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COULD THE TURIN SHROUD BODY IMAGE FORMATION BE EXPLAINED BY MAILLARD REACTION?

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ABSTRACT

Nowadays, after more than twelve decades of studies involving many scientists from all over the world, *we* do not know the originary chemistry of the Shroud of Turin. This state of affairs is due to the uncertainty between two possibilities. The first one, deduced by Heller and Adler, asserts that the surface chemistry is linen cellulose structure. The two scientists have obtained this result by microanalysis of the samples extracted from the Linen of Turin. The second one, deduced by Rogers and subsequently studied with Arnoldi, supports the hypothesis that the linen threads were, in origin, covered with a thin layer of impurities. Also this result has been experimentally obtained. In fact, by microchemical tests, using iodine on thread pieces of the Shroud linen, it was detected the starch impurities presence. This study is an attempt to analyze the Rogers' hypothesis: a Maillard reaction between amines (nitrogen compound with a free $-NH_2$ group), coming through the corpse wrapped in the Linen of Turin and reduced sugars, due to the manufacturing procedure, present on the surface of the above linen cloth. Therefore, as it has already affirmed, we have two different visions. However, we must take also into account that the second one hypothesis needs, at same time, the presence of amines and the absence of aromas and/or burial ointments. The aim of this our study is to see if the above hypothesis (the one of Rogers with Arnoldi) is able to yield on the linen a color distribution characterized by a I(z) correlation between the intensity of color and the cloth-body distance, as it occurs to the Shroud of Turin.

KEYWORDS: Shroud, chemistry, sugar, ammonia, amines, Maillard, linen, fibrils, decomposition

1. INTRODUCTION

Heller and Adler, authoritative scientists of the STURP (Shroud of Turin Research Project) team, investigating the Shroud of Turin, affirmed in their microchemical analysis, performed by samples extracted from the above linen cloth (Heller and Adler, 1981; Jumper et al., 1984), that the coloration was produced by some dehydrative and oxidative processes of the cellulose structure of the linen. In fact, they observed organic groups that are typical of dehydration and oxidation with the formation of conjugated carbonyl groups, as the chromophore. These processes occurred at low temperature with a chemistry similar to the one causing the linen to yellow with age. Therefore, there had been an interaction between the thermal energy emitted by the corpse and the cellulose surface structure of the Linen of Turin.

So, starting from the distribution of the yellowed fibrils on the Shroud body image region (Fazio and Mandaglio, 2011; Fazio, 2014; Fazio et al., 2015), we have demonstrated, describing step by step its formation process, that a very reasonable hypothesis of image formation is the stochastic one (Fazio, Mandaglio and Anastasi, 2019).In detail: the thermal radiation, coming by the corpse wrapped in the Shroud, triggered a stochastic process yielding a latent image with its uniqueness and the 2D and 3D characteristics. Moreover, to confirm the above statement, a correlation exists between the yellowed fibrils density (or image intensity) and the cloth-body distance, well represented by linear regression as occurs to the Shroud (Jackson, Jumper and Ercoline, 1984).

In this paper, we want to investigate another natural process suggested by Rogers (Rogers and Arnoldi, 2002 and 2003; Rogers, 2008): the chemical interaction among ammonia and amines produced during the corpse's decomposition and the crude starch coming by the manufacturing procedure of the threads of linen. This amino-carbonyl Maillard reaction (Miller, Vandome and McBrewster, 2010; Hayash and Namiki, 1986; Zamora and Hidalgo, 2011) is a strong dye. The amines are volatile and rapidly undergo Maillard reaction with the reducing sugars when they are in contact. Also ammonia, with its two free electrons, reacts like amines with reducing sugars yellowing the linen fibrils. In this case, there is a considerable amount of ammonia due to the sweat on the skin of the corpse of a scourged and crucified man.

In fact, it contains a lot of urea which is hydrolyzed in ammonia. However, the diffusion of this gas must occur approximately in the same way from all parts of the corpse and be in sufficient quantity to yield the desiderate effects. Therefore, no interaction between thermal energy and superficial cellulose structure of the linen will be discussed in this article. We will analyze the Maillard reaction between amines and reducing sugars only to investigate the possible existence of an I(z) correlation also in this case. This chemical process has been highly criticized by many scientists. Here, we will cite two authoritative among the above (Fanti, 2011; Jackson, 2017) but only for the comparison with the hypothesis made by Rogers because we do not believe in their miraculous proposed as formation mechanisms. They affirm that it is practically impossible to obtain an image with good resolution (it is about 0.5 cm) and the possibility to have a 3D reconstruction with weak distortions as it has been deduced for the Linen of Turin.

Moreover, we must understand if the thermal energy source had interacted with the cellulose structure, as has already been described in a previous article (Fazio, Mandaglio and Anastasi, 2019) or had favored a reaction between a thin layer of reducing sugars, present on the outside surface of the linen, and the amines coming from the sweat which is on the skin of the corpse of a man who suffered unprecedented violence. Obviously, this last hypothesis could occur only if the reducing sugars were present and the aromas and/or burial ointments were absent. In any case, to be clear, there is no competition between the two hypotheses. In fact, both depend on the originary Shroud chemistry. So, we reiterate that want to find out if an I(z) correlation can be present.

2. ANALYSIS and DISCUSSION

Now, because the amines coming by the corpse's degradation, we have considered two articles to obtain useful information to solve our problems (Bonte and Bleifuss, 1977; Vass et al., 2002). The amines, including Putrescine (1,4-diaminobutane) and Cadaverine (1,5-diaminopentane), are produced during the decomposition by amino acid- decarboxylase interaction. The latter is a bacterial enzyme. The above process yields about 16 different amines but the molecules of our concern (the heavy ones) appear after four, five days.

Therefore, they are not present at the early decomposition time. Within 36-72 hours, a lot of ammonia product from the sweat is present on the entire surface of the body of a person who died after scourging and crucifixion. In this condition, as it has already been affirmed, the sweat contained a large quantity of urea that by hydrolysis was transformed in ammonia (NH_3). Besides, we must remember that gamma-amino butyric acid and beta-alanine (both heavy amines) are present before 36-72 hours but at a very low concentration. These amines increase their presence on the fifth day.

So, in the attempt to understand how the evaporating ammonia molecules, coming from the sweat on the skin, are distributed in the space between body and cloth (the regions where the z cloth-body distance is greater than or equal to zero), we shall use Fick's law, characteristic of the diffusion of gases:

$$\varphi + D \cdot dc/dz = 0 \qquad (1)$$

where, in this approach, φ is the flow of ammonia (mol $\cdot$ cm^{-2} $\cdot$ s^{-1}), D is its diffusion coefficient (cm^2 $\cdot$ s^{-1}) and dc/dz its concentration gradient, with c concentration (mol $\cdot$ cm^{-3}) and z (cm) cloth-body distance. The gas diffusivity coefficients are temperature, pressure and gas type dependent.

Now, for the gases, when the molecular weight increases, the diffusion coefficient D decreases and vice versa. Therefore, respecting Fick's law on the diffusion of gases, when the -φ/D ratio, that represents the dc(z)/dz function, increases its value and a large variation of the concentration appears in a small distance (this occurs to the amines as Putrescine and Cadaverine that are both heavier than air), it means there is a good resolution; otherwise, the image would appear diffuse or blurry, as it is when the resolution is low.

Also the φ flow contributes to the above ratio. So, it is necessary to have an idea of the range of the $(\varphi/D)_{ammonia}$ values as it is time dependent. Moreover, we should know all the appropriate information together with the real values of the parameters involved in this complex chemical process that is the amino-carbonyl Maillard reaction. For example, the slope of the c(z) function [dc(z)/dz] must have such a value that the yellowing fibrils, produced by Maillard reaction, does not exceed the distance of z = R_0 = 37 mm for the frontal image (Jackson, Jumper and Ercoline, 1984). Now, taking this last value into account, it is important to have a large flow of ammonia to increase the slope of the dc(z)/dz function and to respect the distance of 37 mm. Otherwise, we will have very scattered data and, consequently, a poor resolution.

The idea of Rogers (Rogers and Arnoldi, 2002 and 2003; Rogers, 2008) is supported by microchemical tests with iodine that have detected, on the surface of pieces of thread taken from the Shroud, the presence of starch impurities. In the Maillard reaction, it is also necessary to take into account the temperature of the wrapped corpse in the funerary cloth that can also reach 41°C. This thermal state of the corpse could have had a positive effect in the image formation involving the Maillard reaction. This value of the corpse temperature was furnished to Rogers by Dr. Irvine of the Pathology Section, Office of the Medical Investigator, University of New Mexico (Rogers, 2001). The concentration of the reactants, the relative humidity values and pH are also very important. Moreover, it is necessary to remember that the presence of *Saponaria officinalis* has not been confirmed on the Shroud of Turin. The above process occurs in a wide range of temperatures, with a lower limit that is not well-defined. This can also occur at room temperature with effects that appear after hours, days or months. Generally, the Maillard reaction is fast, extremely complex and color producing. The concentration gradient dc/dz, equal to - φ/D ratio, is time dependent because $\varphi = \varphi(t)$. However, in a first approximation we could consider the above ratio roughly constant for the time taken by the cloth to absorb the first gases of ammonia. So, respecting this hypothesis, we should have a function of distribution c(z) represented by a linear regression.

In realty, we must consider the -φ/D ratio not constant, taking into account that we do not know the $\varphi(t)$ function. However, we are in the condition to surpass this impasse considering that the temporal dependence of the ammonia flow will distribute the colored fibrils on the linen, left by the activity of the Maillard reaction, in a scattered way. This picture is due to the comparison with the Linen of Turin when the linear I(z) function was obtained by the fitting procedure with a coefficient of determination (the degree of correlation) $r^2 = 0.60$. A result with a low degree of correlation, in line with the data present on the Shroud that are sufficiently scattered in the (I, z)-plane.

We have extracted from Fig.2 of (Jackson, Jumper and Ercoline, 1984) the 13 pairs of (I, z) values repeating the fitting procedure. For the degree of correlation, we have obtained $r^2 = 0.58$, slightly different from Jackson's value (0.60). This is due to our data capture. Besides, we have extracted the 0.53 value for the χ^2 reduced in line with the presence of scattered data in the (I, z)-plane. These results support our above hypothesis that the c(z) function can be considered as the result of a fitting procedure of data that on the (c, z)-plane are scattered. However, if we had found only a weakly scattered line, we would have discarded the Rogers hypothesis.

Therefore, the maximum presence of the gas is in the cloth-body contact areas. When the cloth-body distance z increases its value, the gas concentration decreases and vice versa. Therefore, the function describing the gas concentration, obtained by Fick's law, is:

$$c(z) = c_0 \, (1 - z/R_0) \qquad (2)$$

where c_0 is the gas concentration for z = 0. We underline that we have considered the diffusion of nitrogen compounds in the air but not in the linen because the image is superficial, its thickness being 20-30 μm.

Consequently, the Maillard reaction could yield on the linen cloth a yellowed fibrils distribution with the same trend of the concentration of gas on the same linen cloth surface. In other words, the correlation between the intensity of Maillard coloration and cloth-body distance I(z) will be a linear regression, as it is on the Shroud of Turin:

$$I(z) = I_b + I_0 (1 - z/R_0) \quad (3)$$

where I_b is the average image intensity due to the natural linen degradation per action of the electromagnetic radiation (before the Maillard reaction). Moreover, due to the low level of the temperature value (about 41 ^{0}C) the above image will be, as on the Shroud, a latent image.

The existence of the formula (3), a correlation between the intensity of color distribution and cloth-body distance, would highlight that in the image region there are codified information between body surface and sheet distance. Therefore, would be possible to obtain a reconstruction in 3D of the image product. However, the presence of only NH_3 gas, with $(P.M.)_{ammonia} < (P.M.)_{air}$, would act negatively on the resolution if the ammonia flow φ is not very large.

Besides, to obtain colored fibrils, by Maillard reaction, it is necessary for the corpse to be in the linen cloth until the first gas emission because, in such a case, a reaction with the carbohydrates, coming by crude starch, is possible. So, after a suitable time, the corpse must be out of the linen cloth. Only in this case, we could explain the uniqueness of the Shroud body image. Indeed, in this way, the successive emissions will not act on the possible image, damaging or destroying it.

These uncertainties characterize the actual situation. In the near future it could be important information due to the interest that the Forensic medicine has for the decomposition chemistry of human remains, in the attempt to improve the postmortem interval (PMI) estimates (Megyesi, Navrocki and Haskell, 2005; Choi et al., 2019). With this state of affairs, only the experimental evidence could explain these open questions.

Unfortunately, the complexity and the difficulty to study the amino-carbonyl Maillard reaction do not allow to understand which of the two hypotheses (Heller-Adler or Rogers) is the right one. Therefore, for now it is not possible to investigate, with the advantage of the knowledge of the originary chemistry, and to describe the interaction that generated the passage from the above chemistry to the current.

3. CONCLUSIONS

The comprehension of the mechanism yielding the Shroud body image is a very important goal. For us, the above process is certainly probabilistic because on the linen cloth, as a final result, there are colored fibrils and others with background optical density (fibrils that did not turn yellow). On the above burial linen cloth the density of the yellowed fibrils, grouped in small bundles, increases when the cloth-body distance decreases and vice versa. Therefore, a function that represents the I(z) correlation between image intensity (or yellowed fibrils density) and cloth-body distance exists. Besides, independently from the number of yellowed fibrils, their optical densities are equal in the region where the body image lies. This result is due to the action of the stochastic process. Consequently, the time required for yellowing, varies from years to decades. In reality small differences are present due to the natural variety of the linen threads and/or to the manufacturing procedure. In fact, these slight variations in color could be attributed to an uneven distribution of impurities on the linen of the Shroud of Turin.

In the case of Rogers' hypothesis, the amino-carbonyl Maillard reaction should be able to obtain a linen fibril coloration with an important characteristic: the one to generate an intensity of the color distribution I that *versus* z cloth-body distance is well represented by a linear regression. However, due to the absence of Putrescine and Cadaverine, both heavier than air, and to the complexity of the above process, it is opportune to think of the realization of various experiments in Legal Medicine areas, taking also into account that the necessary time to obtain a coloration is strongly dependent on the initial thermal conditions, the concentration of the reactants, the pH and the relative humidity.

Just so, we could, at a microscopic level, observe how the yellowed fibrils of linen are distributed in the region where the coloration lies and to compare these results with the obtained ones on the Linen of Turin. Otherwise, due to the complexity of the above process and to the poor knowledge of characteristics and involved parameters, verbal confrontations will continue with many written articles and zero results.

We, like Rogers, believe in a natural mechanism for the formation of the Shroud image. For us, an interaction between thermal energy and linen cellulose structure; for Rogers, a Maillard reaction between amines and reducing sugars. However, there is not competition between the two visions because both depend on the originary chemistry. We decided to support also the Rogers' hypothesis for our intellectual honesty, because we believe in the science rejecting the pseudoscience, excessively abundant in this case, and because those who contribute to the search for truth are no less important than the few who find it.

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