Metal soaps in paintings from the sixteenth to the twentieth century

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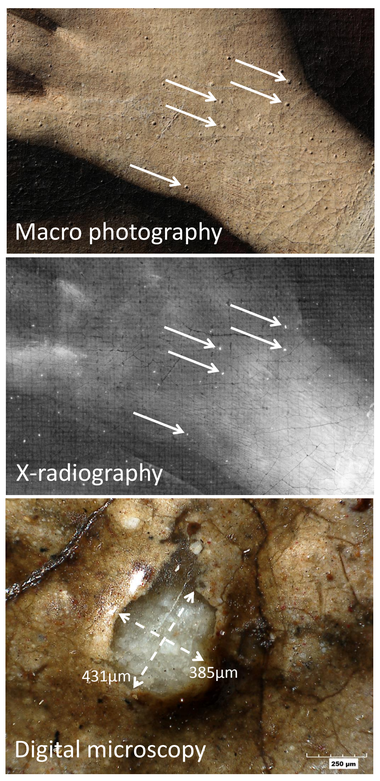
Introduction

The poster reports on the findings of metal soaps in four paintings from different time periods and/or regions. The metal soaps have been characterized using different imaging methods as well as analytical techniques. In three of the four paintings lead soaps were identified, in the fourth painting, zinc soaps were present. By documenting the metal soaps encountered in as much detail as possible, possible triggers for the formation of the soaps might be elucidated in the future .

Massimo Stanzione – Lead soaps

Massimo Stanzione (Italian, c.1586 – c.1656)
Mary Magdalene holding a skull
Private collection

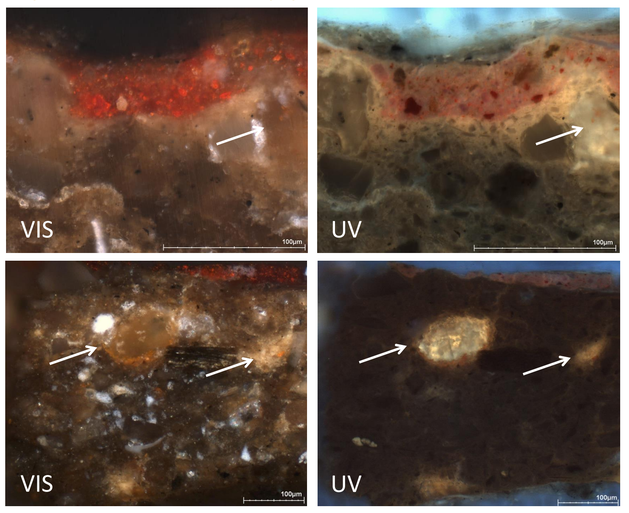
Scientific imagery



Using macro photography the metal soaps could be visualized. In the X-ray images the metal soaps appear as bright white spots, suggesting the presence of heavy elements, such as lead, in high concentration.
The digital microscope image shows a typical protrusion, as can be seen over the complete painting surface.

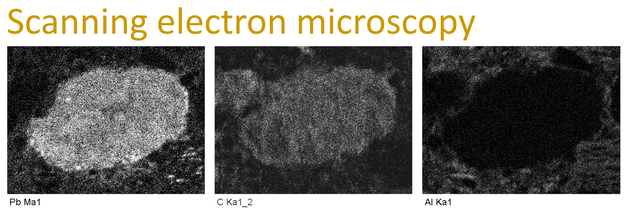
Microscopy on cross-sections

Optical microscopy



Cross-sections of samples from the red borders of the sleeve show a dark ground composed of mainly earth pigments, covered by a red paint layer composed of vermillion, red ochre, a red lake, smalt and chalk. Metal soaps find their origin in the dark ground, which is surprisingly poor in lead white. A few grains of minium can be seen, especially near the edges of the metal soaps.

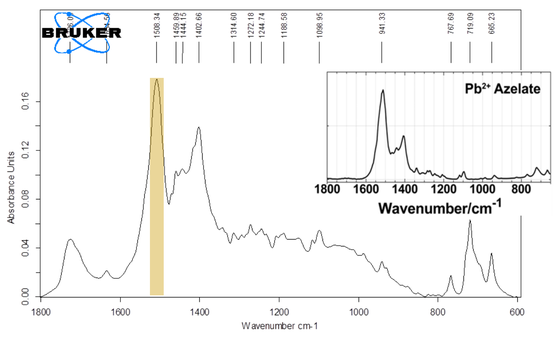
Scanning electron microscopy

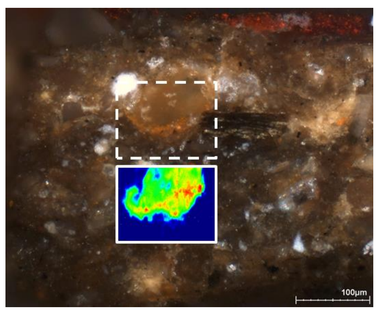


SEM-EDX mapping (Pb, C, Al) of a metal soap confirm the presence of lead.

(Imaging) ATR-FTIR

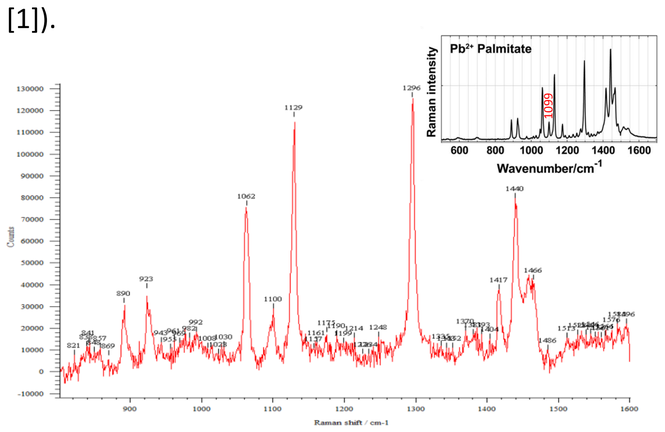
With attenuated total reflection – Fourier transform infrared spectroscopy (ATR-FTIR) the presence of lead soaps was confirmed as shown by the typical lead soap band at c.1508 cm^{-1} and comparison with a reference spectrum (inset; [1]). Imaging ATR-FTIR (integration of the characteristic band between 1583 -1475 cm^{-1}) reveals the lead soap distribution within the cross-section.





Raman spectroscopy

The Raman spectrum (785nm excitation) is characteristic for a lead soap. Based on a smaller band at 1100 cm^{-1}, the presence of lead palmitate is very likely, as seen in the reference spectrum (inset; [1]).



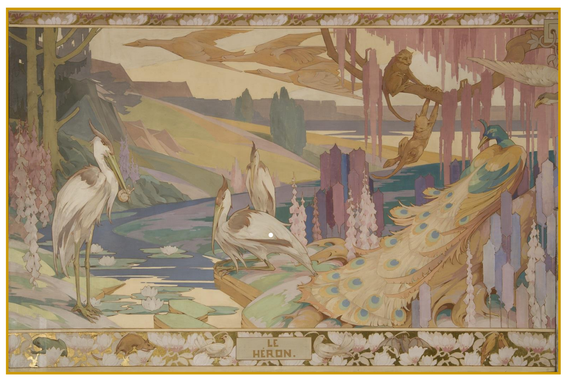
THM-Py-GCMS

Thermally assisted hydrolysis and methylation – pyrolysis – gas chromatography-mass spectrometry (THM-Py-GCMS) with 2.5% tetramethylammonium hydroxide (in methanol) of both the dark ground and a lead soap results in clear differences in proportions of (dicarboxylic) fatty acid, as can be seen in the table.

	P/S	Az/P	Az/Sub
Ground	1.05	0.11	5.02
Lead soap	1.69	1.05	4.62

These results suggest that the relative proportion of palmitic acid vs. stearic acid is higher in the lead soap than in the surrounding ground. Also the dicarboxylic acids seem to be enriched in the lead soap. Results should be interpreted with caution, since they are based on only one measurement of each sample.

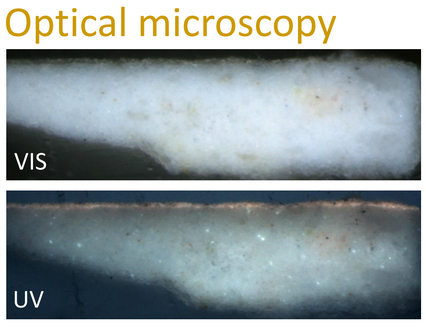
Camille Barthélemy – Zinc soaps



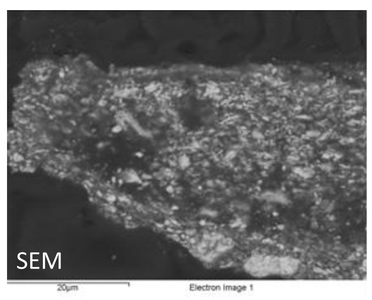
Camille Barthélemy (Belgian, 1890 - 1961)
The Fables of Jean de La Fontaine (detail)
Institut dentaire Georges Eastman, Brussels

Microscopy on cross sections

Optical microscopy

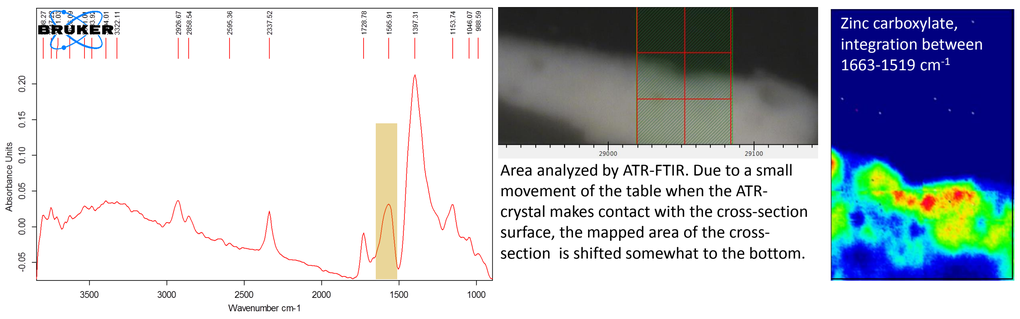


SEM-EDX



Some areas of the painting surface are glossy, while others are mat. A cross-section from a glossy area is shown, revealing a thin fluorescent layer on the surface. SEM-EDX measurements show low density areas in the white paint (rich in zinc white and lead white).

(Imaging) ATR-FTIR

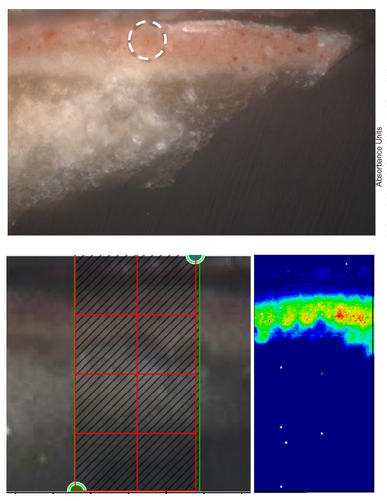


ATR-FTIR analyses on the cross-section reveal the presence of an amorphous zinc carboxylate, characterized by a broad band at c. 1575-1566 cm^{-1} [2]. Integration of this band between 1663 and 1519 cm^{-1} shows the distribution of the zinc carboxylate in the cross-section. The thin layer on the surface does not seem rich in zinc carboxylates. Its identification remains unclear.

Lambert Lombard – Lead soaps

Lambert Lombard (Southern Netherlands, 1505/06-1566), *The Refusal of Joachim's Offering* (reverse side), Musée de l'Art wallon

(Imaging) ATR-FTIR



(Imaging) ATR-FTIR identified lead soaps evenly distributed throughout the reddish top layer, which is composed of red earth and lead white. The dashed circle on the cross-section indicates a lead soap with a transparent halo and minium in the center.

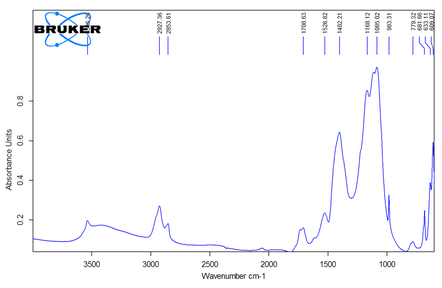
Pieter Brueghel the Younger – Lead soaps

Pieter Brueghel II (Southern Netherlands, 1564/65-1637/38), *Wedding dance,* Private collection

Protrusions can be seen over the whole painting surface. These are identified with FTIR as lead soaps.

Macro photography

FTIR



References:

[1] V. Otero *et al.*, *Characterization of metal carboxylates by Raman and infrared spectroscopy in works of art*, J. Raman Spectrosc. **2014**, *45*, 1197-1206

[2] J.J. Hermans *et al.*, *An infrared spectroscopic study of the nature of zinc carboxylates in oil paintings*, J. Anal. At. Spectrom. **2015**, 1600-1608