

# Decoding Biomolecules and their Networks in Artists' Materials using Layer-by-Layer High Resolution MALDI Imaging and CrossLinking Mass Spectrometry

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Recent technical advances in mass spectrometry (MS) have allowed the emergence of new methods to study ancient biomolecules constitutive of objects of cultural heritage. One major breakthrough is the reliable structural elucidation of proteins, oils and sugars using omics techniques. Spectacular progress has been made throughout the years reducing sample amounts and increasing the quality of output information, producing a deeper knowledge of the artwork and facilitating conservation or resolving treatment issues.

The biggest challenge faced today in heritage MS is the chemical decoding of the networks through the characterization of crosslinked biopolymers, their modifications, degradation and interaction with other components. The newest MS-driven methods such as top down proteomics and hydrogen deuterium exchange MS developed to address this challenge will be presented. We will discuss how their combined use contribute to explaining the molecular complexity of these networks and accessing the original, transformed or degraded forms of the biomolecules in their environment. Among the topics that will be discussed are the protein conformational changes and interactions with pigments that occur during paint manufacture, drying and ageing. Furthermore, several case studies will show how chemical signatures can distinguish a particular restoration procedure, focusing on induced chemical crosslinking.

Finally, the presentation will show how high resolution MALDI imaging can decode the biomolecular organization of paint layers by identifying and mapping both organic and inorganic compounds. We will demonstrate the suitability of the technique to detect intact materials, by-products and complexes within samples, at the surface, within the layers and at layer interfaces of artworks. The informative power of this technique applied for the first time to historic artworks will be illustrated by the study of several master pieces from the Metropolitan Museum of Art's collection