The Future Of Research On The Shroud

BRUNO BARBERIS
Associate Professor of Mathematical Physics, University of Turin
Director of the International Center of Sindonology of Turin

ABSTRACT. The future of research on the Shroud is outlined starting from the present knowledge of it, in particular from the results of the analyses made in 1978 by the STURP scientists and from the results of radiocarbon dating in 1988. Particular reference is made to the most useful techniques for studying the chemical, physical and biological characteristics of the most important typical sites of the Shroud: the cloth, the double image of a human body and the blood stains. A new data collection is proposed in order to significantly develop the research; it would give scientists the possibility to have at their disposal new information for making concrete progress in acquiring knowledge about the characteristics of the cloth and of the image. Several methodologies are proposed like: XRF (X-ray fluorescence), LIBS (Laser-induced breakdown spectroscopy), TOF-SIMS (Time-of-flight secondary-ion mass spectrometry), ICP-MS (Inductively coupled plasma mass spectrometry), UV-VIS (Ultraviolet-visible spectroscopy), RAMAN spectroscopy, NMR (Nuclear magnetic resonance), HPLC-MS (High-performance liquid chromatography mass spectroscopy), HPLC-IR (High-performance liquid chromatography infrared), GC-MS (Gas chromatography mass spectroscopy), etc.

1. INTRODUCTION

Modern scientific research on the Shroud began only in 1898 when the first photograph of it, by Secondo Pia, revealed the negative characteristics of the image. This gave scholars the possibility to study in detail both the cloth and the image, making the Shroud known all over the world. But it is only in the last fifty years that wide, coordinated studies have taken place.

There is no doubt that the most important of these more recent studies have been the analyses made directly on the Shroud between October 8 and 13, 1978 for 120 hours by an international team of 44 scientists, the majority of whom were members of the American association STURP (Shroud of Turin Research Project). The results of these analyses were published in the following years and still today they are the main references of modern knowledge on the Shroud. Since then over 30 years have passed. With the exception of the taking of the cloth sample for radiocarbon dating in 1988 and the removal of the patches and the substitution of the Holland cloth in 2002, no other direct interventions on the Shroud have been done. In order to significantly develop the research, it would be opportune to have the possibility to organize new data collection. This data collection would start from the results of the 1978 analyses and it would give scientists the possibility to have at their disposal new information for making concrete progress in acquiring knowledge about the characteristics of the cloth and of the image.

In my report I will provide a brief description of the possible future lines of research. I will divide my proposals into three sections corresponding to the main fields of research: the cloth, the double image and the blood stains.

2. ANALYSIS OF THE CHEMICAL, PHYSICAL AND TEXTILE STRUCTURE

Several people have asked for a repetition of the radiocarbon dating of the cloth of the Shroud made in 1988. However, as Alan Adler always asserted, this experiment would be significant only after the possible anomalies which might have influenced the 1988 results (pointed out by experiments and research conducted in these last twenty years) have been carefully checked. A detailed analysis of the cloth could be very useful in verifying statements regarding the homogeneity and the representativeness of the sample used for the radiocarbon dating.

In the last decade the American chemist Raymond Rogers claimed that the cloth samples used for the radiocarbon dating in 1988 had anomalous characteristics because he found cotton fiber contaminations. He suggested the hypothesis that these samples had a different composition from that of the whole Shroud due to an invisible darn. In order to confirm such a hypothesis it is necessary to analyze in detail the structure of the threads coming both from the main corpus of the Shroud and from the zone contiguous to the sample taken. The results of these wide-range analyses (microscopy, spectrophotometry, etc.) must be compared among them and with the results present in literature. It could be useful to obtain precise measurements of the dimensions of the threads and of the flax fibers, using not only integrated systems of optical and electron microscopy, but also such new technologies as Atomic Force Microscopy (AFM).

A further interesting argument to study is the comparison between the so-called side-strip and the main corpus of the Shroud, included the stitching thread: although the dimensions of the threads and fibers cannot provide definitive answers, they could give indications about whether the two parts are of the same origin.

The X-ray fluorescence (XRF) spectra obtained in 1978 highlighted the presence on the cloth of iron (8.3-17.5 $\mu g/cm^2$), calcium (150-200 $\mu g/cm^2$) and strontium (2-3 $\mu g/cm^2$). These data are very important for studying the characteristics of the image and of the blood stains. The theories asserting the pictorial origin of the image should be based on a higher content of iron (or other inorganic elements) in the image sites. The data obtained by STURP point out no differences in iron content in image and non image sites. This statement has been criticized by Walter McCrone and other scholars. Their criticisms are substantially based on the statement that the sensitivity of the detection method (XRF) and of the measuring instruments utilized was not able to detect the very low concentrations used to paint the image. In order to settle this controversy it is necessary to analyze inorganic elements, such as iron, calcium and strontium, with more sensitive instruments than the ones used in 1978. It would be suitable to take into account also other detection methods such as Laser-induced breakdown spectroscopy (LIBS), which is useful for the quantitative detection of the metal elements; new mass spectrometry methods like Time-of-flight secondary-ion mass spectrometry (TOF-SIMS), which is a very sensitive analytical technique for surfaces analysis able to detect both molecular organic species and inorganic compounds; and Inductively coupled plasma mass spectrometry (ICP-MS), which is a highly sensitive type of mass spectrometry. The use of highly sensitive methodologies could enable science to characterize and hence to distinguish between sites without image, sites with image and sites with blood stains. These analyses can be done using micro samples. Moreover, it would be useful to repeat some spectroscopic analyses done in 1978 like Ultraviolet-visible (UV-VIS) spectroscopy, Fourier-Transform Infrared Spectroscopy (FT-IR) with microscopic technique, RAMAN spectroscopy with microscopic technique and fluorescence spectroscopy. The limits of the spectroscopic data are often due to low signal resolution or to the superposition of signals on the typical cellulose signals. Hence it should be useful to utilize high resolution instruments. Moreover, it would be opportune to use infrared techniques able to detect only signals coming from the surface layers of the samples, and Nuclear magnetic resonance spectroscopy (NMR) for its huge power in recognizing molecules, in particular organic ones. The only problem with NMR is the significant amount of samples requested, which is of the order of at least some milligrams or more. Hence only high resolution instruments could be used, probably only instruments operating at more than 1000 Mhz.

Rogers deduced the presence of madder (alizarin) or of its aluminum metal complexes since the sample used for the radiocarbon dating when put into water left a yellow material which becomes red after acidification. To verify Rogers' hypothesis it might be useful to study a micro sample of thread using methodologies like High-performance liquid chromatography mass spectroscopy (HPLC-MS), High-performance liquid chromatography infrared (HPLC-IR) or Gas chromatography mass spectroscopy (GC-MS). These tests are very delicate due to the tiny dimension of the samples that it is possible to remove.

To complete the tests on the cloth it would be necessary to provide an in-depth map of the pollens on the cloth using the methods and techniques of modern palynology in order to obtain a detailed pollen diagram that permits precise qualitative and quantitative microscopic analysis. In the meantime it is possible to try to verify the suggested hypothesis of the possible presence of flowers on some sites of the cloth.

Moreover, it would be useful to repeat the ultraviolet (UV) fluorescence photographs made by Vernon Miller and Samuel Pellicori in order to determine the characteristics of the sites without image, of the sites with image and of the sites with blood stains, of the burn marks, of the water stains and of the so called “poker-holes”.

The carbon dust and the residual material found under the patches during the conservation work made in 2002 (which has been carefully collected and catalogued) could be studied using microscopic techniques: UV-VIS spectroscopy, fluorescence, infrared and RAMAN Spectroscopy with microscopic technique. Researchers must carefully define the success probabilities of these analyses because it is well-known that in several cases the collecting and interpretation of spectral data of carbon material is hard. Moreover, these analyses could be used to evaluate the hypothesis of a possible influence of the Chambéry fire on the radiocarbon dating. The analysis should be an enzymatic hydrolysis of the cellulose wastes with the examination of the hydrolysis products with the aim to verify the presence of alkylated or carboxylated glucose derivatives.

Specific color measurements in well defined sites contiguous to the burn marks could be very useful. These measurements should be done using precise calibration processes so that it is possible to evaluate possible color variations with time: this could highlight any possible increase in cloth decay. These results could provide important indications for improving the conservation conditions.

The edges of the poker-holes could be studied using spectroscopic methodologies (UV-VIS, IR, RAMAN, TOF-SIMS, etc.) in order to verify the hypothesis that their origin is not due to combustion.

Moreover, it could be opportune to repeat spectroscopic analyses on the water marks, also using mass spectrometry and measurements of their iron content in order to compare these results with the ones obtained in sites without water marks and in sites with image.

Finally, spectroscopic tests could be done on the Holland cloth and on the patches removed in 2002 in order to compare the characteristics of the cloth sites – both those exposed to air and those that are not – for studying the aging of the cloth.

3. ANALYSIS OF THE IMAGE CARRIED OUT USING VARIOUS EXPERIMENTAL METHODS

The most important research is without any doubt to investigate in the deepest possible way the nature of the image with the aim of trying to clear up its origin and giving objective considerations about the several hypotheses about its formation proposed in these last years (vaporograph, pictorial origin, thermal origin, light origin, oxidation-dehydration, electromagnetic radiation, etc.).

The most important and detailed data regarding the study of the image were given by the papers of the scientists of STURP and of other scholars after the scientific investigations of 1978. The nature of the image is clearly the central argument of research on the Shroud. Therefore it is very important to widen and deepen the acquired knowledge. The fundamental arguments to deepen are the following ones.

a) Comparison between the iron concentration of the sites with and without image. This research must only be done on sites certainly not contaminated by the presence of blood because otherwise the iron content would be increased. The measurement methodologies must ensure very high precision, sensitivity and repeatability. It will be very useful to determine previously in the laboratory (working on control samples) the iron concentration able to give a Shroud image-like optical density and then to evaluate its spectroscopic characteristics.
b) Test on the presence of proteins. Also in this case it is necessary to work on sites certainly not contaminated by the presence of blood because otherwise proteins are surely present. The chosen methodologies should be able to give an unequivocal answer, that is due only to the presence of proteins and, if possible, to determine the type of the source organism.
c) It would be prudent not to exclude the hypothesis that the binder used by the possible forger is of plant origin and hence with a polysaccharide structure.
d) In order to confirm the hypothesis of a process of oxidation-dehydration as the cause of formation of the image (as suggested by STURP), it would be important to have data connected to the chemical structure of the molecules responsible for the yellow colour of the surface of the flax fibres in the sites with image.
e) Examination of different sites with image in order to point out possible chemical and physical heterogeneities. In particular it would be opportune to carry out a comparative study of the frontal and dorsal image so as to highlight possible differences in their characteristics and formation processes. The three-

dimensional reconstruction of the frontal image should be extended in detail also to the dorsal image.

f) It would be important to propose a detailed study of the sites of the nose, of the knees and of the heels, because some scholars assert the finding of traces of aragonite in these sites. It could be interesting to confirm its presence, and at the same time to verify the possible presence of aragonite also in other sites of the Shroud.
g) To study the various hypotheses on the formation of the image, it would be important to confirm the absence of the image under the blood stains.

The answers to the above mentioned problems can be obtained through a systematic comparative study of flax samples treated with the above techniques (iron oxide and proteins for the pictorial hypothesis, thermal treatment of the sample for the thermal origin of the image, etc.) and Shroud samples with and without image. The methodologies are fundamentally the same as those already described for the study of the sites without image. In short:

a) Microscopic observation and recording of the sites using optical microscopy, electron microscopy and AFM. Using these techniques it is possible to enhance the possible presence of extraneous material due to pictorial techniques.
b) Measurement of iron concentrations using high precision and repeatability instruments and techniques: LIBS, TOF-SIMS, XRF, ICP-MS, etc.
c) Spectroscopic characterization in UV-VIS (reflectivity and fluorescence), IR and RAMAN.
d) Photography with ultraviolet light and recording of only fluorescence light, and other photography techniques such as thermography using thermographic cameras with high sensitivity.
e) The presence of proteins is detectable using mass spectrometry methods like TOF-SIMS, and in particular Matrix Assisted Laser Desorption/Ionization-Mass Spectrometry (MALDI-MS). This last technique is commonly used today for studying proteins (proteomic) and very big databases of MALDI spectra are today available. The only limitation of the application of this technique to the Shroud samples is due to the necessity of having significant quantities of proteins.
f) These same techniques are able to provide information on the nature of the substances present on the sample also if these substances are neither proteins nor iron oxide.
g) Several of the above-mentioned techniques are not destructive. Therefore careful planning of the experiments could give interesting results also using few samples of very little dimensions.

4. ANALYSIS OF THE BLOOD STAINS

In spite of the large amount of data collected in 1978 on the blood stains, several criticisms have been raised about the results obtained. Therefore it would be necessary to repeat on the blood sites the same tests already proposed for the cloth and for the sites with image, in order to point out the presence of substances typical of blood structures and to study them from the points of view of chemistry, physics, biology and forensic sciences. The fundamental arguments to deepen are the following ones.

a) The detailed documentation of the extraneous material present on the fibers in the blood sites. This study must be done with microscopic images with different enlargements and different techniques: optical microscopy with bright field illumination, dark field illumination and phase contrast illumination; electron microscopy; AFM, etc.
b) To check in detail if in this extraneous material there is iron with a higher concentration than in other Shroud sites and if there are no traces of mercury. In reality the presence of iron is not contested, but knowledge of its concentration in the blood sites is very interesting. Confirmation of the experimental results given by John Heller and Alan Adler about the absence of such microelements as manganese, nickel and other elements that are usually present together in the mineral iron pigments could be very important. Likewise, the presence of mercury sulfide should be carefully studied in order to state whether it is accidental, as claimed by Adler, or systematical, as claimed by McCrone. Moreover, it would be useful to check the possible presence of potassium and chlorine ions. In all this research it is necessary to use methodologies able to check the various elements at a level of microtraces, like TOF-SIMS, LIBS, ICP-MS, XRF with high sensitivity instruments.
c) To check in detail for the presence of proteins. Unlike for the sites with the image only, the presence of proteins on the blood sites is not denied because, in the opinion of McCrone and of his supporters, proteins are used in the preparation of temperas in order to thicken them and to carry the iron pigments. However, detection of the presence of proteins and in particular their characterization is a fundamental point and their analysis must be done using both spectroscopic methodologies (UV-VIS spectroscopy, FT-IR and RAMAN spectroscopy), and mass spectrometry methodologies (in particular TOF-SIMS and MALDI-MS). The research and characterization of proteins on blood sites is very important in particular if its results are compared with the results of the same research made on sites with the image only. In fact the possible detection of proteins on blood sites

and the contemporary absence of proteins on the image only sites should have significant diagnostic importance. The data obtained by STURP for the fluorescence spectra of blood sites show the absence of fluorescence, while fluorescence has been detected on the edges of the blood spots. Therefore it would be advisable to repeat this research.

d) A study strictly connected to the presence of proteins is the detection of systems relevant to human blood, made with the use of methods typical of biology and biochemistry. Working on the blood material taken in 1978, Pierluigi Baima Bollone proved the presence of iron and, using fluorescent antibodies methodologies, the presence of human blood. It would be important to repeat these studies with modern systems using still today antibodies reactions for their high specificity. Moreover, it would be useful to verify and carefully document whether the blood present in different sites of the Shroud belongs to the same man and if in some sites it is the blood of a living man and in other sites blood that came out from a corpse. In particular the borders between the blood and the serum spots should be studied in detail. Finally, it will be useful to verify and repeat the research regarding identification of the blood type.

e) It would be interesting to try the use of the detection techniques of blood traces used by police forensic teams.

f) The methodologies used for studying the blood stains could be usefully used also for the scourge marks.

5. CLOSING COMMENTS

1) Any future research must take into account the research proposals advanced by the STURP scientists at the end of their studies on the data collected on the Shroud in 1978. These proposals were officially presented on October 16, 1984 to Card. Anastasio Ballestrero, the Papal Custodian of the Shroud at the time.
2) It is fundamental and unavoidable to choose very carefully the sites to examine. It is absolutely necessary to distinguish very carefully among the various sites: without image, with scorches, with burns, with “poker-holes”, with water stains, with image, with blood traces, mixed.
3) In order to avoid too invasive interventions, it is absolutely necessary to use samples of very little dimensions and hence any taking of samples must be done only with the use of microscopic techniques.
4) With the aim of both reducing the number of samples to be taken and of maximizing the information obtained, every sample must be used to make several

tests. Therefore the research must be planned in a such a way as to first carry out on each sample all of the not destructive measurements (for example the recording of UV-VIS, IR and RAMAN spectra) and only afterwards the measurements which can modify the nature of the samples (for example: extraction with inert or reactive solvents, the recording of MALDI spectra, etc.).

5) Before taking any sample from the Shroud it is necessary to simulate on samples prepared in a laboratory all the measurements and experiments planned on the Shroud, in order to verify their feasibility, answer types, utility and invasiveness.