Thermochimica Acta 617 (2015) 169–171

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Short Communication

There is no mass spectrometry evidence that the C14 sample from the Shroud of Turin comes from a "medieval invisible mending"

Marco Bella[a,*], Luigi Garlaschelli[b], Roberto Samperi[a]

[a] Department of Chemistry, Sapienza University of Roma, P.le Aldo Moro 5, 00185 Roma, Italy
[b] Department of Chemistry, University of Pavia, Via Taramelli 10, 27100 Pavia, Italy

ARTICLE INFO

Article history:
Received 6 July 2015
Received in revised form 1 August 2015
Accepted 3 August 2015
Available online 28 August 2015

Keywords:
Mass spectrometry
Pseudoscience
Shroud of Turin

ABSTRACT

This is an editorial regarding a paper published on Thermochimica Acta (R.N. Rogers, Thermochimca Acta, 425 (2005) 189–194). A close-up analysis of the pyrolysis-mass spectra reported in the original paper reveals that the differences found between the samples coming from different parts of the Shroud are just due to the presence of a contaminant with a long aliphatic chain. Except for the presence of the contaminant, the two pyrolysis-mass spectra look alike rather than different. Therefore, the pseudoscientific theory stating that the C14 sample might come from a "medieval invisible mending" remains unsupported by evidences.

This editorial regards a paper by the late Dr. Raymond Rogers published on Thermochimica Acta [1]. The Shroud of Turin is a linen which has impressed a faint image of a man and some color spots (supposedly blood). A popular tradition born in the second half of the XIV century recognizes it as being the burial cloth of Jesus Christ. In 1988, three independent laboratories dated this object between 1260 and 1390 (95% confidence interval, 2σ) by means of the C14 analysis [2]. After the publication of these data, several theories have been proposed to explain a discrepancy with the "sought" date of the linen, which according to tradition should be around 33 AD. Among those, a popular one is the so called "invisible mending", disclosed by S. Benford and J. Marino and based on the analysis of low resolution (JPEG format) pictures of the Shroud [3]. According to these authors, the part of the Shroud from where a C14 sample was obtained does not belong to the main linen, but is a Middle Age addition which precisely matches the kind of weaving, and moreover has been painted to exactly match the color of the main Shroud. No one has hypothesized this before 1988 (before C14 analysis gave an "undesired" date for the linen); no textile experts who could examine the Shroud in person during the collection of the C14 sample reported any evidence of this late addition [2].

Thus, we read with great surprise the above-mentioned article [1], which, by means of mainly mass spectrometry analyses, concludes that the C14 sampling area might indeed be different from the rest of the cloth, giving credit to the theory known as the "invisible mending".

Although this can be debated, we will assume that all the samples that Rogers tested do come from the Shroud of Turin. He analyzed three kinds of samples:

a) 32 adhesive-tape samples from all areas of the Shroud and associated textiles taken in 1978.
b) Some samples of both warp and weft threads coming from the C14 sample (for which there is no evidence about their origin besides private correspondence), which were cut from the center of the C14 sample area and received by Rogers in 2003.
c) Some yarn fragments (14) coming from the "Raes sample", a piece of linen cut in 1973 to be examined by the textile expert Gilbert Raes, and which Rogers in an early publication did not report to be different to the main linen [4], but now he considers them to be part of the "medieval invisible mending".

The author performs some qualitative chemical testing on these samples. He tests for the presence of vanillin, giving insufficient details to enable the reproduction of this analysis besides observing a change of color. He could not detect any vanillin on the main Shroud but apparently he could detect "some" vanillin in the Raes sample (sample c). He analyzes the Raes sample (sample c) and C14 sample (sample b) with a microscope, supposedly identifying a pigment, alizarin, by means of its change of solubility by pH variations. His conclusion is "*The presence of alizarin dye and red lakes in the Raes and radiocarbon samples indicates that the color has been manipulated. Specifically, the color and distribution of the coating*

* Corresponding author.
E-mail address: Marco.Bella@uniroma1.it (M. Bella).

http://dx.doi.org/10.1016/j.tca.2015.08.002
0040-6031/

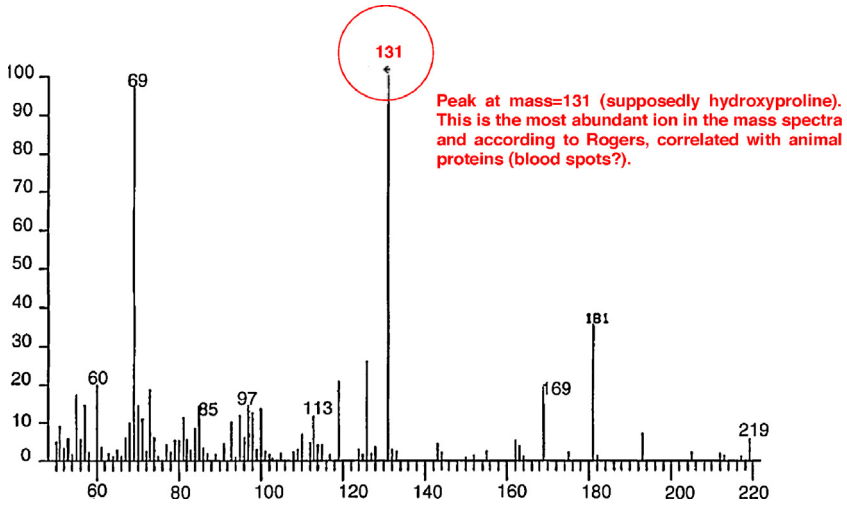

Fig. 1. Fig. 4 from the paper of Rogers: mass spectra obtained from the pyrolysis of a "Shroud-image fiber", (sample a), "Surely authentic Shroud sample".

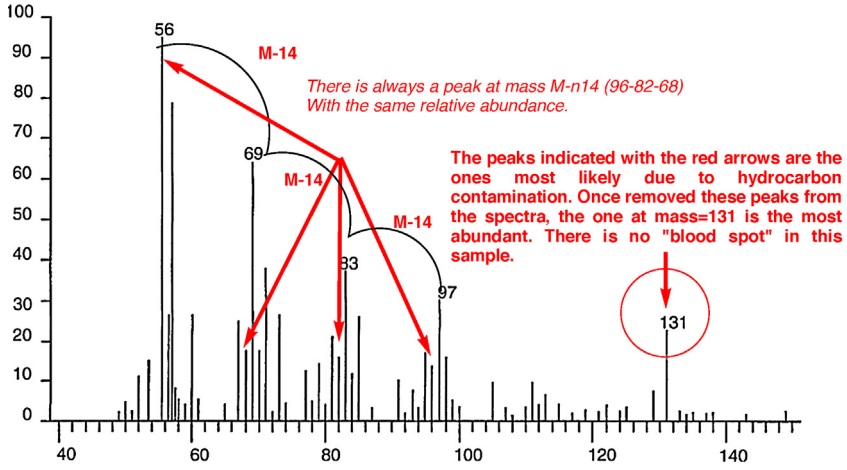

Fig. 2. Fig. 5 from the paper of R. Rogers: mass spectra obtained from the pyrolysis of a Raes sample-fiber (sample b, supposedly coming from the "invisible mending").

implies that repairs were made at an unknown time with foreign linen dyed to match the older original material." [1]. On the basis of solubility tests, Rogers hypothesizes the presence of pentosans rather than cellulose on the Raes samples (sample c).

According to the Author, however, the key evidence to support his thesis is the analysis of two pyrolysis spectra. The first (Fig. 1) is a mass spectrum obtained from the pyrolysis of a shroud-image fiber (sample a). He identifies the peak at mass = 131 as hydroxyproline, a hypothesized pyrolysis product of animal proteins, and hydroxymethylfurfural (mass = 126) a hypothesized pyrolysis product derived from cellulose. The intensity of the latter peak (less than 30%) does not differ significantly from the baseline noise and other unidentified peaks. The second is the mass spectra from the low-temperature pyrolysis of fibers coming from the Raes sample (sample b, see Figs. 2 and 3). He detects a signal at mass = 96 and could not detect the weak peak at mass = 126, concluding that the sample contains a significant amount of pentosan.

However, the mass spectra from the Raes sample (sample b, Fig. 2) shows the characteristic peak pattern derived from the fragmentation of a molecule with a long hydrocarbon moiety [5]. These peaks are so intense that they cover most of the other signals. The supposedly diagnostic peak at mass = 96 appears to be just one of the many peaks due to the contaminant. Furthermore, once the peaks of the contaminant are removed from the spectra, the major peak left is actually the one at mass = 131. Should that peak be

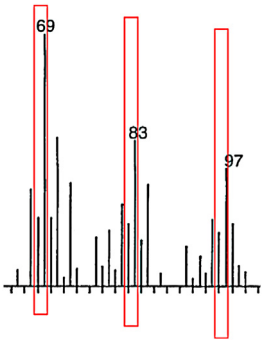

Fig. 3. Detail from Fig. 5 (Rogers paper) decomposition pattern of the contaminant with a long aliphatic chain: the peak at mass = 96 is likely to belong to the peak pattern of the contaminant rather than to another distinct molecule.

associated with the presence of animal proteins (from blood?), it should not be there where no image or blood stains are present. The different threshold level of the two spectra does not allow to confirm the absence of the peak at mass = 126, should that be of any relevance.

Therefore, the only significant difference between the two reported mass spectra is the presence of a hydrocarbon-derived contaminant in the second one. An example of a similar spectrum,

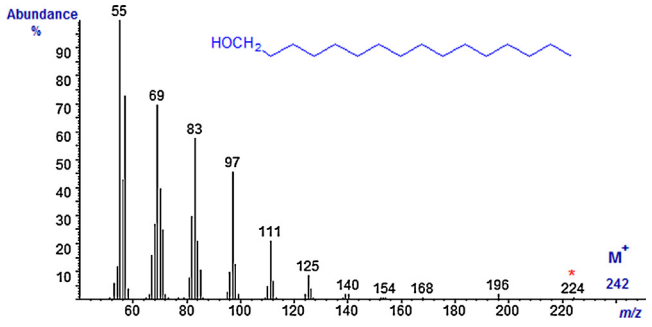

Fig. 4. Example of mass spectra from a molecule with a long aliphatic chain (exadecan-1-ol), which fragmentation pattern is similar to the contaminant presents in the Raes sample (sample b).

with analogous isotopic pattern, is reported in Fig. 4 [5]. In fact, once the "alien" peaks are removed, the two spectra look alike. This actually denies rather than confirms the hypothesis of Rogers.

In conclusion, the unspecific qualitative chemical tests presented by Rogers are in no way confirmed by instrumental analysis (mass spectrometry). No diagnostic peak in the pyrolysis mass spectra indicates a significant difference in the two samples, besides hydrocarbon-derived contamination. Therefore, none of the presented data supports the conclusion by Rogers.

The work of the late Dr. Rogers has been exploited to support a pseudoscientific hypothesis, which is in no way confirmed by the reported data. Regardless of the debate on the hypothetical authenticity of the Shroud, the scientific community and the general public can only be misled by this paper.

Acknowledgements

Authors thank Andrea Nicolotti and Gian Marco Rinaldi for a helpful discussion.

References

[1] R.N. Rogers, Thermochim. Acta 425 (2005) 189–194.
[2] P.E. Damon, D.J. Donahue, B.H. Gore, A.L. Hatheway, A.J.T. Jull, T.W. Linick, P.J. Sercel, L.J. Toolin, C.R. Bronk, E.T. Hall, R.E.M. Hedges, R. Housley, I.A. Law, C. Perry, G. Bonani, S. Trumbore, W. Woefli, J.C. Ambers, S.G.E. Bowman, M.N. Leese, M.S. Tite, Nature 337 (1989) 611–615.
[3] See references 8 and 9 of Roger's paper: (a) M.S. Benford, J.G. Marino, http://www.shroud.com/pdfs/textevid.pdf; (b) M.S. Benford, J.G. Marino, http://www.shroud.com/pdfs/histsupt.pdf
[4] L.A. Schwalbe, R.N. Rogers, Anal. Chim. Acta 135 (1982) 3–49.
[5] For several examples of hydrocarbons mass spectra see: http://lipidlibrary.aocs.org/ms/ms35/index.htm