PUBLICATIONS (1)
PAPERS & ARTICLES

Spectrometry in 'Studies on the Radiocarbon Sample'[4]

In the last issue I reviewed a "short communication" to Thermochimica Acta by Marco Bella et al.[5], showing that Raymond Rogers's diagrams attempting to demonstrate different chemical structures of Raes sample threads and those of the main body of the cloth did not necessarily support his argument, and could simply be due to a minor hydrocarbon contaminant on the former. This paper has been challenged by Mario Latendresse[6], and the challenge responded to by Bella.[7]

The dispute arises from two spectrographs published by Ray Rogers, which bear looking at impartially before we get drawn in to the arguments. Rogers describes the origin of these diagrams thus:

"One of the analytical methods used during the STURP studies was pyrolysis mass spectrometry. The Midwest Center for Mass Spectrometry (MCMS) at the University of Nebraska, Lincoln, made

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[4] *'Studies on the Radiocarbon Sample from the Shroud of Turin'*, Raymond N. Rogers, Thermochimica Acta 425 (2005) 189-194

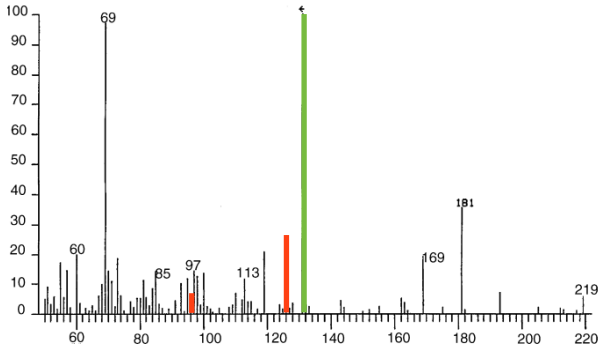
[5] *'There is no mass spectrometry evidence that the C14 sample from the Shroud of Turin comes from a 'Medieval Invisible Mending'*, Marco Bella et al., Thermochimica Acta 617 (2015) 169-171.

[6] *'Comments on the mass spectrometry analysis of a sample of the Shroud of Turin by Bella et al.'*, Mario Latendresse, Thermochimica Acta 624 (2016) 55-58.

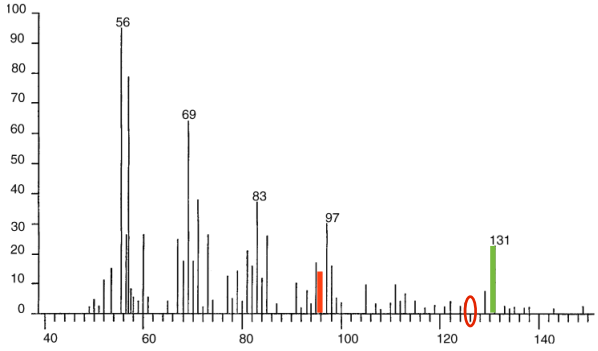
[7] *'Comments on the analysis interpretation by Rogers and Latendresse regarding samples coming from the Shroud of Turin'*, Marco Bella et al., Thermochimica Acta 632 (2016) 52-55.

dozens of scans on different samples in 1981. The chemical-ionization system used was the most sensitive MS at the time, sufficiently sensitive to detect parts-per-billion traces of oligomers from the polyethylene bag that Gonella had used to wrap the Raes threads. The instrument at MCMS is equipped with a pulsed source that has a time resolution of 100ns, and it produces a series of mass spectra as the sample heats up."

Here are Rogers's diagrams, at their original relative sizes. Note that they have different horizontal scales. The lines he draws attention to are those at mass 96 and mass 126, which I have highlighted in red (one, circled, has no line at all); and later mass 131, which I have highlighted in green.



from a main Shroud fibre (at least 260°C)

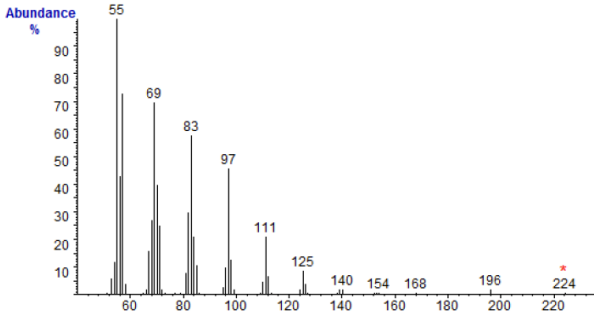


from a Raes sample fibre ('low temperature')

Rogers claims that the cellulose of which the Shroud is mainly composed breaks down at about 260°C to produce hydroxymethylfurfural (mass 126), which itself decomposes to produce furfural (mass 96), both of which are represented in the 'main Shroud fibre' diagram'. The Raes sample, however, produced furfural even at "low temperatures", before the cellulose began to decompose, as shown by the lack of signal at mass 126. Roger attributes this to the decomposition of a pentosan, a constituent of a plant gum, which he thinks coated the Raes sample, and which does not produce hydroxymethylfurfural but does produce furfural.

It has to be said that Rogers's use of these diagrams is very over-selective. Almost as an aside to this paper he comments that other STuRP spectrographs, of "blood spot" fibres, showed strong peaks at mass 131, suggesting hydroxyproline, which he thinks is a derivative of blood. While this could be supportive of the identification of the blood-spots as actual blood, he does not comment on why both the spectrographs above also show just such a peak, although neither is a blood-spot, and although Heller and Adler, in their exploration of the Shroud fibres, specifically excluded the possibility of animal protein anywhere else. Rogers also fails to comment on the very large peak at mass 69 on the main Shroud fibre diagram, which is very remiss, as it is surely significant, and not a characteristic of the decomposition of cellulose.

Marco Bella disputed that the Raes sample fibre spectrograph shows pentosan-derived furfural, and claimed that the peak at mass 96 was merely one of a series of peaks derived from a simple contaminant, "a molecule with a long hydrocarbon moiety". These decompose to produce a series of regularly spaced peaks, decreasing in intensity. Hexadecan-1-ol, for example, shows decreasing peaks at mass 55, 69, 83, 97, 111, 125 etc. as shown in the spectrograph over the page, taken from lipidlibrary.aocs.org, and quoted by Bella. Note that each peak emerges from a surrounding cluster of minor peaks.



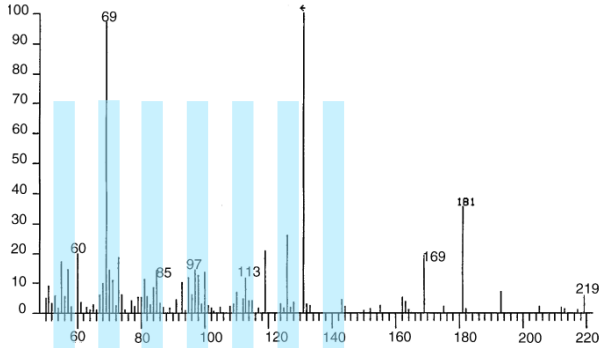
mass spectrograph of hexadecan-1-ol

It was Bella's contention that if the peaks attributable to a contaminant were removed from Rogers's Raes sample diagram, it would look much the same as the main Shroud diagram, and that the peak at mass 96 that Rogers identified as from a plant gum was actually an artifact of the contaminant.

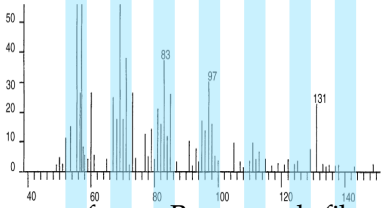
In fact, if the three diagrams are shown to the same horizontal scale, it can be seen that a series of similar clusters of peaks is present on all three spectrographs, although only the lower two show them very pronounced (see opposite).

Mario Latendresse felt that Bella had not proved his case at all, and attacked his communication on three, not always complementary, grounds.

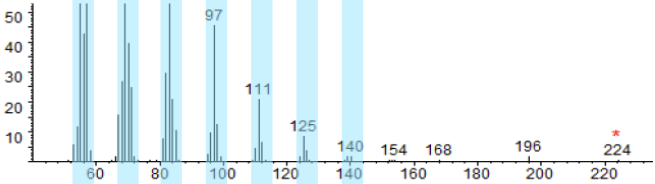
Firstly, he explained that Rogers's spectrographs were merely corroborative evidence for a conclusion already justified from microscopy, and not definitive in themselves. Secondly, he showed that, mathematically, the simple subtraction of the hexadecan-1-ol peaks from the Raes sample graph does not, in fact, give a result that closely resembles the main Shroud fibre diagram. And finally, he suggested that even if there were a contaminant present, it could as well be derived from human sweat, and therefore not unsurprising on the Raes sample.



from a main Shroud fibre (at least 260°C)



from a Raes sample fibre ('low temperature')



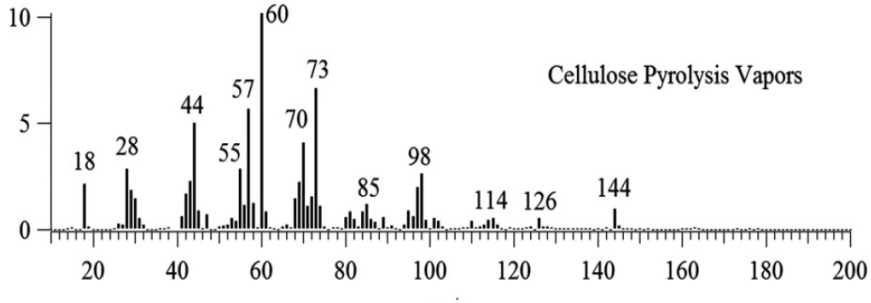
from hexadecan-1-ol

Unfortunately, Latendresse illustrated one of his arguments with an erroneous spectrograph for hexadecan-1-ol (that of trimethylsilyl hexadecan-1-ol), which spoilt his credibility, as the two are very dissimilar.

Marco Bella's reply pointed out that as Rogers gave very few details about the process by which his spectrographs were achieved, especially the range of temperatures involved, and as the material of the

Shroud may consist of, or at least contain, several compounds, all of whose pyrolysis breakdown products would be represented in one form or another, only general conclusions could be drawn, one of which was certainly the possibility of a contaminant, as Latendresse seems to have agreed by suggesting a derivative of sweat. Bella went on to suggest that any such contaminant would certainly have been removed from the C14 sample by the cleaning process (and thus would have had no effect on the date discovered), and that had it been present on the main body of the Shroud, the STuRP team's careful removal of the fibres from the sticky tape (which they describe as "laborious cleaning") would have removed it from there too. In short, Ray Rogers's spectrographs do not support, far less "prove" (his word), the presence of a plant-gum on the Raes fibres, calling into question the hypothesis that the radiocarbon sample was not part of the original Shroud.

The only well described mass spectrograph of cellulose that I can find comes from an academic paper by Calvin Mukarakate[8]. This is from the pyrolysis of 50mg of cellulose at 500°C for 35s.



It compares quite well with Rogers's main Shroud fibre spectrograph, although at this temperature almost all any hydroxymethylfurfural (mass 126) generated has decomposed, and the peak at mass 96 (furfural) is correspondingly larger. There is no huge peak at mass 69.

[8] *'Real-time monitoring of the deactivation of HZSM-5 during upgrading of pine pyrolysis vapors'*, Calvin Mukarakate et al., Green Chemistry, 2014, 16, 1444.