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Chemical characterization of painting layers by means of electron and FT-IR microscopy

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In the reported study paint and preparation layers of a copy of “The rape of Europe” of Paolo Veronese, which is currently being restored at Croatian Conservation Institute, were studied. The suitability of two different analytical techniques, both rapid and requiring a very little amount of sample, was investigated.

Microscopic samples were taken from the painting which original size had been increased by adding a piece of canvas on the right side. Moreover, unlike the original painting, the sine of Europe was covered with a white drapery. The aim of the study was to help dating the artifact, to determine the presence of any remakes as well as to determine when the canvas was enlarged and which materials have been used in the repainting as in the original part.

Samples were embedded in polyester resin and the obtained cross-sections were analyzed with different microscopic techniques. First of all the sections were observed by optical microscope in order to determine the number of layers, their thickness and color. The composition of the pigments was determined by SEM/EDS using a Quanta FEG 250 FEI and IR spectrum of each layer was acquired using a Bruker Tensor 27 FTIR spectrometer coupled with infrared microscope Hyperion 1000 fitted with a MCT detector and a micro ATR objective in Ge crystal. The results obtained with both techniques have been compared in order to confirm the findings.

Micro FT-IR analyzes showed that both the original canvas and the subsequently added part were prepared with a ground preparation made of gypsum and animal glue and that above this layer a white colored imprimature was applied, composed by a mixture of white lead and barium sulfate. Above the layer of imprimature pigments were applied. All collected spectra of the paint layers shown characteristic peaks due to the presence of oil (particularly well visible C-H and C=O stretching bands at $3800-3000\text{ cm}^{-1}$ at $1730-1750\text{ cm}^{-1}$ respectively) which indicate the nature of the binder. The structure of the painting's layers in the added part of the canvas was practically the same as the one found in the original piece. The ground, the imprimature, the binder and the pigments had the same composition. In both canvas parts pigments have been mixed with white lead before being laid on the canvas. The only difference was observed in the imprimature; optical microscope analysis has shown that the one in the original canvas contained black small particles of carbonized wood that gave it a grayish tone. The imprimature on the added part of canvas has the same composition as the original but did not contain those particles, which indicates that the piece of canvas was added and painted at a later time. It can be assumed that the canvas has been enlarged in order to adapt the size of the painting to the new frame or site of exposure.

The cross-section analyzes have proved the first assumption that the sine of Europe has been overpainted at a later time. The microscope image clearly shown a pinkish layer covered by a thin white layer, which indicates that the painting was primarily identical as the original Veronese's one. SEM/EDS as the μ FT-IR analyzes have shown that this repainting was done using white lead.

The composition investigations have shown that the repainting on the Europe's sine, as well as the paint layers on the added canvas, were made with the same pigments used in the original part, which indicates how all the remakes were probably made by the same hand or workshop and in a relatively short period of time. By the identification of the pigments and the determination of the composition of the imprimature (prussian blue used for the sky and barium sulfate crystals present in the imprimature) it was possible to narrow the dating frame, at first carried out on the basis of style, to the end of the 18th to the first half of the 19th century.

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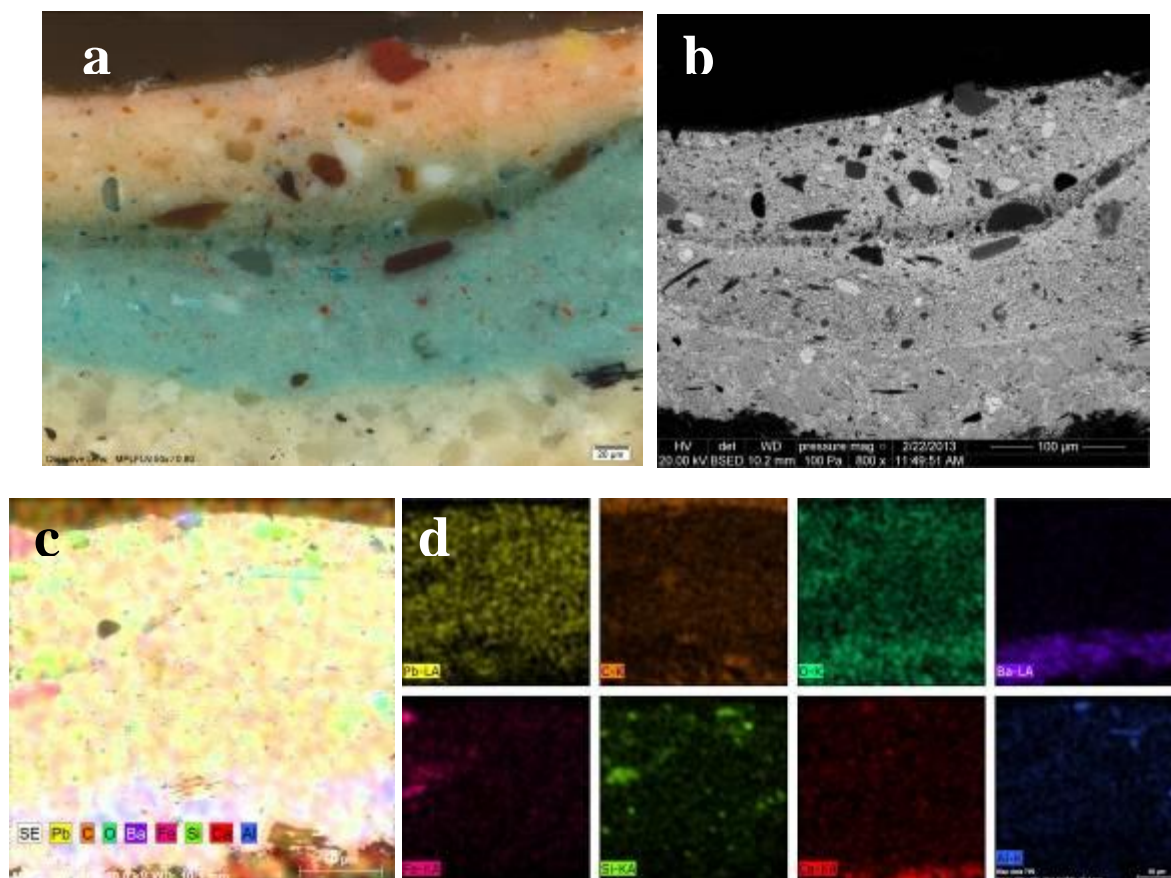


Figure 1. Sample 4; **a.)** optical microscopic image; **b.)** BSE SEM image; **c.)** EDS map; **d.)** EDS maps of singular detected elements.

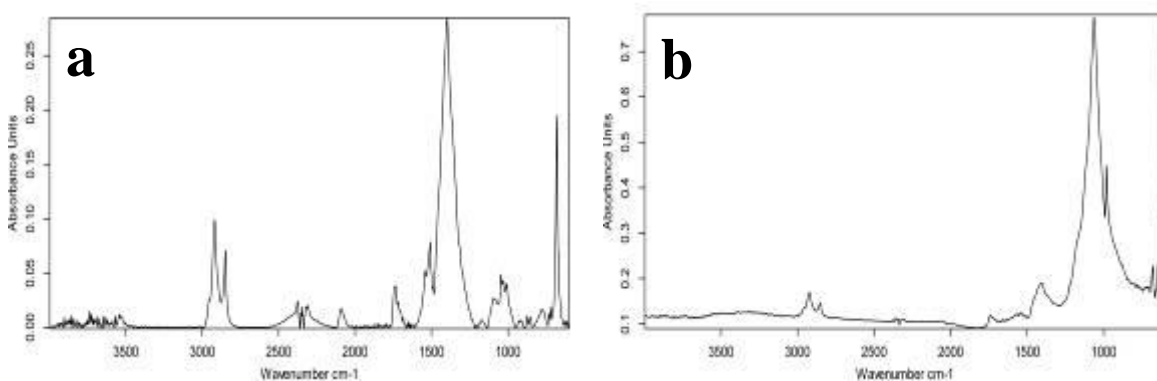


Figure 2. **a** μFT-IR spectrum of the blue pigment (white lead, prussian blue, ultramarine blue, oleic binder); **b** μFT-IR spectrum of the imprimatura (barium sulfate, oleic binder).