Identification of insoluble oil paint film structure after innovative soft chemical depolymerization and high resolution MALDI FTICR MS analysis. Application to Cultural Heritage and environment samples

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Oil paint binders are made from triacylglycerol of polyunsaturated fatty acids which crosslink by exposition to light and atmosphere by a mechanism named siccativation. Despite their wide use as binders in artworks for centuries; little is known about the structure of the 3D-crosslinked polymeric film of oil paints, and the mechanism of their siccativation is still under debate. Three oils were used: walnut, linseed and poppy oil which differ only by the number of unsaturations of their fatty acids. Until now there is no robust method to identify which oil was used from a painting sample, which is an important information for historians of arts and restorers.

To solve this problem, we developed a new methodology for the analysis of insoluble paint films starting by an innovative soft chemical depolymerization protocol which is a transamidation reaction using dimethylaminopropylamine (DMAPA) which breaks the ester bonds. This catalyst was selected also to improve the mass spectrometry ionization and to enhance the cleavage by participation. The resulting depolymerized paint films were then analyzed using MALDI ionization on an ultra-high resolution Fourier transform ion cyclotron resonance mass spectrometry (FTICR MS) 9.4 Tesla. In a first step, we made mock-up samples using different oils, pigments, driers and ageing conditions as temperature or UV exposure. We identified successfully the remaining traces polyunsaturated fatty acids of the original paint, their modifications induced by the siccativation process and the crosslinking dimers and oligomers. The products obtained were shown to be very dependent and characteristic of the initial oil. In a second step, this sensitive method was applied to museum size samples on painting from the XIX\textsuperscript{th} and XX\textsuperscript{th} centuries to identify the oil used by the artist according to the period but also to the pigments which bring the desired colour.

We will show that this methodology works for other polyester polymers such as alkyd paints which are formed of phthalic or isophthalic part, polyols and unsaturated fatty acids and polyethylene terephthalate after natural or accelerated ageing. For identifying the diols or polyols which are water soluble, we modified slightly the above protocol starting by a water-free transesterification with methanol and derivatization of the alcohols by benzyolation with dimethylaminobenzoyl chloride.