



P.01-VS

VS-melted tendons



To:

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Subject:

Peptide mass fingerprint analysis of tendon and binding material from the panel painting “Martin Luther” by Lucas Cranach the elder, 1529, Museum zu Allerheiligen, Schaffhausen, Inv.Nr. A1950, destroyed by fire (World War II).

Background:

Previous peptide mass fingerprint (PMF)^{1,2,3,4} analysis of fibrous material from medieval wooden panel paintings identified cattle as the source of the material. The source of associated binding material was identified as sheep or mixed sheep/pig. See reports DBG05202016 and DBG08252016. PMF analysis was requested to identify materials from the Cranach panel painting. Wibke Ottweiler supplied samples and accompanying documentation.

Summary of results:

Original Sample ID	Sample Description	PMF Result
P.01-VS	CH_MAS_A1950, Lucas Cranach d. Ä., Martin Luther, <i>fire damaged</i> . <i>Fiber mass covering a panel joint, recto (front side).</i>	Cattle tendon
P.02.RS	CH_MAS_A1950, Lucas Cranach d. Ä., Martin Luther, <i>fire damaged</i> . <i>Fiber mass covering a panel joint, verso (backside).</i>	Cattle tendon
P.02.RS-BM	CH_MAS_A1950, Lucas Cranach d. Ä., Martin Luther, <i>fire damaged</i> . Binding media of P.02.RS.	Cattle tendon, sheep binder
VS-melted tendons	CH_MAS_A1950, Lucas Cranach d. Ä., Martin Luther, <i>fire damaged</i> . Sample of melted tendons from a burned region, recto (frontside).	Weak but consistent with cattle

Analysis:

PMF analysis involves the enzymatic digestion of proteins followed by Matrix Assisted Laser Desorption-Ionization Time of Flight mass spectrometric (MALDI) analysis of the resultant peptide mixture. In the case of skin, hide, tendon, bone and mammalian-based glues, collagen is the major constitutive protein, and for each mammalian source, the amino acid sequence of collagen is unique. Thus, the mixture of peptides is unique—a “peptide mass fingerprint.” Marker ions⁵ in the MALDI spectra from known reference materials are compared with those from unknown samples for identification. Sample locations and respective MALDI spectra are shown in figures 1-3 below.

A sample of melted tendon from a burned region was also analyzed to determine the possibility of PMF analysis for severely degraded materials. Albeit weak, the PMD data was consistent with cattle (not shown).

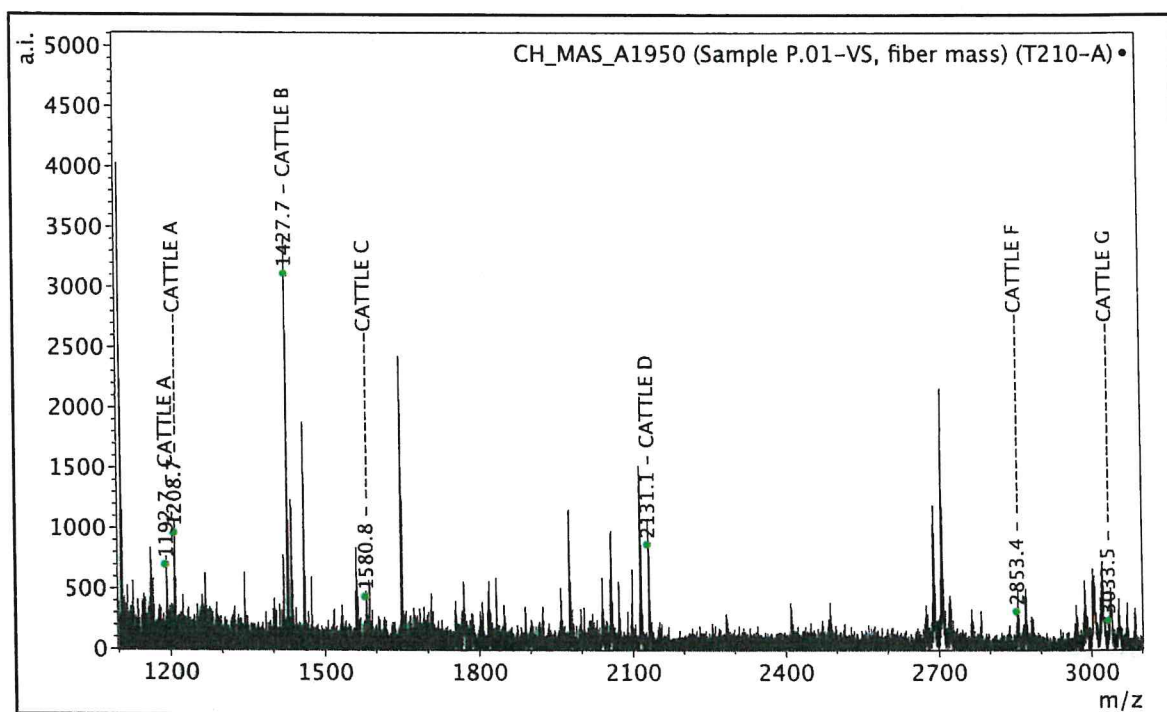
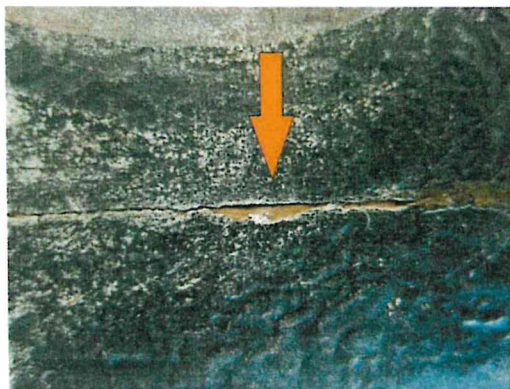


Figure 1. Sample P.01-VS Recto. Fiber mass covering a panel joint. CH_MAS_A1950, Lucas Cranach d. Ä., Martin Luther, fire damaged. MALDI (PMF) spectrum with cattle markers indicated.

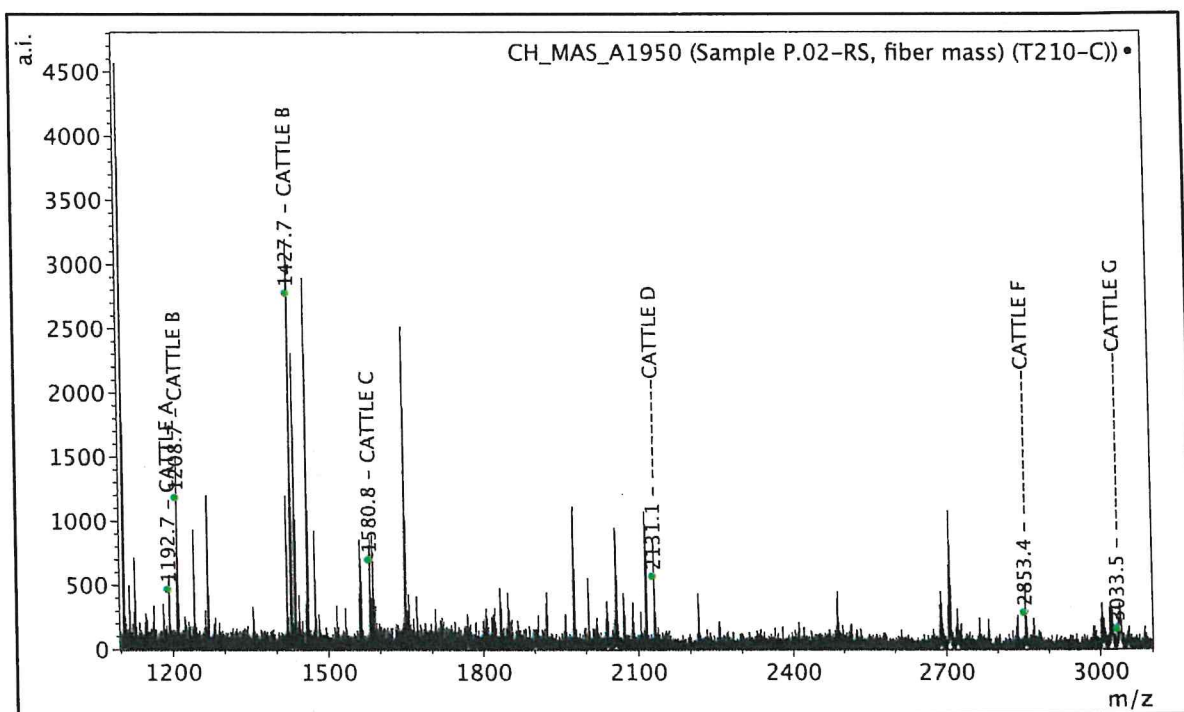
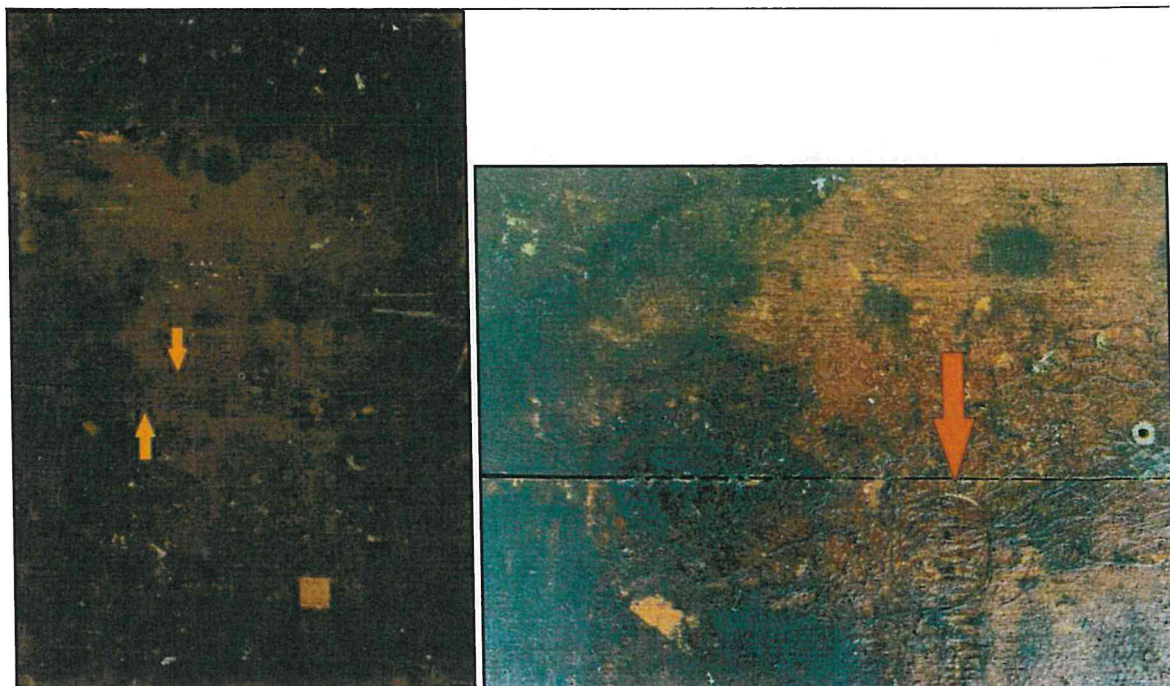


Figure 2. Sample P.02-RS Verso. Fiber mass covering a panel joint. CH_MAS_A1950, Lucas Cranach d. Ä., Martin Luther, fire damaged. MALDI (PMF) spectrum with cattle markers indicated.

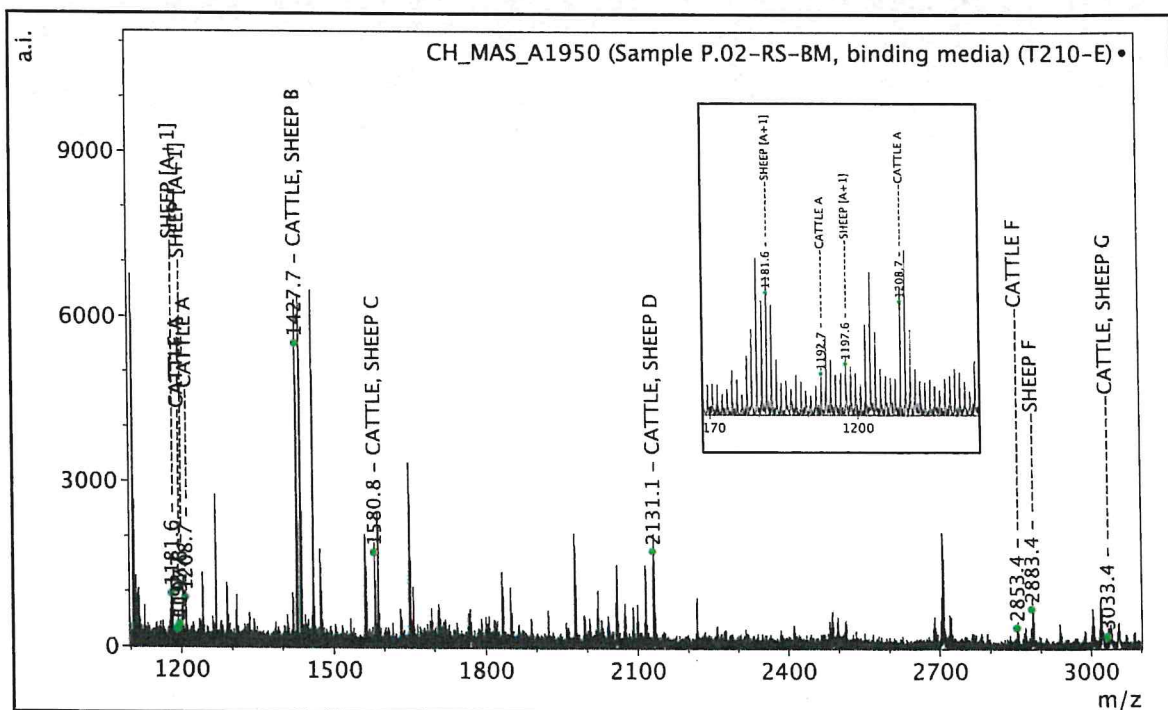
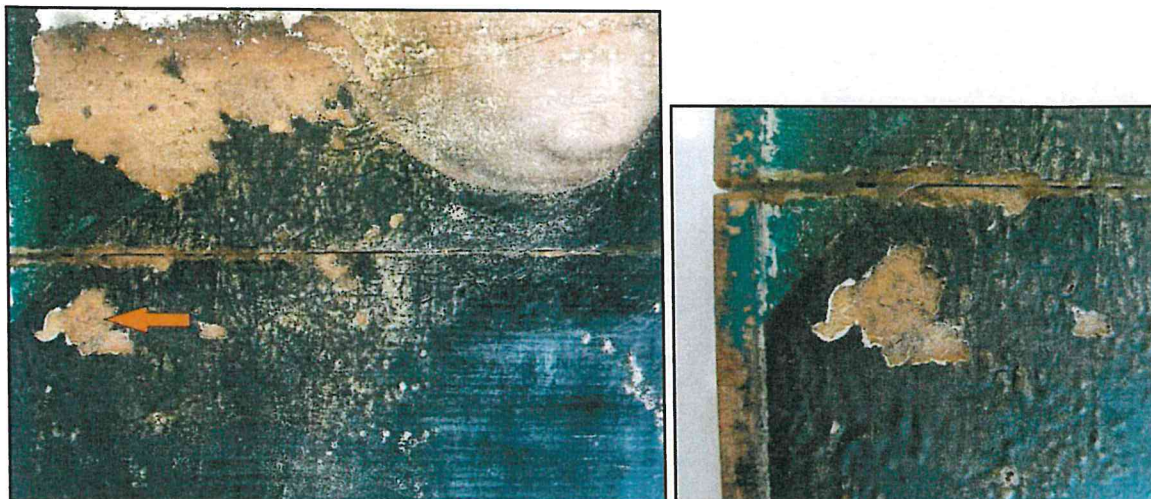


Figure 3. Binding media of P.02.RS. CH_MAS_A1950, Lucas Cranach d. Ä., Martin Luther, fire damaged. MALDI (PMF) spectrum with cattle and sheep markers indicated. The inset shows the A-markers used to differentiate cattle and sheep along with the F-markers in the main spectrum.

¹ Kirby, D. P., N. Khandekar, J. Arslanoglu and K. Sutherland, "Protein Identification in Artworks by Peptide Mass Fingerprinting," Preprints, ICOM-CC 16th Triennial Conference, Lisbon, Portugal, (September, 2011).

² Kirby, D., M. Buckley, E. Promise, S. Trauger and T. R. Holdcraft 2013, "Identification of collagen-based materials in cultural heritage," Analyst (138) 4849-4858.

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- ³ Promise, E., T. Rose Holdcraft, D. Kirby, and S. Haakanson, "Identifying collagen-based materials: A cross-cultural collaboration," Preprints, ICOM-CC 17th Triennial Conference, Melbourne, Australia (September, 2014).
- ⁴ Henzel, W. J., C. Watanabe and J. T. Stults 2003. "Protein identification: the origins of peptide mass fingerprinting," J. Am. Soc. Mass Spectrom. (14) 931-942.
- ⁵ M. Buckley and M. J. Collins, *Antiqua*, 2011, (1) 1-7.

