Application note

Analysis of a Tintoretto stratigraphy with micro-FTIR spectroscopy

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Introduction

In this application note, a painting sample (stratigraphy) of Tintoretto's work at the Scuola Grande di San Rocco (Venice, Italy) was analyzed in order to verify the composition of its five pictorial layers. Specifically, the analysis sought to determine if:

- The top of layer (1) contained oil as a binder
- The intermediate layer (2) has tempera grassa (a mixture of protein and oil) as a binder, and what pigments it contains
- The greenish layer (3) is the result of mixing malachite and earth pigments
- The earth pigments in the ground/preparation layer (4) are mixed with biacca or cerussite, and if proteins are present as the main binder

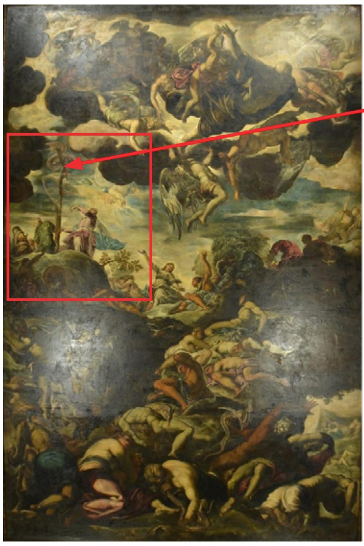
Fourier transform infrared (FTIR) spectroscopy has long been utilized in art restoration to investigate stratigraphy structure, specifically to identify binders, pigments, and other materials used in the preparation layers. Thanks to the availability of spectral libraries, it is possible to easily identify all the spectra acquired.

Sample

The stratigraphy sample, kindly provided by Dr. Eleonora Balliana, was taken from the ceiling of the Scuola Grande di San Rocco in Venice (Figure 1). Ten years after the completion of the Sala dell'Albergo, between 1576 and 1577, Tintoretto completed the large canvases in the Sala Capitolare. The decorative cycle focuses on scenes from the Old and New Testament. The ceiling analyzed in this application note in particular shows three main moments of the Jewish people's journey to the Promised Land.

Figure 1. Sala Capitolare of the Scuola Grande di San Rocco in Venice.

The sample is a purple veil fragment collected from the glaze used to coat a depiction of a snake (Figure 2).



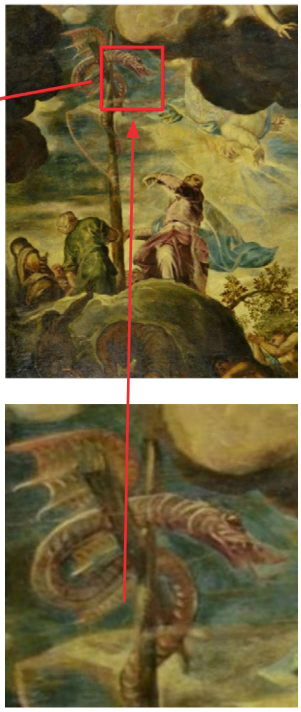


Figure 2. Close up of the painting region sampled for this application note.

Sample preparation

The painting sample was embedded in resin in order to obtain the stratigraphy along with visible, ultraviolet (UV), and scanning electron microscopy energy dispersive spectroscopy (SEM-EDS) images. The sample consists of four well-defined layers and a sketched fifth layer containing many small inclusions.

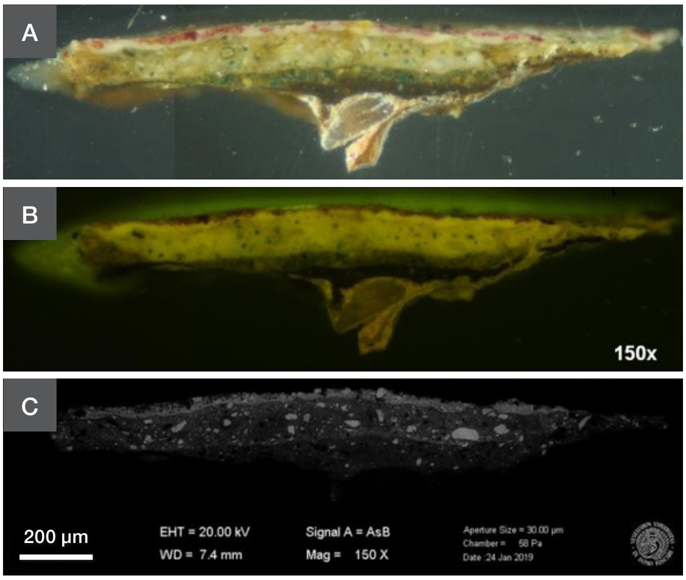


Figure 3. Cross section of the painting sample embedded in resin, shown with visible, UV, and SEM-EDS imaging (A to C).

This sample exemplifies Tintoretto's pictorial technique, where thin layers are applied on top of each other. The presence of a dark ground layer (4) is also typical for Tintoretto; it is used to create shadows and facilitate the application of the surrounding areas. Layers 2 and 3 are expected to consist of pictorial drafting of the snake's body, which was then detailed through the application of a purple glaze (1) mixed with other materials.

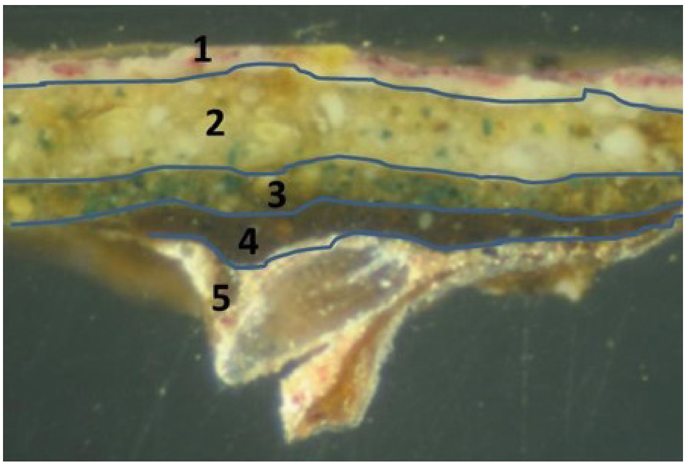


Figure 4. Close up of the painting sample showing its pictorial layers.

Analysis

The sample was analyzed using a Thermo Scientific™ Nicolet™ RaptIR™ FTIR Microscope, which offers precision and agility for streamlined sample analysis, producing rapid, actionable results. It can often be a lengthy and difficult process to pinpoint the intricacies of a sample and find the answer you need. Any amount of time savings can make a world of difference in delivering prompt, actionable results. The research-grade Nicolet RaptIR Microscope is not just suitable for users of all experience levels, but also for numerous disciplines. The objectives, infrared capability, and clear images are useful in a diverse range of fields including pharmaceuticals, environmental research, forensics, art restoration, as well as polymers and materials research.

Figure 5. The Thermo Scientific Nicolet RaptIR FTIR Microscope with a Nicolet iS50 FTIR Spectrometer.

Methods

First, a visual mosaic was collected using the 4x objective, followed by a visual and IR mosaic using the 15x objective. The resulting spectral resolution was 8 cm^{-1} with a 1 second acquisition time for each spectrum.

Multiple maps mode

Spectra were acquired in ATR mode using a germanium crystal with pressure control in order to avoid damaging the sample.

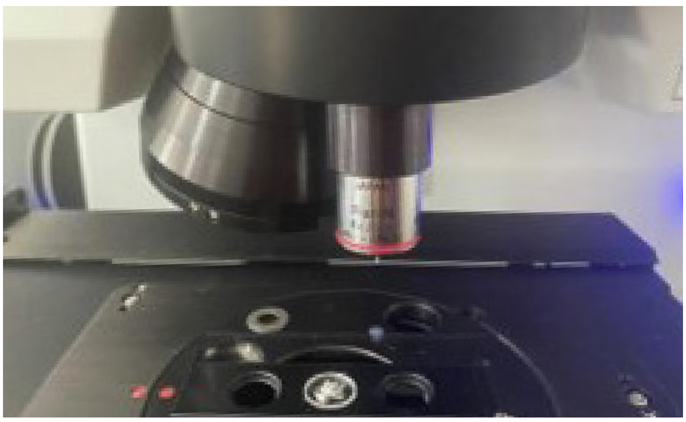


Figure 6. The 4x and 15x objectives of the Nicolet RaptIR FTIR Microscope.

Results

The 4x visual mosaic provided a picture of the regions within the stratigraphy; the subsequent 15x visual mosaic provided greater detail for each region of the sample.

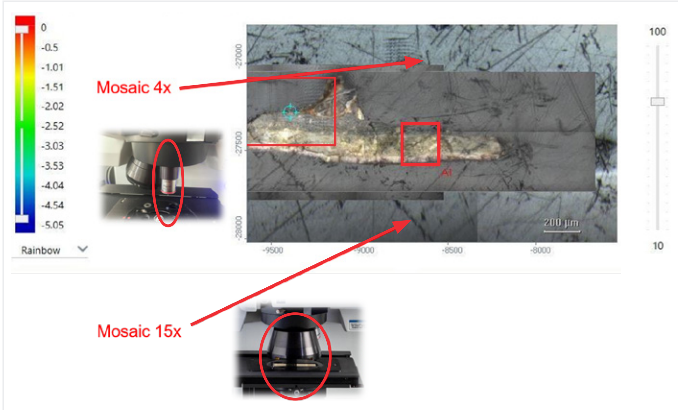


Figure 7. 4x and 15x maps and objectives.

Multiple maps were acquired in ATR mode to obtain more information from different regions of the sample (Figure 8).

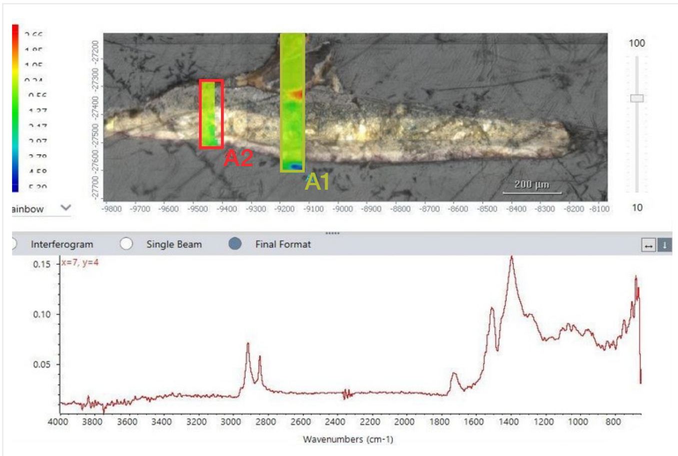


Figure 8. 15x mosaic, maps, and a real-time spectrum. An in-progress correlation with organic substances is boxed in red. A1 shows a map that has already been acquired, A2 shows the active acquisition. The corresponding spectrum is shown in real time.

Correlation maps were created using the correlation function of Thermo Scientific™ OMNIC™ Paradigm Software in order to evaluate the presence of the different materials.

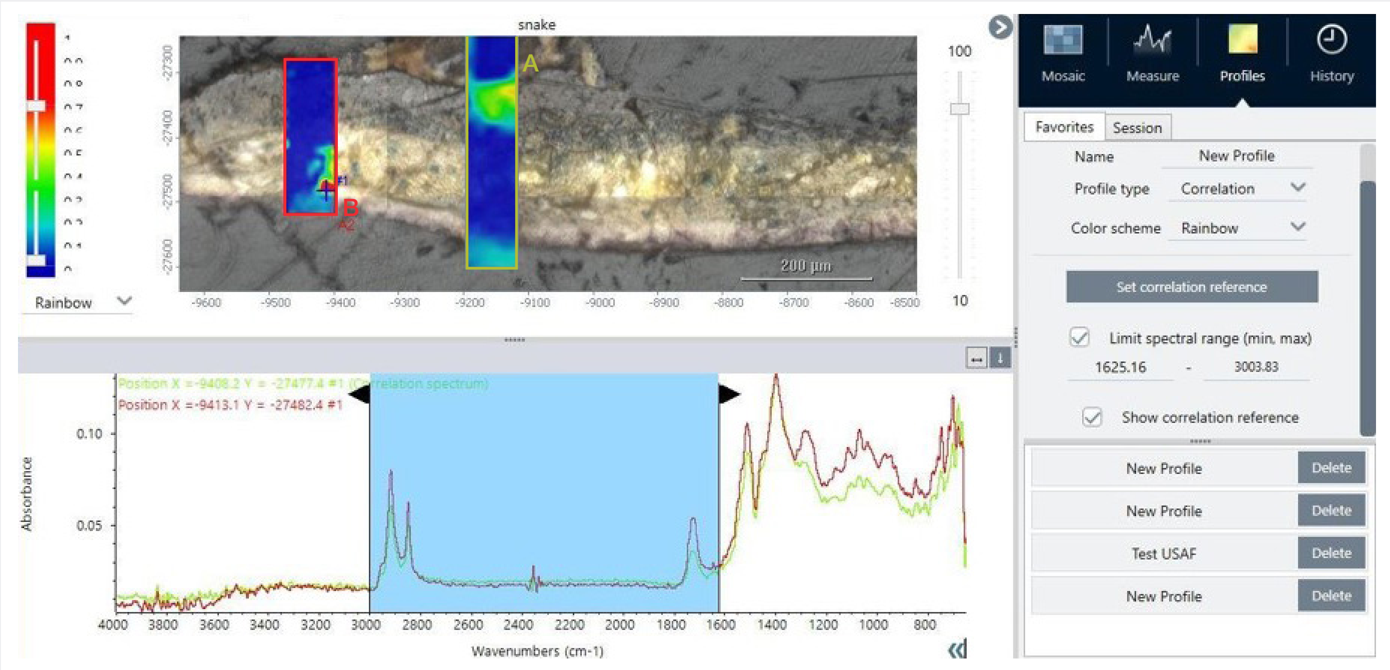


Figure 9. Oil correlation maps. Labels A and B indicate regions where oils are present. A corresponds to the upper pictorial film (1) and B corresponds to the preparation layer (4).

Oil correlation maps

Using OMNIC Paradigm Software, it is possible to correlate all the spectra acquired in the mosaic with the characteristic bands of natural oils, as seen in Figure 9. The results (marked A and B) indicated the presence of a lipidic binder, most likely linseed oil, which was detected not only in the upper pictorial film (1) but also in the preparation layer (4). There are also signals that are linked to the presence of proteins, silicate, etc. This was expected, as the use of oil and protein mixtures is typical for Tintoretto.

Protein correlation maps

The presence of protein (likely animal glue) was found in the ground/preparation layer, close to the canvas (Figure 10). Animal glue was commonly mixed with white lead or earth pigments by Tintoretto to create an ideal optical layer and drastically reduce the absorptivity of the canvas. Signals associated mainly with gypsum and lead carbonate are also visible.

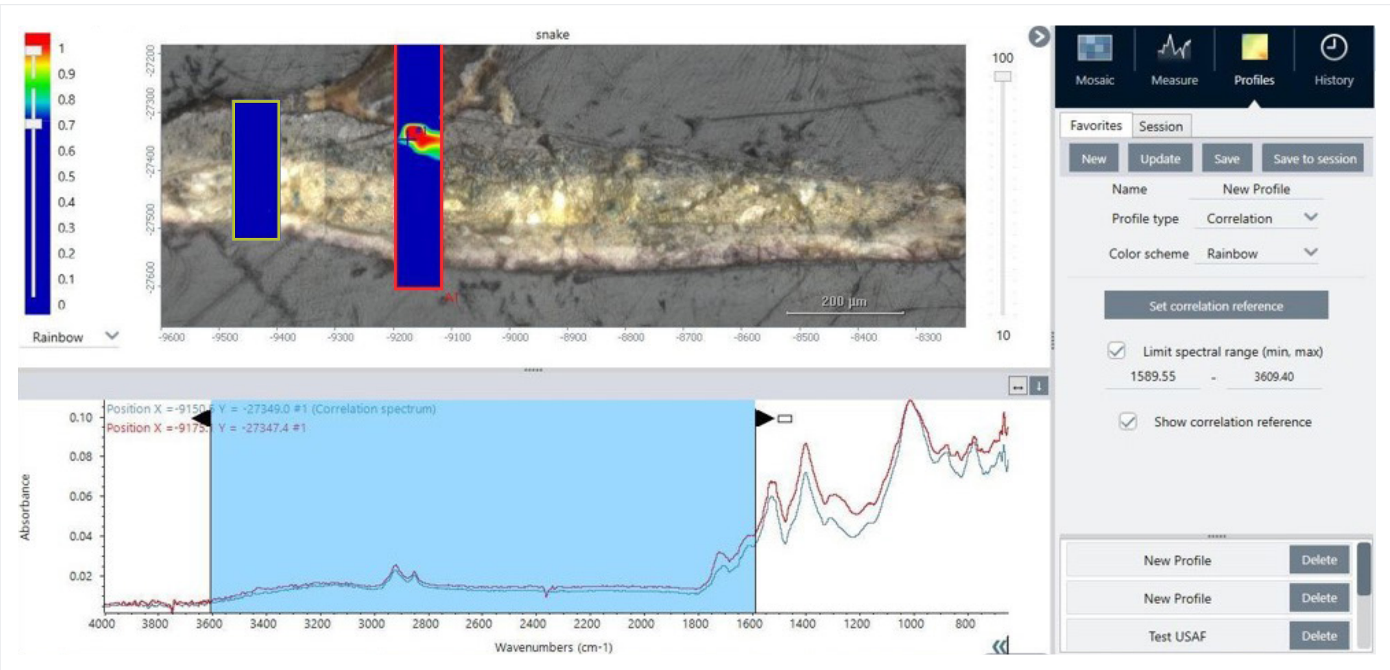


Figure 10. Protein correlation map, with a heatmap showing the presence of proteins.

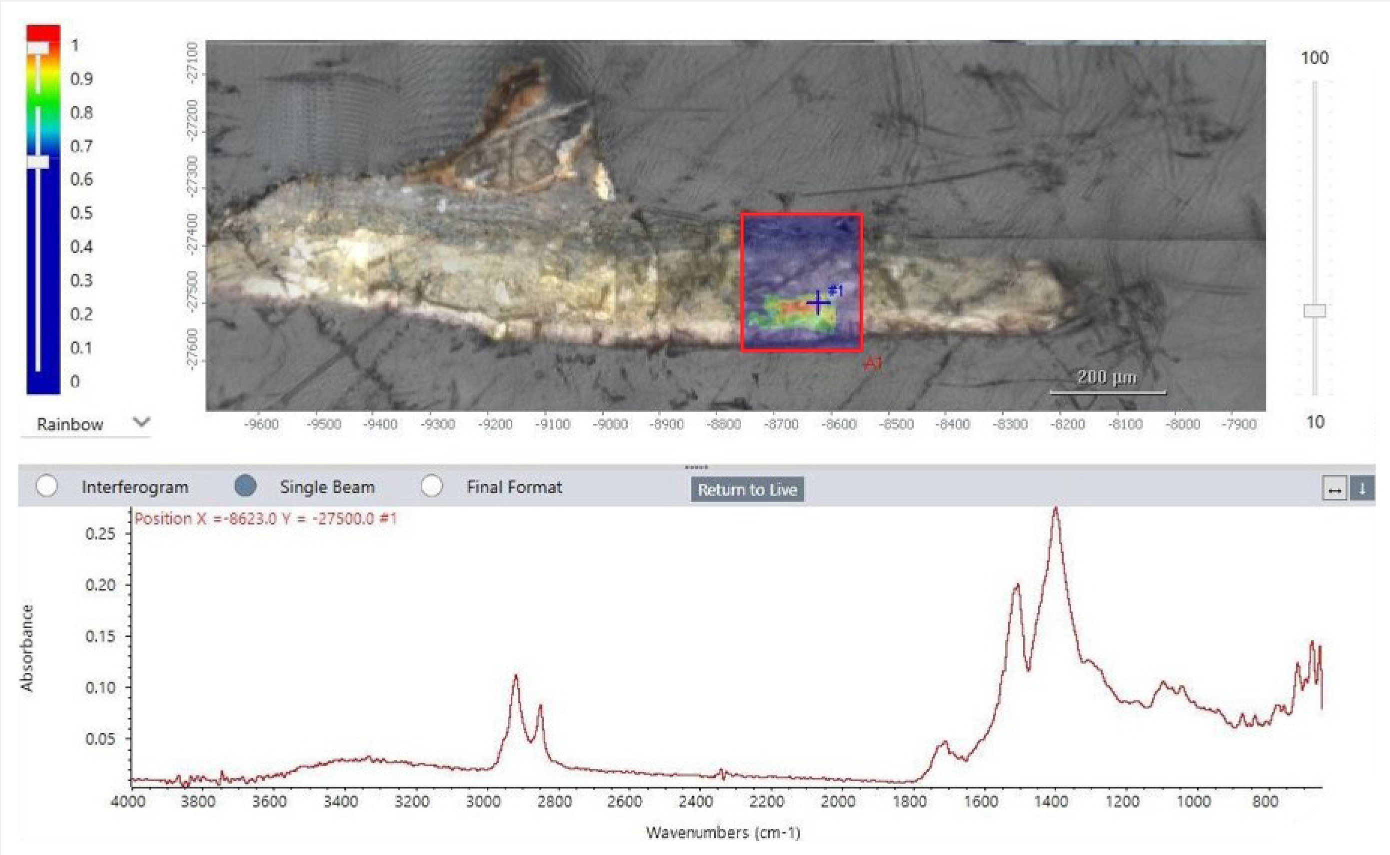


Figure 11. Oil correlation map including ATR data. The heatmap in the red box indicates where oils are present.

Oil correlation map including ATR

Figure 11 shows the presence of oil in the pictorial film. The use of oil allowed Tintoretto to easily spread paint, resulting in more vibrant colors, especially when using lacquers or pigments made of precious materials.

Spectra acquired in the regions containing protein also showed signs of other components such as pigments and oils. Using the multicomponent search function in OMNIC Paradigm Software, it was possible to easily identify all of these additional compounds without the need for any further data collection.

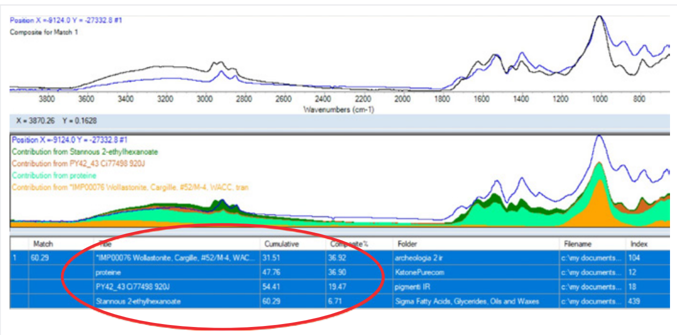


Figure 12. Multicomponent search function in OMNIC Paradigm Software.

Azurite correlation map

The correlation map in Figure 13 shows the presence of azurite, which was corroborated by copper signal in the SEM-EDS analysis. Tintoretto reserved the use of important and expensive pigments for the decoration of small parts. To vary the intensity of the composition, he played with the size of the pigment grains as well as the application of thin pictorial layers to create vibrant textures.

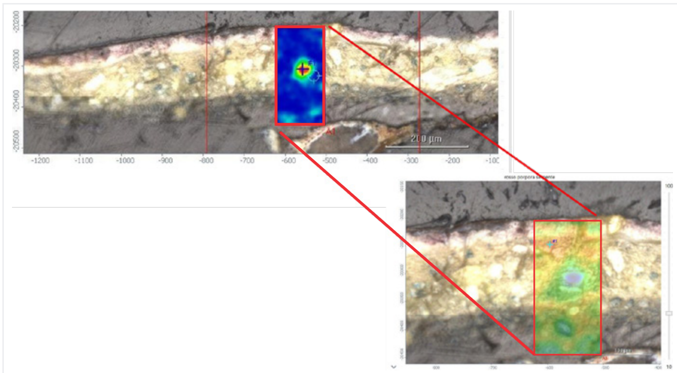


Figure 13. 15x visual map with an overlaid azurite correlation map. The close up clearly shows an azurite grain.

Magnesite correlation map

Correlation maps, corroborated by SEM-EDS analysis, identified the presence of magnesite, which was used as filler to produce vibrant surfaces and reduce the use of precious pigments.

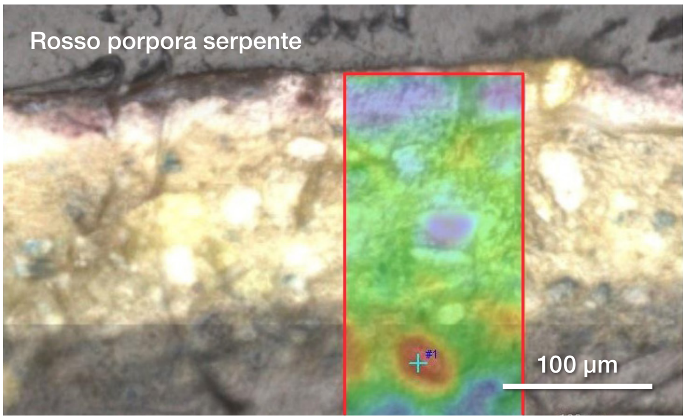


Figure 14. 15x visual map with an overlaid magnesite correlation map; magnesite grains can clearly be seen.

Malachite correlation map

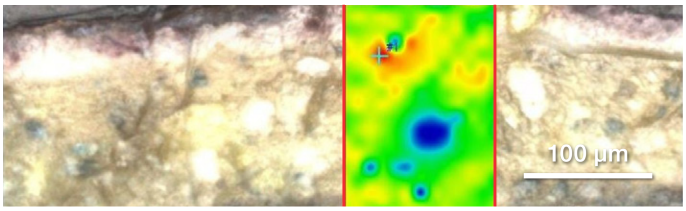


Figure 15. 15x visual map with an overlaid malachite correlation map.

Carbonate correlation map

As identified in the correlation maps, carbonates appeared mainly in the preparation layer. The presence of cerussite is common in all layers and was likely added not only for optical reasons, but also to facilitate and speed up the drying process of the pictorial film.

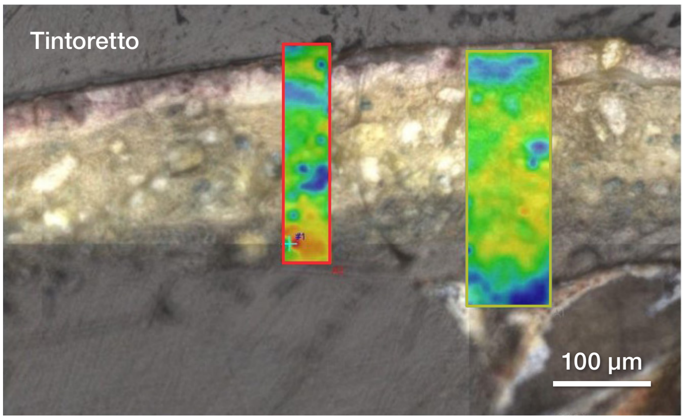


Figure 16. 15x visual map with overlaid carbonate correlation maps.

Conclusions

All materials that were expected to be found in the paint sample were successfully identified using the Nicolet RaptIR FTIR Microscope, combined with the multicomponent search function of OMNIC Paradigm Software. Overall, the following materials and their locations were identified:

- Linseed oil, not only in the upper pictorial film, but also in the preparation layer
- Proteins in animal glue, which are commonly mixed with white lead or earth pigments
- Azurite
- Magnesite
- Malachite
- Calcium and magnesium carbonates

These results were corroborated with SEM-EDS. Overall, this application note demonstrates the versatility and utility of micro-FTIR spectroscopy in the analysis of painting sample cross sections.

References

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