummy wrapping from the period 3000-3500 BC.

3.1. Dating Linen using FT-IR Spectroscopy

A series of tests were performed using a Nicolet 5700 Spectrometer to establish whether the there was a clear relationship between observable characteristics seen in the FT-IR spectra produced by these samples and their age. This research was helped by previous studies which had established the resonance frequencies of the different cellulose molecular bonds. For example, it was known that the C—O—C glucose linkage has an asymmetric stretching vibration that absorbs infrared radiation at wavenumber 1160 and that the intensity in that band of the spectrum is affected by any decrease in cellulose crystallinity. Fanti and his colleagues used this information to identify those areas of the infrared spectrum where age-dependent changes in radiation intensity were most likely to be observed before deciding to focus their tests on four specific frequency ranges. However, before running their tests, some initial assessments were made of the thirteen remaining samples to determine whether there were any irregularities in their spectra that indicated they had been subjected to some form of treatment that could have affected the natural degradation process. Five anomalous samples were eliminated as a result of this process, including two samples of flax paper that appeared to have been chemically treated during the production process and another sample which had been bleached.

The aggregate intensities in the absorbance spectra produced by each of the eight remaining samples were then measured across each of the four selected frequency ranges. Two of those regions, from wavenumber 2600 to 3080 and from 3070 to 3600, showed an intensity increase with age, with the other two regions showing no change. In theory, the degradation of cellulose was expected to be a first order reaction which would produce an exponential decay curve and this was evident in the spectroscopy results. Various mathematical ratios of these aggregate intensity measurements were evaluated and some of these ratios showed a close alignment between the calculated values for each of the eight samples and the predicted decay curve. Separate dating formulas were then established for use with two of these ratios, R_1 and R_2:

$$D = 1730 + 1809 \ \log_e(R_1)$$

$$D = 1706 + 2379 \ \log_e(R_2)$$

where D is the sample date [2].

Pearson's Correlation Coefficient was used to determine the accuracy of each of these equations based on the FT-IR measurements made using the eight samples. This test provides a measure of the accuracy on a scale of -1 to +1, where +1 means that the calculation produces results which perfectly match the test data. When the Pearson's test was applied to the two equations above, it gave results of 0.899 and 0.947 respectively, which is an extremely positive validation of the accuracy of these two formulas considering a value of 0.7 is considered to be evidence of a strong correlation between the equation and its associated measurements.

The level of uncertainty for dating measurements made using this FT-IR process was also assessed and calculated to be ± 200 years for a 68% confidence level and ± 400 years for 95% confidence.

3.2. Dating the Shroud using FT-IR Spectroscopy

As outlined above, the Shroud was known to have been exposed to the heat of at least one fire in its history and this was a concern since excessive heat was known to increase the rate of cellulose degradation. In order to understand the impact this would have on the measured date, samples of modern linen were woven to closely match the quality of the Shroud fabric and then heated in an oven.

Different combinations of temperature and time were used for each sample, with temperatures ranging from 150°C to 250°C and exposure periods ranging from five minutes to five hours. This produced various levels of discoloration, which were then compared with the color of the Shroud fabric. The color of three of these samples matched the Shroud color: those heated to 250°C for five minutes, 200°C for thirty minutes and 180°C for one hour. These values were therefore assumed to be the upper limit of the conditions that would have caused the discoloration, as age-related yellowing would also have contributed to some of the Shroud's color.

FT-IR spectra were then obtained for these three samples, which were then compared with the spectrum produced by a sample of the same linen cloth that hadn't been exposed to heat. There was a difference of 18% in the value of the two intensity ratios obtained from the unheated cloth compared to the samples which had been heated and so this percentage value could therefore be used to correct FT-IR dating measurements of Shroud material for the effects of heat exposure during its history.

The test was conducted using linen threads taken from a small piece of fabric that was retained when the radiocarbon dating sample was removed in 1988. The two intensity ratio values, $R1$ and $R2$, were calculated from an analysis of the FT-IR spectrum and these were increased by 18% to allow for the effect of the Chambery fire. These corrected values produced dating results of 200 BC and 297 BC respectively, giving a mean value of 250 BC± 400 years at a 95% confidence level (table 1). This equates to a date range of 650 BC to 150 AD, which is more than a millennium earlier than the result produced by the 1988 radiocarbon dating test. This date range does however cover the lifetime of Jesus Christ.

Table 1. The ratio values derived from the FT-IR spectrum produced by Shroud material and the resulting dates.

Property	R_1	R_2
Calculated Intensity Ratio Value	0.291	0.365
Corrected Intensity Ratio Value	0.344	0.431
Calculated Date	-200	-297

3.3. Dating Linen using Raman Spectroscopy

A similar process was used to determine whether Raman spectroscopy could offer another technique for measuring the age of linen [1]. The same thirteen samples that were made available for the FT-IR research were evaluated and this showed that Raman spectra were less sensitive to contamination and chemical treatments than the FT-IR spectra. Only eight of these samples had been considered suitable for use in the FT-IR dating research but when assessments were made of the thirteen samples to determine whether there were any irregularities in their Raman spectra, eleven passed this screening process.

There are several frequency bands in the Raman spectrum produced by linen which show a decreasing intensity with age, with the largest variance in intensity at wavenumber 1097. This corresponds with the symmetric stretching mode of the C—O—C bond in cellulose, the molecular bond which connects glucose molecules in the cellulose chain. In contrast, the Raman spectrum intensity at wavenumber 3251, which corresponds with the hydrogen bonded C—OH linkage, is unchanged with age. The ratio of these two intensity measurements is therefore a value that could potentially be used for dating flax.

A Bruker MultiRAM FT-Raman spectrometer was used to record Raman spectra for each of the eleven flax samples. However, one issue with the Raman method is that it causes some materials, including flax, to produce electromagnetic fluorescence across a range of frequencies. This affected the two bands at wavenumbers 1097 and 3251 which the scientists needed to measure. The fluorescence could be minimized by reducing the frequency of the laser beam but it wasn't possible to eliminate its effect completely and so it contributed to the peaks seen in the Raman spectra produced by the eleven samples. It was however possible to subtract the remaining fluorescence from the intensity of the spectrum signal using a baseline correction feature on the MultiRAM spectrometer.

The eleven samples produced varying amounts of fluorescence and each sample was categorised as being either high or low fluorescence. This distinction was necessary because it was apparent that the amount of fluorescence affected the relationship between sample age and the ratio of the two intensity measurements. The fluorescence was quantified by defining a fluorescence value, which was the ratio of the fluorescence intensity at wavenumber 2890 divided by the band intensity after baseline correction at the same wavenumber. Samples which gave a fluorescence value between 0.2 and 1.5 were categorised as low fluorescence and values between 1.5 and 5 were categorised as high fluorescence. Seven of the eleven samples were categorized as low fluorescence with the remaining four categorized as high fluorescence. The average fluorescence value given by the low series was 0.786 and the high series, 1.825.

Plots of the results obtained for both the high and the low fluorescence sets of samples showed a close correspondence to the first order exponential decay curve expected for cellulose degradation. This was similar to the outcome of the FT-IR spectroscopy dating research but instead of one formula to derive the date, this method required two different dating equations:

$$D = 2451 + 2299\ \log_{\mathrm{e}}(R)$$; for the low fluorescence samples

$$D = 7498 + 4871\ \log_{e}(R)$$; for the high fluorescence samples

The accuracy of these two formulas was evaluated using Pearson's correlation coefficient test, which gave values of 0.907 and 0.947 for the low and high fluorescence equations respectively. Once again this demonstrated a close correspondence between each formula and its related measurements. The test results were also used to determine the level of uncertainty for dating measurements made using each of these formulas, which were calculated to be ± 400 years for low fluorescence and ±600 years for high fluorescence, both at 95% confidence.

Just as with the FT-IR research, tests were conducted to evaluate the effect of heat exposure but it made little difference to the Raman spectra and had only a marginal impact on the age measurements. The age difference due to heat was well below the uncertainly levels for these measurements and so it wasn't necessary to make dating adjustments to allow for exposure to the Chambery fire.

3.4. Dating the Shroud using Raman Spectroscopy

Raman spectroscopy measurements were obtained from the same Shroud threads that had been used for the FT-IR dating test. These gave an intensity ratio of 0.233 and a fluorescence value of 1.55, which was between the average values for the high and low series of fluorescence samples used for calibration of this technique, 1.825 and 0.786 respectively.

Two lines corresponding to the high and low fluorescence equations are charted in figure 6, along with a horizontal line representing the Shroud intensity ratio result of 0.233. The points of intersection between this horizontal line and those representing the high and low fluorescence formulas are also shown. The red and blue vertical dotted lines in the diagram show that for a measured intensity ratio of 0.233, a fluorescence value of 1.825 corresponds with a date of 402 AD, while a value of 0.786 corresponds with 897 BC. These extremes represent the maximum and minimum possible date values for the Shroud threads. However, since the fluorescence intensity of the Shroud sample was 1.55, it's possible to interpolate a more precise date value as illustrated in figure 6.

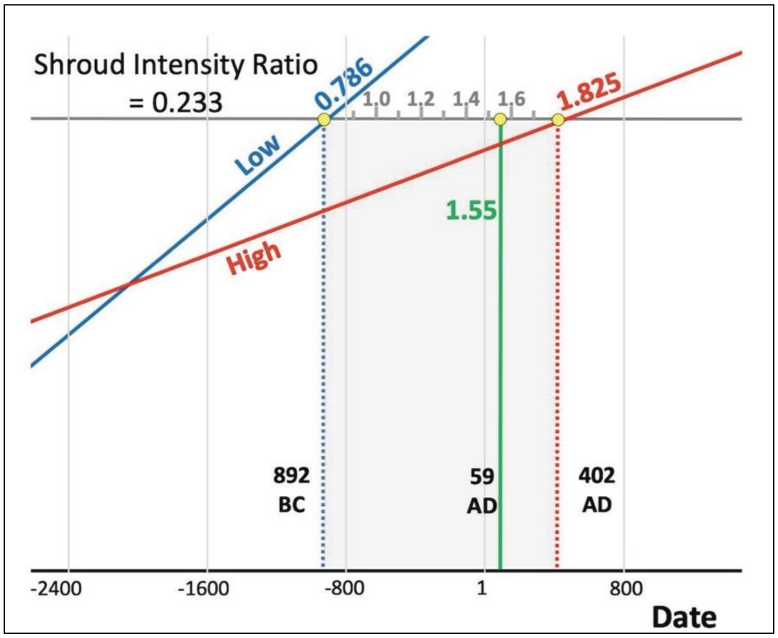

Figure 6. A linear scale marks values along the Shroud Intensity Ratio line between the points of intersection with the high and low fluorescence formulas. The vertical green line is positioned to intersect this scale at value 1.55, which is the measured Shroud fluorescence value. This corresponds to a date of 59 AD ± 400 years. © Giulio Fanti.

A linear scale has been added between the two points on the Shroud intensity ratio line which intersects the red and blue lines representing the high and low fluorescence equations. A vertical green line representing the Shroud fluorescence value of 1.55 has been added which intersects the horizontal Shroud intensity ratio line at the point corresponding to 1.55 on the linear scale. This positions the Shroud fluorescence value proportionally between the high and low values, resulting in a more accurate calculation of the Shroud's age, which gives a date of 59 AD with an estimated measurement uncertainty of ± 400 years for a 95% confidence level.

Once again, this flax dating method has produced a result which contradicts the radiocarbon dating measurement but is compatible with a first century origin for the Shroud.

4. Mechanical Methods of Dating Linen

Age-related degradation of cellulose also affects the physical attributes of flax fibres. The long cellulose molecular chains slowly fragment into smaller pieces over time causing the cellulose structure to become less crystalline and increasingly amorphous. This increases the mobility of molecular chains within a flax fibre, resulting in changes to some of the fibre's mechanical characteristics, such as its strength and elasticity.

Initial tests conducted by Giulio Fanti confirmed that fibres from newer samples could withstand much higher loads than those from older fabrics, which indicated that there was a link between sample age and the breaking load. However, it was necessary to design and custom-build highly sensitive equipment that was capable of measuring the minute stresses and strains acting upon flax fibres under tension in order to perform research into this potential new dating technique. Under the guidance of Professor Giulio Fanti, Pierandrea Malfi successfully built a Microcycling Tensile Machine that could measure forces to a resolution of 2 micronewtons and elongation to a resolution of 0.1 micrometres.

The extreme sensitivity of this equipment made it possible to subject a flax fibre to successive loading and unloading cycles, during which the stress and strain could be measured. These measurements could then be used to plot a stress-strain curve for the fibre (fig. 7), which enabled values for the breaking load and several other mechanical properties to be measured.

Once the microcycling tensile machine had been built, Fanti and Malfi began to establish whether there was any correlation between the age of a linen textile and the mechanical properties of its fibres [3]. The test process followed the same pattern as those used for when evaluating and calibrating the FT-IR and Raman Spectroscopy dating methods. Fibres were taken from the same set of linen samples dating from 3500 BC to the present day and subjected to some initial screening tests, which included both microscopic inspections and mechanical tests for evidence of structural defects in the fibres. Eleven of the samples passed this initial screening and were considered to be suitable candidates for use in this research.

Several fibres were taken from each of the samples and although most fibres originating from the same sample produced similar results, approximately 10% gave stress-strain curves that were distinctly different. These anomalous results were discarded as they were almost certainly caused by fibre damage that the screening tests had been unable to detect.

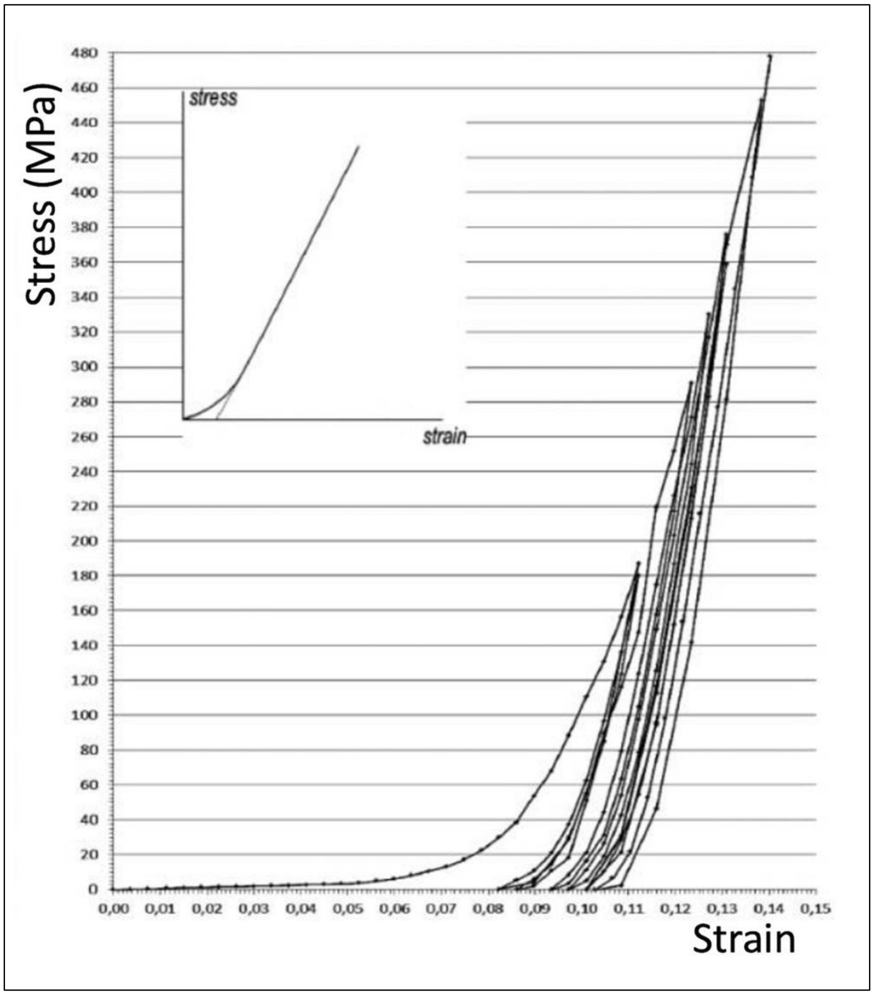

Figure 7. A typical stress-strain curve for a flax fibre obtained from multiple load-unload cycles made using the microcycle tensile machine. MPa, or megapascal, is the unit of measure for the stress force. Inset: The expected shape of a single load-unload cycle for a textile fibre. © Giulio Fanti.

The values of several different mechanical properties were then derived from the stress-strain curves produced by the remaining fibres. Five of these properties showed a clear correlation with the sample age:

- *Breaking Load.* The maximum load recorded divided by the cross-sectional area of the fibre.
- *Elastic Modulus.* Also known as Young's modulus. This is the ratio of tensile stress to tensile strain and was measured just before the peak of the loading cycle.
- *Decreasing Elastic Modulus.* This is the stress-strain ratio measured at the start of the unloading cycle, just after the peak of the loading cycle.

- *Direct Loss Factor.* The ratio of the amount of energy lost or dissipated during the last complete load-unload cycle, divided by the total energy applied to the fibre during that cycle.
- *Inverse Cycle Loss Factor.* This is a similar ratio to the direct loss factor. It couples the unload phase of the last complete cycle with the last loading phase that ends when the fibre breaks. The loss factor is calculated by dividing the energy dissipated during this inverse cycle by the total energy applied to the fibre.

The results obtained from three of these properties, the Breaking Load, Elastic Modulus and Decreasing Elastic Modulus, varied exponentially with increasing sample age. This is characteristic of a decay involving a first order chemical reaction and was consistent with the results obtained from the spectroscopic dating measurements. However, the Direct Loss Factor and Inverse Cycle Loss Factor both showed a linear variance with age.

These five property values were calculated for each sample by averaging the results obtained from tensile tests of each of its fibres. A dating formula was then derived and calibrated for each of the five properties, along with the respective uncertainties. Pearson's correlation coefficient tests once again confirmed a high degree of accuracy for each of the five formulas, with all five equations giving results of 0.9 or above as shown in table 2.

Table 2. A list of the formulas used to calculate the date (D) of flax fibres from measurements of five micro-mechanical properties.

Property Measured	Formula	PCC
Breaking Load (σ)	$D = 1032 \ln \sigma - 5095 \pm 336$ years	0.943
Elastic Modulus (E_f)	$D = 1407 \ln E_f - 2575 \pm 418$ years	0.915
Decreasing Elastic Modulus (E_i)	$D = 1647 \ln E_i - 3466 \pm 537$ years	0.910
Direct Loss Factor (η_d)	$D = 5450 - 723\eta_d \pm 193$ years	0.955
Inverse Cycle Loss Factor (η_i)	$D = 3707 - 871\eta_i \pm 385$ years	0.900

Extreme temperatures were known to alter the mechanical properties of flax and so the effect of heat from the 1532 AD Chambery fire was also assessed. Fibres were taken from three of the samples which had been used to determine the effect of heat on spectroscopic measurements. These were then subjected to tensile tests and the results were compared with those obtained using fibres taken from an unheated sample of the same fabric. The heat exposure had slightly affected the measurements, causing a marginal difference in the date calculations of less than one hundred years. However, this difference was well below the measurement uncertainties and so it was unnecessary to make significant adjustments to account for the effect of the fire on the Shroud date.

4.1. Dating the Shroud using Mechanical Dating Method

Several fibres that had been found in the aspirated dust taken in 1978 from the back of the Shroud in an area corresponding to the pelvis were examined and screened for any defects.

Eight of these were considered suitable for tensile testing and the dating results obtained from measurements of the five mechanical properties are shown in figure 8. Four of the five results are quite similar but the date derived from the Direct Loss Factor measurement was considerably older than the rest. This was believed to be a consequence of the difficulties involved in connecting the fibres to the equipment, which caused some plastic deformations in the fibres.

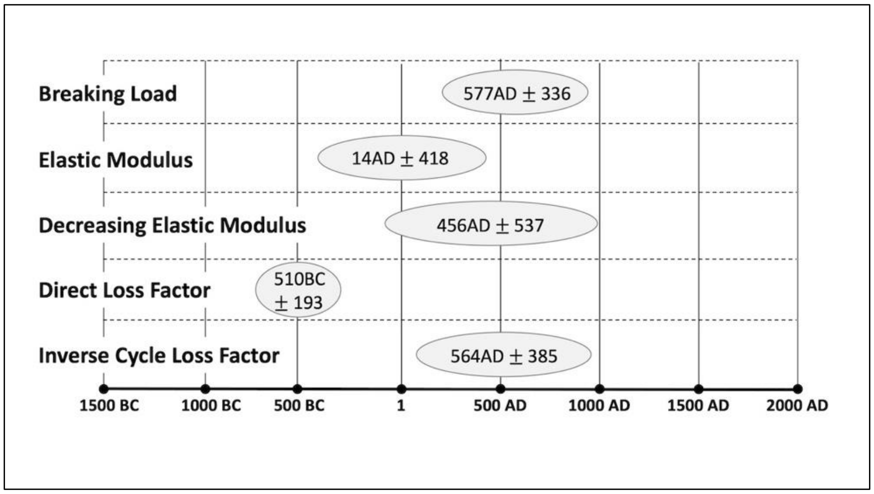

Figure 8. Shroud dating results calculated from the five mechanical property measurements. © Giulio Fanti.

The arithmetic mean of these five results gives a Shroud date of 220 AD but this is a very simplistic way of combining the results. Some of these measurements, such as the Direct Loss Factor, appeared to be affected by fibre plasticity as the fibre did not return to its original length after a complete load-unload cycle. Fanti and Malfi accounted for these plastic slippages by assigning a greater weight to the mechanical property measurements which theoretically would have been less affected by these effects. A weighting of three was given to the Decreasing Elastic Modulus and Inverse Cycle Loss dates, the Breaking Load date was given a weighting of two, with the Elastic Modulus and Direct Loss Factor dates given a weighting of one. The weighted mean was therefore calculated using the following formula:

$$Mean\ Date = \frac{2D(\sigma) + D\left(E_f\right) + 3D(E_i) + D(\eta_d) + 3D(\eta_i)}{10}$$

This gave a weighted mean of 372 AD ± 400 years with a 95% confidence level, which was rounded up to 400 AD ± 400 years to take account of the marginal effect that the heat of the Chambery fire would have had on the measurements. This result was once again compatible with a first century origin for the Shroud and several centuries earlier than the 1988 radiocarbon dating result.

Although the microcycling tensile machine had proved to be very effective at measuring the mechanical properties of minute flax fibres, it was clear that there was room for some improvements to both the equipment and the process. For example, the method of mounting fibres was problematic, causing approximately 30% of the fibres to break before any tension had been applied. To help address this problem, the machine was fitted with an improved fibre clamping system and the components used to measure the applied force and fibre displacements were also enhanced.

After completing this equipment upgrade, Giulio Fanti and Roberto Basso then used this upgraded equipment to perform another dating test of the Shroud using a flax fibre from the wrist area of the Shroud that had been removed during a 1978 examination [4]. Fibres from two fabrics of known age were also tested: a modern, unbleached linen cloth and the wrappings of an Egyptian mummy known to date from the period 2826 to 2478 BC. As in the previous series of tests, these fibres were subjected to a series of load-unload cycles but the approach adopted in this series of test involved running many more cycles before reaching the breaking point. Each fibre was initially stressed with a tensile force corresponding to about 20% of its expected breaking load before releasing the tension and his was repeated five times. The first three cycles showed evidence of the fibre plasticity outlined above but by the fourth and fifth cycles, the internal structure of the fibre had stabilised and so its length at the start and end of each of those cycles was usually the same. The load was then increased, followed by another five cycles and this process was repeated until the fibre eventually broke in two.

This new approach of using a low tensile force in the first cycles before gradually increasing the load changed the previously evaluated relationship between the loss factor values and the age of the fibre. It was clear that it would be necessary to recalibrate these formulas using the new equipment and the revised test method. However, the existing breaking load formula proved to be even more reliable using the new system and so this property was measured for fibres from each of the three linen samples.

The results of these dating tests are outlined in table 3, which shows that the fibres taken from the modern linen fabric and Egyptian mummy wrappings gave dates consistent with their known age. The date of the Shroud fibre was calculated to be 110 AD ±400 years with a 95% confidence level, a result which was in a similar range to that obtained in previous mechanical tests and compatible with a first century origin.

Table 3. Comparison between the claimed and measured dates of the three samples tested

Sample	Claimed Date	Measured Date
Egyptian Mummy Wrappings	2826 – 2478 BC	2112 BC ±400 years
Modern Linen	2000 AD	1901 AD ±400 years
Turin Shroud	30-33 AD	110 AD ±400 years

5. Dating linen using Wide Angle X-Ray Spectroscopy (WAXS)

Another spectroscopic technique which has recently been evaluated as a possible method for dating linen has also produced promising results. In 2019, a team of scientists led by Liberato de Caro of *Istituto di Cristallografia, Consiglio Nazionale delle Ricerche* conducted research to determine whether wide-angle X-ray scattering (WAXS) could also be used to measure age-related structural degradation of linen threads. At certain wavelengths and incidence angles, X-rays are reflected and scattered by the lattice planes of crystalline material, producing a scatter pattern with peaks in intensity that reveal details of the material's crystalline structure. The age-related degradation of cellulose results in crystalline cellulose zones becoming increasingly unstructured or amorphous, reducing the crystalline content of cellulose over time and producing measurable changes in the X-ray scatter profile.

Threads were taken from nine of the linen samples used for the tests described above for the purposes of this research. Each of these thread samples produced a scatter pattern which was then analysed to create a chart that showed how the signal intensity varied with the angle of scatter (fig. 9). The diffraction peaks in the region where *q* (the x-axis of the chart) is between 9 and 16 are produced by the crystalline structure of cellulose in the linen thread. This region of the chart is therefore where age-related changes due to cellulose degradation should to be found and indeed the peak intensity in this region became lower with increasing age, which confirmed that there was a correlation between the signal intensity and the age of the material.

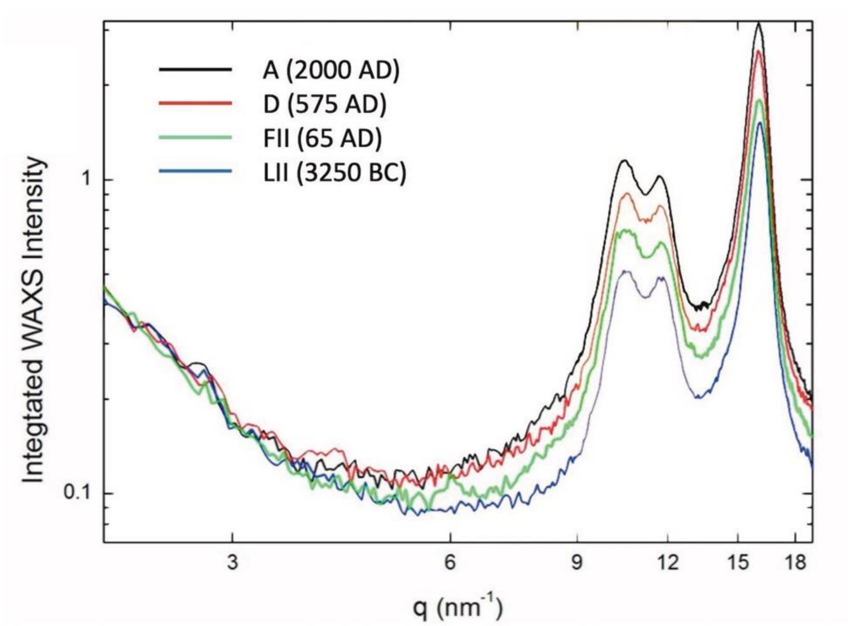

Figure 9. WAXS profiles produced by four of the test samples. The intensity of the signal decreases with increasing sample age, particularly at the signal peaks. From *X-ray Dating of a Turin Shroud's Linen Sample* by Liberato De Caro et al., Heritage 2022, 5, 860–870

The tests also revealed that where the cellulose degradation is only due to natural ageing effects, the relationship between the WAXS measurements and the sample age is almost linear up to an age of between 2,500 and 3,000 years. Beyond this point there was only a slight further reduction in the intensity measurements, which indicated that the number of cellulose chain breaks was approaching a saturation point.

The chemical process that causes chain breaks in cellulose is an Arrhenius reaction, with a reaction rate that increases with rising temperature and humidity. Consequently, some historical linen samples degrade faster than others as a result of different environmental conditions and so samples of the same age from different locations could give different WAXS measurements. However, it's possible to make assessments of the average storage temperature and humidity from knowledge of where each sample had been kept. This allows a reaction rate adjustment factor to be calculated that compensates for the effect of different environmental conditions.

WAXS profiles were taken from two of the nine linen samples, one from Masada known to date from 55 to 74AD and an Egyptian fabric that dated from 544 to 605AD. These were used to calibrate an equation that could calculate the age of linen threads from their WAXS measurements, average temperature and relative humidity and this equation was then used to determine the age of threads removed from another four of the linen fabrics. This gave impressive results with the age derived from the WAXS measurements being very close to the known age (table 4). A regression analysis of these results confirmed that this is a reliable technique when used with linen fabrics that are less than 3,000 years old and have aged naturally at temperatures below 23 degrees.

Table 4. Comparison of WAXS age measurement results with the known age obtained from historical records and carbon-14 measurements. The upper limit of the uncertainties is greater than the lower limit for measurements made using samples approaching 3,000 years of age as these limits are close to the degradation saturation point.

Sample Provenance	Age obtained from Historical Records and C^{14} tests (years)	Age obtained from WAXS measurements (years)
Jericho, Israel	950 ± 80	940 [-70, +70]
Engedi, Israel	2,310 ± 60	2,350 [-290, +510]
From a mummy, Egypt	2,390 ± 40	2,390 [-230, +280]
From a mummy, Thebes, Egypt	2,880 ± 140	2,770 [-360, +600]

5.1. Dating the Shroud using WAXS

Before using this method with material taken from the Shroud, it was important to determine what effect its exposure to the heat of the 1532 Chambery fire would have on the WAXS scatter profile. WAXS patterns were obtained from a piece of linen both before and after placing it in an oven at 200^{o} centigrade for up to thirty minutes. Although the heat of the oven caused a distinct yellowing of this linen sample, it made almost no difference to the WAXS profile (fig. 10). This was found to be due to the fact that during a fire, the relative humidity drops to a very low level, reducing the reaction rate by at least one order of magnitude and counteracting the rate increase caused by the rise in temperature [6].

A tiny linen thread measuring 1 mm by 0.5 mm was then taken from a small piece of Shroud fabric that was retained when the radiocarbon dating sample was removed. A WAXS analysis of this Shroud thread produced the scatter profile which is shown in figure 11, along with those previously obtained for the samples depicted in figure 9. It's clear from this chart that the peak intensities obtained from the Turin Shroud sample are almost identical to those obtained from sample FII, which was the label given to a sample from the archaeological ruins of the Siege of

Masada and dating from the period 55 to 74 AD. The close match of these two WAXS profiles clearly suggests that the thread removed from the Shroud also had a first century origin.

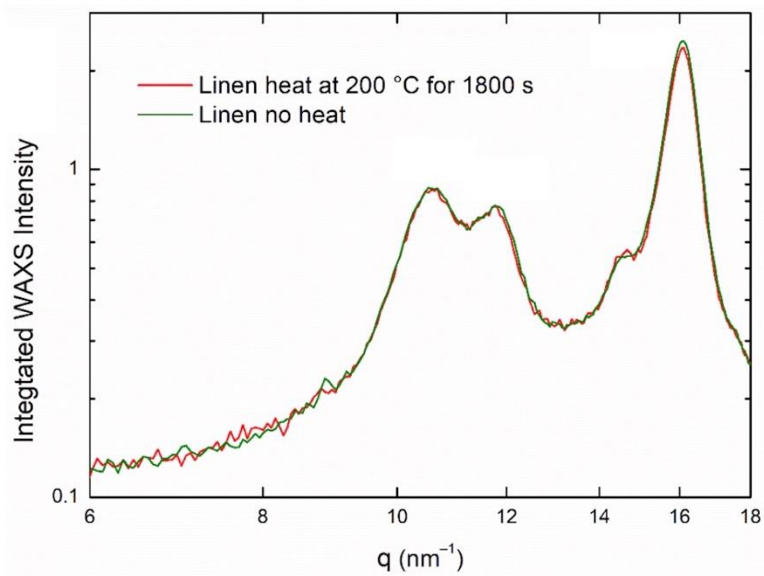

Figure 10. The red curve is the profile obtained after exposing a piece of linen in oven at a temperature of 200° C for half an hour. The green curve is the profile before the thermal treatment. From *X-ray Dating of a Turin Shroud's Linen Sample* by Liberato De Caro et al., Heritage 2022, 5, 860–870.

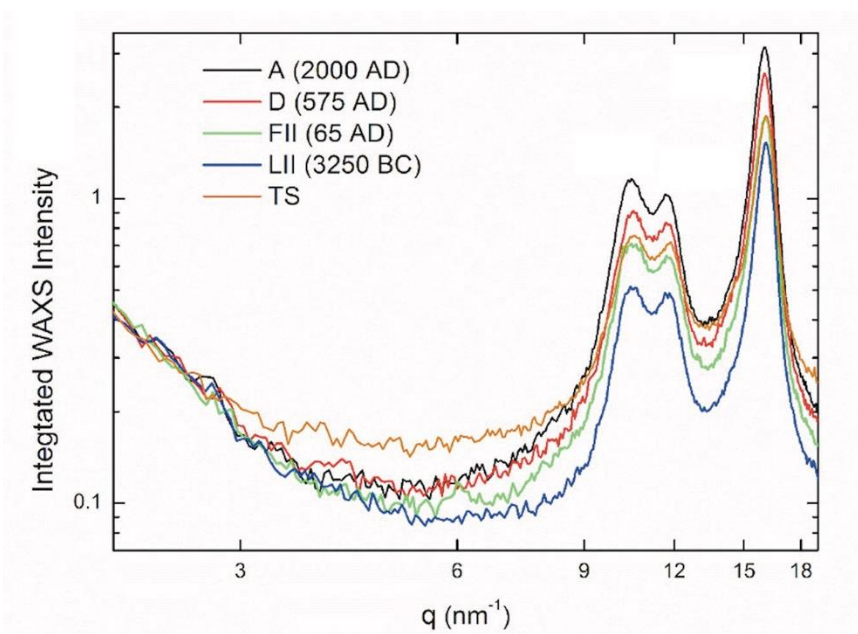

Figure 11. WAXS profiles produced by the Turin Shroud (TS) and four of the test samples. Note that the intensities of the signal peaks produced by the Shroud sample (brown line) are almost identical to that of sample FII (green), a first century linen fabric from an archaeological site in

Masada.From X-ray Dating of a Turin Shroud's Linen Sample by Liberato De Caro et al., Heritage 2022, 5, 860–870.

The radiocarbon test of the Shroud suggested that it was only seven hundred years old but this conflicts with the amount of age-related cellulose degradation revealed by the WAXS test of the Shroud sample. In fact, if the Shroud is just 700 years old, it would need to have been kept at an average temperature of over 27.5º centigrade to have produced this WAXS result. Only the hottest places on Earth, such as Mali in Africa, experience such high average temperatures and this is clearly well above both the 12.5º centigrade average temperature of Turin and the European average of 9º centigrade.

6. Conclusion

The controversies and concerns surrounding the 1988 radiocarbon dating test and its conclusions were the driving force behind the efforts to find alternative methods of dating linen fabric. There have been many other instances where radiocarbon dating of ancient items have delivered contentious results and any doubts are usually resolved by obtaining more samples and repeating the test. Clearly, this is not a viable option for a sacred relic such as the Shroud. The relevant church authorities have not allowed any further samples to be removed and have also rejected requests for further scientific examinations of the fabric in the years since the 1988 dating. Consequently, scientific research has been constrained to tests involving the use of only the small amount of material that was authorised for removal during scientific examinations of the Shroud in 1973, 1978 and 1988.

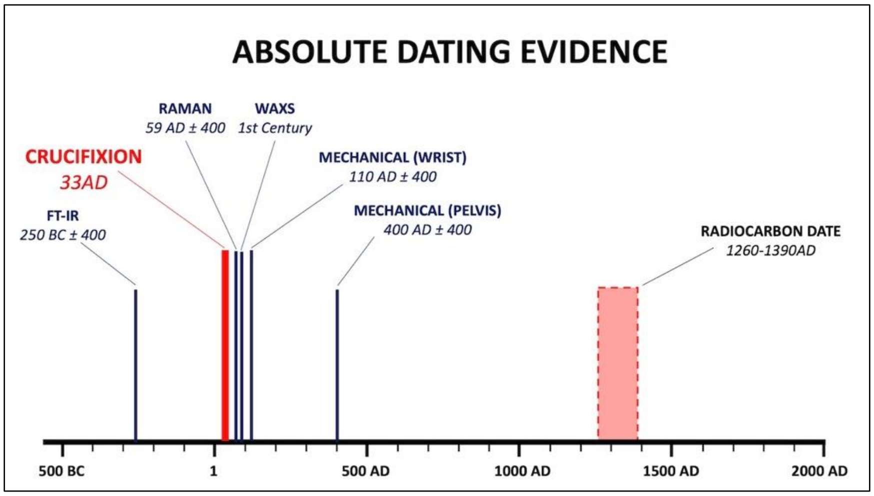

Figure 12. A summary of the absolute dating measurements made using spectroscopic and mechanical dating techniques.

However, some of the most extraordinary scientific accomplishments are often born out of adversity and these new, alternative dating methods are examples of innovation and ingenuity overcoming the most severe constraints. All these methods are non-destructive and require only minute amounts of material to be able to determine the age of the originating fabric. Unlike radiocarbon dating, which today is a precise technique which has benefited from over seventy years of research and development improvements, these new methods are still in their infancy.

However, the mutual compatibility of the age measurements obtained by these diverse, innovative techniques is nonetheless extremely significant. The fact that every one of these new dating methods has obtained a result for the Shroud that not only contradicts the radiocarbon dating result but also supports claims that the Shroud originated in the first century, is an outcome that must be considered relevant to any discussion concerning the age of the Shroud.

7. References

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Author's Biography

Michael Kowalski graduated in Physics at the University of Manchester in 1976 and subsequently spent three years working in the textile industry, during which he earned a post-graduate diploma in Textile Technology. He subsequently changed careers, joining a multi-national computer company where he worked for thirty seven years, specialising in the development and implementation of core banking systems used by many of the UK's major financial institutions.

Since taking early retirement in 2016, he has devoted much of his time to a study of the Holy Shroud of Turin. He is a member of the Shroud Science Group, a closed forum used by Shroud researchers from around the world to encourage communication and collaboration on matters relating to the Shroud. He is the editor of the British Society for the Turin Shroud Newsletter and the author of a book about the Shroud titled *'The Shroud of Christ: Evidence of a 2,000 Year Old Antiquity'*.