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Short communication

Comments on the analysis interpretation by Rogers and Latendresse regarding samples coming from the Shroud of Turin

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ABSTRACT

The presence of a "invisible mending" has been proposed as an explanation for medieval radiocarbon dating measurements made on the Shroud of Turin. Here we show that the chemical analysis which was to support this theory is not consistent, and no scientific data confirm these speculations. Specifically, the samples of the Shroud image fibers underwent a different cleaning procedure with regards to those allegedly belonging to the medieval mending. There is no reliable indication of the supposedly diagnostic compounds (e.g. gum Arabic, pentoses). The only detectable difference between the samples is the presence of a compound with an aliphatic chain which cannot be identified more in detail, e.g. as sebum.

In 2005, Raymond N. Rogers published an article in *Thermochimica Acta* in which, on the basis of chemical tests and pyrolysis mass spectrometry analysis, he gave credit to the theory of an "invisible medieval mending" on the Shroud of Turin [1]. We have shown that by pyrolysis mass spectrometry analysis the only significant difference found between the sample taken by the image zone of the Shroud and that supposedly belonged to the "invisible mending" is due to an external contaminant [2]. We have identified this contaminant as a chemical specie bearing an aliphatic chain.

Recently, in a comment, Mario Latendresse addressed some points of our editorial, stating that ". . .the technical analysis of Bella et al. of the mass spectra is *incorrect* and their main conclusion is *unconfirmed*" (our emphasis). He proposed that the contaminant is sebum [3]. It was not our intention to discuss this subject any further and will not discuss the controversy about the Shroud of Turin dating, but we have to stress that Latendresse misinterprets mass spectra [4]. Let's remember that Rogers used three kinds of samples.

a) From the image area of the Shroud of Turin (considered "surely authentic" by Rogers);
b) From the "Raes Sample", a piece cut by Raes in 1973 and kept in a plastic bag, and
c) From the C14 fragment cut in 1988.

According to Rogers, samples *b)* and *c)* would both supposedly come from the medieval invisible mending.

While no details about the samples are given in Rogers' *Thermochimica Acta* paper [1], other works by Rogers clarify that samples *a)* were collected by an adhesive tape on the surface of the Shroud and given to microscopist Walter McCrone who, in Rogers' words, "contaminated" them and that they had to be "laboriously cleaned", also by washing with xylene, by Joan Rogers. No cleaning treatment was instead applied to samples *b)* and *c)* [5],[1] This fact alone (omitted in Ref. 1) might be sufficient to explain any chemical difference (for instance the presumed content in vanillin) or dissimilarity observed at the microscope (for instance the amount of cotton or the presence of gum Arabic) between the Shroud image samples and the others. There is no need to invoke any kind of "invisible mending".

To support his hypothesis, Rogers shows two pyrolysis mass spectra, one coming from a fibril taken in the image area of the Shroud, sample *a)*, and another from Raes sample, *b)*. Latendresse [3] has explained Rogers's reasoning [1], showing its fallacy. According to Rogers and Latendresse, during pyrolysis cellulose (made of hexoses) would show peaks at $m/z = 96$ (due to furfural)

[1] Rogers wrote: "···Walter McCrone had ignored agreements on how the STURP samples were to be observed, and he contaminated all of our samples by sticking them to microscope slides. All of the fibers were immersed in the tape's adhesive, Joan Janney (now Joan Rogers) laboriously cleaned and prepared Shroud fibers for analysis at the MCMS···[Midwest Center for Mass Spectrometry]". "···No xylene was used to clean the fibers [of Raes sample], because they were not obtained as part of the tape sampling. . ."

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and $m/z = 126$ (5-hydroxymethyl furfural), while pentoses (such as arabinose, which is present in gum Arabic) would show just one peak at $m/z = 96$. The presence of peaks at $m/z = 96$ in both samples and the absence of a peak at $m/z = 126$ in the Raes sample *b)* should support this reasoning. Latendresse correctly points out that Rogers did not give any reference for his hypotheses, but Latendresse himself cites a paper by Kato presumed to support Rogers' statements [6]. From this paper, the only relevant information which can be drawn is that the thermal degradation products of cellulose are, among many others, furfural (at a temperature above 160 °C) and 5-hydroxymethyl furfural. The words "gum Arabic" or "mass spectrometry" are not even mentioned. Furthermore, arabinose is just one of the molecules found in gum Arabic. It is not even the major carbohydrate component (the other carbohydrates are hexoses). It is not clear why the presence of pentose should "suppress" the evolution of 5-hydroxymethyl furfural generated from the linen of the supposed "invisible mending" and from the other hexoses which are anyway present in gum Arabic.

Even if we were to accept Rogers and Latendresse's reasoning (based only on Rogers' opinion) there are multiple issues for which the presence of these peaks have hardly any diagnostic value. First, Rogers reported scarce details of the instrumental apparatus employed for the mass spectrometry analysis and for the analysis itself. We are unaware of the pyrolysis temperatures of the two samples or even if they were the same, making any meaningful comparison difficult if not impossible.

The major peaks in the first spectrum (from sample *a)*, Shroud image fibres) are at $m/z = 69$ and at $m/z = 131$. The second spectrum (from Raes sample *b)*, supposedly belonging to the invisible mending), presents some clusters of peaks with a repetitive pattern differing for 14 units of atomic mass, which is consistent with the fragmentation of a compound bearing a long aliphatic chain, and a peak at $m/z = 131$ (see the figures of our previous editorial, Ref. 2). In our previous analysis, we concluded that no diagnostic difference could be found between the two spectra except for the peaks due to the contaminant. They show the fragmentation of a compound with a long aliphatic chain, therefore they are unlikely to come from cellulose. There is no evidence about the presence of gum Arabic or pentoses.

In our editorial, we also included the spectrum of hexadecan-1-ol as an example of a compound bearing a long aliphatic chain [2,7]. This was solely to illustrate the characteristic fragmentation pattern of this class of compounds, with the repetitive peak pattern differing by 14 unit of atomic mass (Fig. 1, top). Latendresse challenges this point in an unfortunate way. He incorrectly believes that the GOLM database reports a different spectrum of hexadecan-1-ol (Fig. 1, bottom), with also reading below $m/z = 50$. No direct comparison would be significant, since the two spectra are acquired with different instrumental settings. However, the GOLM database does not report any mass spectrum of hexadecan-1-ol, but only of its trimethylsilyl (TMS) derivative (Fig. 1, bottom) the name of which is specified [8]. Still, Latendresse believes that it refers to hexadecan-1-ol. The mass spectra are different because of the fragmentation by the TMS group. The spectrum of trimethylsilyl-hexadecan-1-ol has been cut (with no comments by the author), hiding the major molecular peak, see Fig. 2 for a comparison.

Latendresse acknowledges that chemical compounds cannot be confidently identified solely by their molecular peaks.[2] It must be added that different instrumental settings and the presence of other compounds might sensibly affect the relative height of the peaks. However, in mass spectrometry the ratio of the peaks are not constant when experimental conditions change even slightly, therefore the argument that the peak at $m/z = 126$ should have been approx. 5% if present is not correct.[3]

Furthermore, the intensities of the supposedly diagnostic peaks are weak (less than 30% of the base peak, which has not been assigned) and comparable with a multitude of other peaks if not with baseline noise. Should we consider acceptable Rogers and Latendresse's identification within these limits, we could find the presence of almost any other chemical substance, not only gum Arabic. The identification of a complex mixture as gum Arabic, discriminating on the presence or absence of a peak with intensity 5% or zero, has little diagnostic value.

Mass spectra cannot be simply arithmetically subtracted, especially if acquired under different conditions. Therefore, as we said in our editorial, it is not possible to confirm that any part of the peak at $m/z = 96$ is due to furfural. The only correct observation is that the relative heights of the peaks are similar within the recurring patterns, therefore the contribution to the supposed peak of furfural with $m/z = 96$ would be minimal, if present at all. It is the responsibility of who proposes the existence of the "invisible mending" to give evidence. A peak at $m/z = 96$, overlapping another again at $m/z = 96$ surely belonging to the contaminant, is actually no evidence at all.

With regards to the contaminant, Latendresse confidently believes it might be identified as sebum, and shows the spectrum of tripalmitin (a compound with long aliphatic chains, exactly as we hypothesised the contaminant should have), one of the components of sebum [9]. Latendresse misinterpreted the mass spectra of hexadecane-1-ol and trimethylsilyl-hexadecan-1-ol. He does not seem to realize that by hypothesizing the presence of tripalmitin (see chemical structure, Fig. 3, top) he actually acknowledges the presence of a contaminant with a long aliphatic chain, thereby confirming rather than confuting our thesis. Sebum is not constituted of tripalmitin alone, but of a complex mixture of lipids. Therefore, the pyrolysis of sebum cannot show just one component and none of the others. The spectrum of tripalmitin is also shown without the "undesired" peaks.[4]

Even if the contaminant would be sebum (it is not) or another compound with an aliphatic chain, this would only show that Rogers did not discuss its presence. It would not support the "invisible mending" theory. Were that sebum really present, basically any difference between the Shroud image fibres and the Raes/C14 samples could just be due to sebum, with no need of the "invisible mending" theory. It is also worth mentioning that the apolar compounds of the hypothetical sebum would have been most likely washed off by the xylene used in the cleaning of Shroud image

[2] Latendresse also observes that "All of the mass spectra of the GOLM database for [what he believes to be] that compound show intense peaks between $m/z = 40$ and 50." The absence of any peaks below $m/z = 50$ in Rogers's hexadecan-1-ol is most likely due to an instrumental setting that cuts off all these peaks with little diagnostic value.

[3] Latendresse's concludes: "In summary, although the analysis of Rogers of the mass spectrum is incomplete because it does not compare it to other spectra and is missing precise contextual details, in particular temperatures, the spectrum does not appear to give a counter indication that gum Arabic was not present on the Raes fibers." So, it is not known if gum Arabic was present, it is not known if it had been removed on the other samples by the "laborious cleaning", it is not known why it should give certain signals in the spectra, it is not clear if these hypothetic signals are actually present, but there are no "counter indication that gum Arabic was not present." Accepting these limits there are no are counter indications regarding the presence of *any* chemical compound.

[4] According to Latendresse: "Second, Bella et al. argue that the reading of the peak at m/z 126, in the second spectrum, is not really zero if we take into account the "contaminant", which has higher intensity peaks than m/z 131, the highest peak in the first spectrum. But the best we could say is that the m/z 131 peak went from intensity 100 to slightly above 20, that is, a reduction by a factor of 5, which if applied to m/z 126 would have gone from intensity of about 25–5, not zero. In other words, and based only on the m/z 126 peak, we cannot conclude that the mass spectra are identical once this unknown "contaminant" is removed. This peak was essential in the identification of gum Arabic".