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A. Vichi[a], A. Artesani[b], C. S. Cheung[a], A. Piccirillo[c], D. Comelli[b], G. Valentini[b], T. Poli[d], A. Nevin[e], P. Croveri[d,c], H. Liang*[a]

[a]School of Science & Technology, Nottingham Trent University, Nottingham NG11 8BS, UK;

[b] Center for Cultural Heritage Technology (CCHT), Istituto Italiano di Tecnologia (IIT), Via della Libertà 12 - Venezia Marghera, IT;

[c]Fondazione Centro Conservazione e Restauro dei Beni Culturali La Venaria Reale, 10078 Venaria Reale, Torino, IT;

[d]Università degli Studi di Torino, Torino, IT;

[e]CNR-IFN, Istituto di Fotonica e Nanotecnologie, 20133 Milano, IT

*Haida.Liang@ntu.ac.uk

ABSTRACT

The formation and growth of metal soaps is of interest in heritage science, as soaps have been linked to a range of alteration and degradation phenomena potentially affecting works of art. However, current approaches detect metal soaps mainly in an invasive way or only at a late formation stage when the metal soaps are formed on the surface of the artwork. In contrast, Optical Coherence Tomography (OCT) has been proven to be a very suitable tool to obtain subsurface morphological information of complex multi-layered systems, such as paintings, in a non-invasive way. In this work, the capability of detecting metal soaps with an 810 nm ultra-high resolution (UHR) OCT in a selection of real and mock-up samples has been explored with OCT virtual cross-section images complemented with invasive structural and chemical analysis (SEM-EDX and ATR-FTIR spectroscopy and imaging). Although the visualization of metal soaps with OCT was evident in some samples, we also show that this is not always the case. In addition, the results of this work show that extra care is needed when interpreting OCT cross-section images to avoid the risk of misinterpreting features present in the paint stratigraphy.

Keywords: Metal soaps, paintings, OCT, non-invasive analysis, ATR-FTIR spectroscopy

1. INTRODUCTION

Amongst many deterioration phenomena, the origin of degradation products in paintings is widely investigated as they can either derive from intrinsic reactions or can be induced by external agents[1]. One of the most serious deterioration processes comes directly from the reactions between the lipid fraction in the binding medium (e.g. oil or egg tempera in paintings), and the inorganic (metal carbonate-based) pigment dispersed in it. This type of product is known as metal soap[2,3]. The presence of metal soaps has been recognized in the formation of protrusion or crater-like holes at the oil painting surface[4,5,6]. Metal soaps originate from the agglomeration of crystalline metal carboxylates that form after metal ion leaching from pigment particles into the binding medium. The first interaction process in paint film takes place at the organic-inorganic interface, as the fatty acids (R-COOH) present in the binding medium bind to the polar surface of pigment particles[7,8]. Although this adsorption initially guarantees a good dispersion of the pigment in the polymeric film, a rapid consequence of pigment particle functionalization is the release of metal ions, which remain attached to the fatty acids head and are leached in the binding medium. In this way, the pigment is dissolved and the binding medium becomes rich in metal carboxylate (R-COOM) structures that comprises both covalent and ionic bonds and has thus been referred to as an ionomer network[9]. The aggregation of the ionomer network initially assumes an amorphous structure[5,10]. The final step of this inorganic-organic evolution is the formation of crystalline structures which can grow up to hundreds of micrometers and can be easily recognized with an optical microscope[3]. Metal soaps usually form in the inner paint layers. As the leaching of metal ions from the pigment particles to the binding medium occurs, the ionomer network starts to form. Then, metal

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soaps crystallize, expand and migrate through the paint stratigraphy. As metal soaps have a tendency to migrate to the surface, they can cause severe damage to the appearance of the paint film, due to the formation of eruptions and protrusions on the paint surface[11].

At present, several analytical approaches are employed to characterize the metal soaps both chemically and morphologically. Scanning Electron Microscopy (SEM) often serves to visually identify the presence of metal soap agglomerate and if combined with Energy Dispersive X-ray (EDX) analysis, it can provide a first elemental identification of the metals[5]. For a chemical evaluation, Fourier Transform Infrared (FTIR) spectroscopy and mapping and/or Raman spectroscopy can be useful for recognizing the metal carboxylate structure with the former and the organic fatty acid chains with the latter[12,13]. Currently, these methods can reveal both morphology and composition of metal soaps. However, surface measurements cannot reveal what is happening within a paint layer and cannot provide information on the size and distribution of aggregates in multi-layer systems. For this, a cross-section sample is necessary to understand the chemistry within a paint[14]. Therefore, the development of non-invasive methods to identify the presence of metal soap before their eruption would be helpful.

One interesting aspect of metal soap structure is its specific optical features with respect to the surrounding paint layers. Under light microscopy, metal soaps are reported to appear translucent to whitish opaque[5] and this observation inspired the present research. Optical Coherence Tomography (OCT) is capable of probing subtle changes in the optical properties of complex stratified materials[15]. The method is non-invasive, non-contact and can be applied directly on top of a painting surface, providing information up to hundreds of microns below the surface depending on the paint mixture[15]. In the last couple of years, there has been considerable interest in the community to explore the potential of using OCT for the non-invasive imaging of metal soaps in paint films. Here, we present results of exploratory research on the use of OCT for metal soap detection on samples of different origin, in order to probe the limits and possibilities of this method. In particular, micro-samples from wall painting with problems of metal soap formation, were collected and analyzed with both conventional analyses and OCT. Due to the complexity of these case studies, the measurements were carried out on cross-section samples for better identifying the presence of crystalline agglomerate of metal soaps. Secondly, we tested the method as a potential non-invasive approach, with the aid of mock-up samples. In this case, the metal soap formation was evaluated directly from the top of the surface, without sampling the paint film. The results of both conditions are critically discussed, and limitation and potentiality of OCT in detecting metal soap structures are presented at the end of this work.

2. METHODOLOGY

2.1 Ultra-high Resolution Optical Coherence Tomography system

An in-house built Fourier domain ultra-high resolution (UHR) OCT instrument was used. This system has a supercontinuum broadband laser source (NKT, SuperK Versa), with output centered at 810 nm. The instrument design and data processing have been described in detail in Cheung et al.[15]. This system allows a depth (axial) resolution of 1.2 µm to be obtained in paint and varnish layers. The resolution in the transverse plane is 7 µm. All samples were scanned by selecting an area of 2×2 mm with 500 × 500 depth profiles (A-Scans) collected. The OCT data cube was processed and re-sampled such that the voxels have 1:1:1 aspect ratio in order to better visualize the features of in the OCT images such that they are comparable with the microscopic images.

2.2 Attenuated Total Reflection - FTIR spectroscopy and imaging

Two different set-ups to collect ATR-FTIR data were used. A portable FTIR spectrometer (Cary 630 Agilent) fitted with a diamond ATR crystal unit (crystal size 2×1 mm) allowed single spectra to be rapidly collected in order to check the presence of metal soaps. The spectral range selected was 4000 – 600 cm^{-1}, and a total of 128 scan were coadded at 8 cm^{-1} spectral resolution.

A Hyperion 3000 FTIR microscope attached to a Bruker Vertex 70 spectrometer (Bruker Optics) was used to collect FTIR chemical images to confirm the location and size of the metal soaps in the area analyzed with OCT. The microscope is fitted with a 20x magnification ATR objective and a germanium crystal (Ge refractive index ~4) which has a contact surface of 100 µm. The microscope is equipped with a Focal Plane Array detector (active window of 64×64 pixels) which, coupled with the ATR objective, gives a chemical image of ~ 30×30 µm size. The spectral range available with the FPA detector is 4000 – 900 cm^{-1}, and FTIR spectra were collected by co-adding 64 scans with 4 cm^{-1} spectral resolution. OPUS software (Bruker) was used to process the data collected.

2.3 SEM-EDX

Scanning electron microscopy images and element analysis were obtained with a Zeiss EVO60 microscope equipped with an EDX Bruker QUANTAX 200 microprobe (scientific laboratories of Venaria Reale, Italy). The cross-sections were coated with gold or graphite and were analyzed in variable pressure mode (VP 20 Pa).

3. RESULTS AND DISCUSSION

3.1 Cross-section samples from real artworks

Cross-sections prepared from samples taken from different polychrome multilayered artworks were prepared in the scientific laboratories of Venaria Reale, Italy. All samples were embedded in resin and polished to reveal the stratigraphy. The first cross-section was prepared from a sample taken from the stucco decoration of the ceiling of The Queen's bedroom, Moncalieri Castle (Torino, IT) (Figure 1a, b and c). The second sample (Figure 1d, e and f) was taken from the mural panting of the Crucifix Chapel, dated to the 18th century, of the San Francesco d'Assisi Church in Torino, IT. The third sample (Figure 1g, h and i) was taken from a polychrome stone (carbonate) sculpture dated around the 15th -16th century. It is worth noticing that these three cross-sections were considered as representative examples of metal soaps in different materials and substrates and they are proposed as a first trial of the detection limits of OCT.

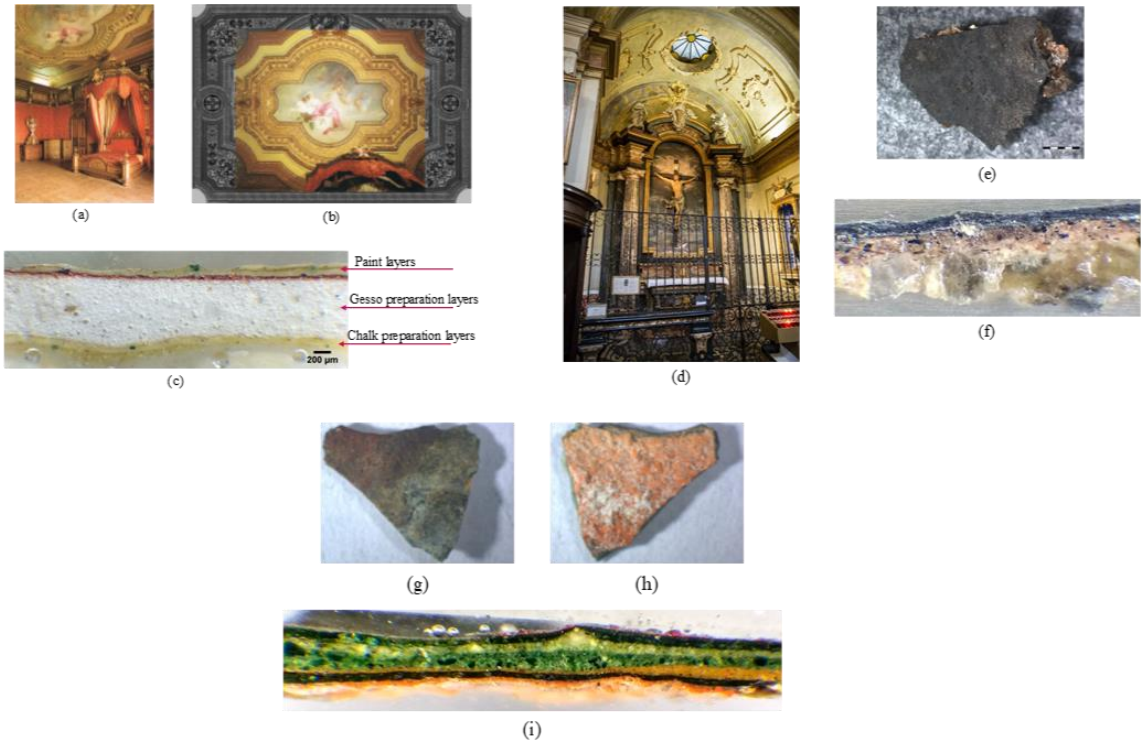

Figure 1. a) The Queen's bedroom, Moncalieri Castle, Torino, IT[15] b) the virtual reconstruction by E. Bottino[16] of the ceiling destroyed in a fire in 2008 and c) the cross-section "Bottino" prepared from a sample of the stucco decoration of the ceiling shows a green agglomerate in the paint layers; d) The Crucifix Chapel, dated to the 18th century, of the San Francesco d'Assisi Church (Torino, IT); e) the sample from the mural painting prepared as a cross-section reveals the mortar support with different colored layers with oily media and f) the cross-section of the sample shows the presence of white agglomerates indicating the formation of metal soaps in the lower oil layers; g) Front and h) back side of the fragment taken from a polychromatic statue dated 15th-16th century. Many painted layers are present mixed with different binding media (gum, oil and protein) i) the cross-section of the fragment reveals white protrusions forming particularly in the oil-based paint layer.

Because of the brittleness of the cross-section samples, ATR-FTIR measurements were not carried out to avoid the risk of crushing the agglomerates of metal soaps through indentation. On these real case studies, the presence of metal soaps was confirmed by FTIR measurements, collected from the areas close to the sampling point. The details of the stratigraphic morphology of the inclusions, as well as their elemental composition were obtained with SEM-EDX. Finally, 810 nm UHR OCT imaging was performed on samples after gently re-polishing the cross-sections which were coated with graphite for the analysis with the SEM (Bottino and Assisi cross-sections).
The first cross-section from stucco decoration by Bottino, presented a clear green translucent protrusion in the top yellow paint layers (Figure 2a). SEM-EDX analysis confirmed the protrusion was mainly composed of carbon, oxygen and copper, and for this reason tentatively identified as an organic copper complex. The cross-section sample was scanned with the OCT such that the OCT virtual cross-section images cut across the identified metal soap (as illustrated in Figure 2d and 2e) and are perpendicular to the microscopic images of the cross-section sample (Figure 2b and c). In the OCT virtual cross-section image extracted from the location of the soap (Figure 2e and f), a transparent "lump" was distinguishable from the surrounding paint materials and this proved that the copper soap was detected with the UHR OCT.

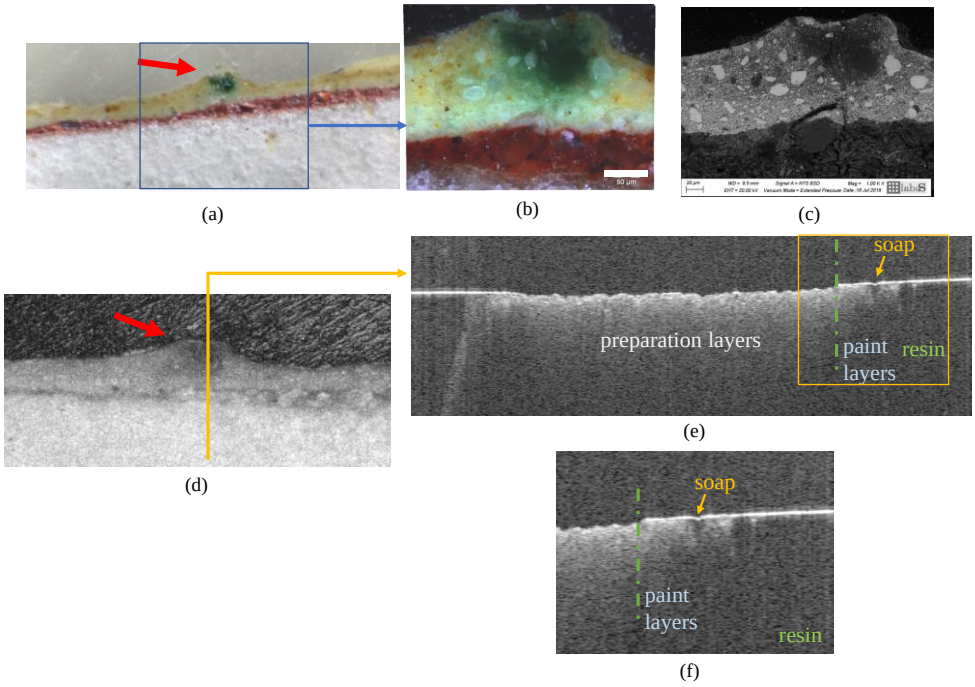

Figure 2. Visible microscopy at a) 10x and b) 1000x magnification of the cross-section "Bottino" from the stucco decoration of the ceiling of The Queen's bedroom, Moncalieri Castle (Torino, IT) showing a green translucent protrusion identified as soap (the scale bar in figure b is 50 µm); c) SEM backscattered image of the metal soap (the scale bar is 20 µm); d) the enface OCT image averaged in depth of the area scanned with the 810 nm UHR OCT around the metal soap; e) an OCT virtual cross section image shows in the paint layer a darker area identified as the metal soap surrounded by the more scattering paint material and f) zoom-in of the OCT image presented above of the copper soap. The OCT cross-section images is 1.8 mm width × 0.6 mm depth (optical depth corrected by assuming a refractive index of 1.5).

The cross-section from a polychrome statue showed visible white protrusions forming in the fourth paint layer (L4, Figure 3a) just below two darker green layers (labelled L2 and L3). In this case, the agglomerate results in an opaque appearance. SEM-EDX analysis (Figure 3b) showed that lead was one of the main elements present in the protrusion, along with oxygen, indicating it was probably a lead soap. The UHR OCT virtual cross-section images (Figure 3d) helped to distinguish the dark green layers (L2 and L3). However, in the virtual cross-section images extracted from the lead soap location (Figure 3d, bottom), the soap aggregate cannot be distinguished from the other materials in the paint stratigraphy.

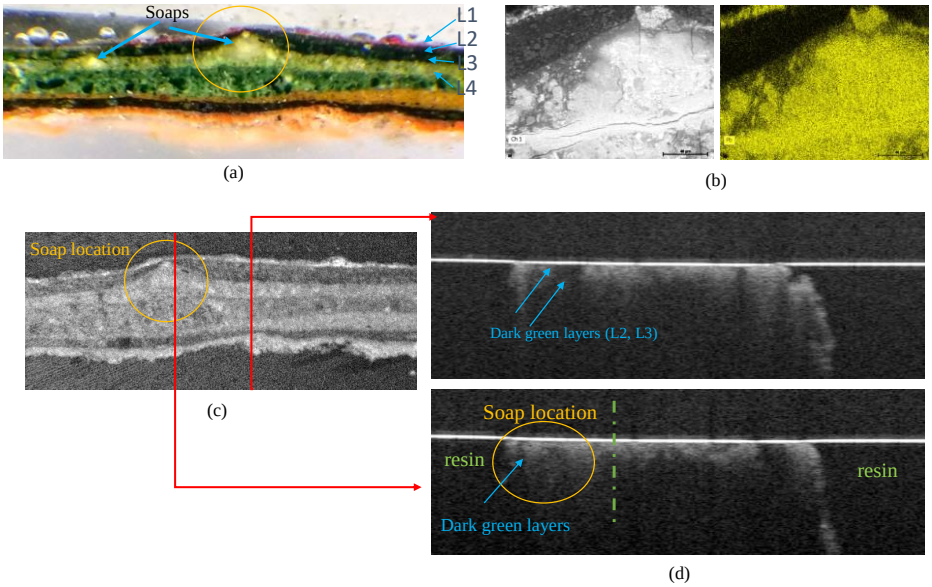

Figure 3. a) Image in visible microscopy at 10x of the cross-section of a polychromatic statue shows white protrusions present in the 4th pain layer associated to metal soaps. A yellow circle indicates the larger protrusion analyzed; b) SEM-EDX analysis of the larger protrusion strongly indicates the protrusion is a lead soap (Pb map on the right, the scale bar is 50 µm); c) Enface UHR OCT image averaged in depth shows the area of the larger lead soap; d) Virtual OCT cross-section images extracted from an area near the soap (top) and the area of the lead soap (bottom). The top cross-section shows a darker area associated to the dark green pain layer 3. The second OCT cross-section, extracted from the lead soap protrusion area, shows it is difficult to distinguish the metal soap from the surrounding paint materials. The OCT cross-section images are 0.8 mm width × 0.27 mm depth (optical depth corrected by assuming a refractive index of 1.5).

In the third sample from the mural panting of the Crucifix chapel in Assisi Church, the cross-section showed a large agglomerate in the paint layers below the surface, resembling the morphology of a metal soap (Figure 4a). SEM-EDX analysis indicated that it was potentially a lead soap. As for the soaps in the polychrome statue presented in Figure 3, the lead soap in the mural painting cross-section with a whitish opaque appearance was not clearly discernable in the virtual OCT cross-section image extracted from the same location of the soap (Figure 4c and d).

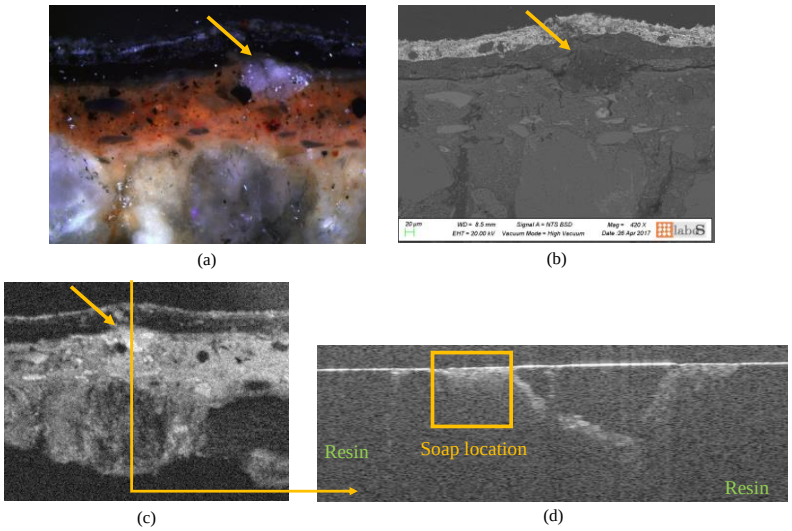

Figure 4. a) Image in visible microscopy at 200x of the cross-section of a sample from the mural panting in the Chapel of the Crucifix in Assisi Church (Torino, IT) shows a large white protrusion (yellow arrow) forming below the surface associated to

metal soaps; b) SEM-EDX analysis of the white protrusion indicates it is most certainly a lead soap (the scale bar is 20 µm); c) Enface UHR OCT image averaged in depth shows the area of the lead soap and the location the virtual cross-section in d) was extracted; d) UHR OCT virtual cross-section image extracted from the soap location shows that OCT does not clearly help to distinguish the metal soap from the surrounding materials in the paint and preparation layers. The OCT cross-section image is 1.2 mm width × 0.37 mm depth (optical depth corrected by assuming a refractive index of 1.5).

3.2 Mock-up paint films

Since the final aim of this study is to explore a non-contact and non-invasive way for the identification of metal soap agglomerate in inner layers, a selection of paint mock-ups prepared on microscope slides were also analyzed from above the top of the surface. This second approach allowed us to better understand the feasibility of visualizing metal soaps with OCT without taking sample. First, ATR-FTIR spectra were collected from the selected mock-ups, in order to evaluate the presence of metal soaps, secondly the same areas were scanned with OCT. The paint mock-ups analyzed along with the metal soaps detected with FTIR spectroscopy are listed in Table 1.

Table 1 List of paint mock-ups and their composition. The presence and composition of possible metal soaps was confirmed with ATR-FTIR spectroscopy.

Paint mock-ups on microscope slide	**Metal soaps**
Natural malachite + egg tempera (13 years old)	Cu soaps
Azurite + egg tempera (13 years old)	None
Smalt + linseed oil (7 years old)	K soaps

The malachite and azurite in egg tempera mock-ups were both prepared in 2006 and kept in normal laboratory conditions. ATR-FTIR spectra revealed that only in the malachite paint film copper soaps (sharp band at IR band at 1585 cm^{-1} assigned to the COO^- stretching of the copper carboxylate[13]) were present. On the other hand, in the azurite paint, FTIR bands of metal soaps were not detected. Despite both pigments are copper carbonate hydroxides, it has been reported that malachite has the tendency to form Cu soaps with the free fatty acids of lipid binders, whereas Cu soaps would form in azurite only when this has transformed to malachite[16]. Therefore, these mock ups were used to compare OCT images of paint film with or without metal soaps in the same area the FTIR spectra were collected. In the UHR OCT cross-section images, the malachite paint film appeared to be fairly scattering with a few sporadically dispersed transparent particles of about a few micrometers in size (Figure 5c, top). These particles due to their size, distribution and the similarity in overall appearance with the copper soap observed in the paint cross-section "Bottino" (Figure 2) might be copper soaps.

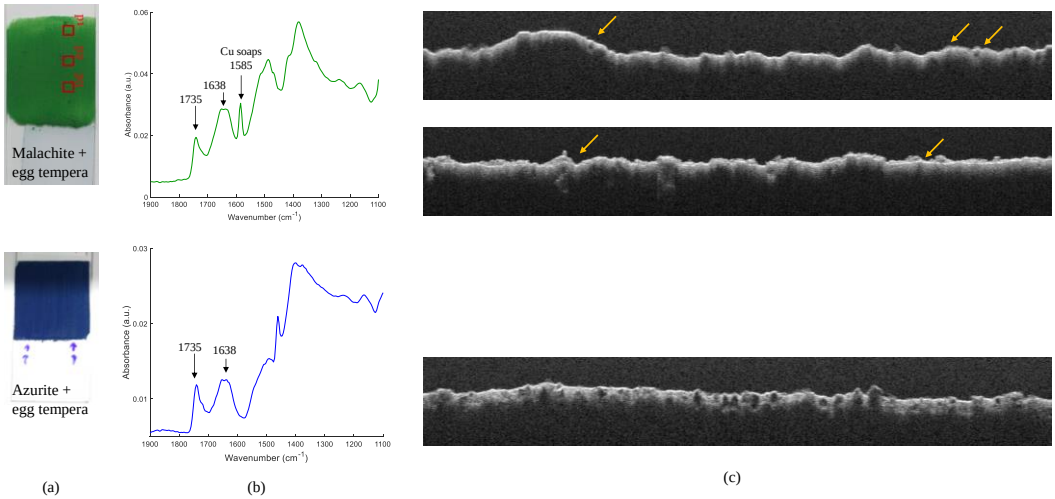

Figure 5. a) Malachite (top) and azurite (bottom) in egg tempera on microscope slides; b) ATR-FTIR spectra shows the presence of copper soaps in the malachite paint (1585 cm^{-1}, egg tempera bands at 1736 and 1638 cm^{-1}), whereas this band is not present in the azurite spectrum indicating the possible absence of metal soaps in the azurite paint; c) UHR OCT cross-

section image of the malachite paint (top) with yellow arrows indicate possible Cu soaps and of the azurite paint (bottom) showing transparent particles. It is evident that it might be difficult to differentiate with OCT potential Cu soaps with transparent pigment particles. The OCT cross-section images are 2 mm width × 0.17 mm depth (optical depth corrected by assuming a refractive index of 1.5).

The complexity of paint films might also imply the presence of elements/particles with a range of optical properties that are not necessarily associated with metal soaps. This is the case of the second mock-up sample made of azurite in egg tempera. The OCT cross-section images of the azurite mocks-ups show transparent particles resembling the ones visible in the OCT images of the malachite paint film (Figure 5c, bottom), even though ATR-FTIR did not detect soap formation in the azurite film. These transparent particles might be associated with the azurite pigment grains, therefore suggesting that OCT might not be capable in differentiating pigment particles with specific optical properties from metal soap agglomerates.

In the third paint mock-up made of smalt in linseed oil, the ATR-FTIR spectra showed that potassium soaps were present on the paint surface (IR bands at 1563 and 1462 cm^{-1}). The ATR-FTIR chemical image (Figure 6c, false color image obtained by plotting the integrated absorbance of the IR spectral region 1596-1530 cm^{-1}) helped to localize the metal soaps and the same area was analyzed with the UHR OCT (Figure 6e and f). The OCT virtual cross-section image shows clearly the transparent layer of smalt over the microscope glass slide (Figure 6e). In the area where soaps were detected, it was possible to note some more scattering agglomerates which could be associated with the potassium soaps.

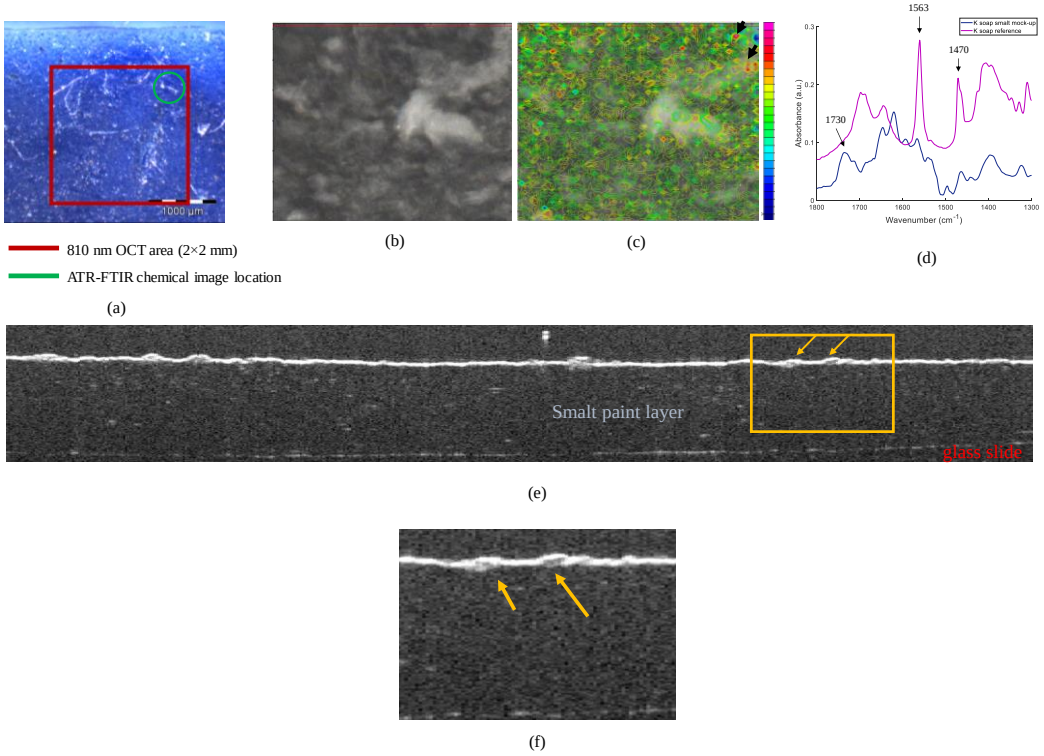

Figure 6. a) Smalt in linseed oil on microscope slide; b) Picture in visible microscopy 20x of the area analyzed with ATR-FTIR imaging and c) the false color chemical image (color scale indicates blue for low absorbance and red for high absorbance) obtained by integrating the IR spectral region 1596 – 1530 cm^{-1} (image size 30×30 µm) which shows the distribution and size of potassium soaps in the smalt paint (indicated with black arrows in the false color image); d) the extracted FTIR spectrum (blue line) from the false color image presents bands characteristic of K soap at 1563 and 1470 cm^{-1} as visible in the reference FTIR spectrum of K soap (purple line). The binding medium oil shows the characteristic IR band at 1730 cm^{-1}; e) UHR OCT cross-section image from the area analyzed with the FTIR microscope shows the transparent smalt pain layer and some less transparent agglomerates (yellow arrows) on the surface which could be associate with the potassium soaps. The OCT cross-section image is 2 mm width × 0.19 mm depth (optical depth corrected by assuming a refractive index of 1.5).

4. CONCLUSIONS

In this explorative work, we showed that OCT can be used for metal soap detection in combination with other complementary techniques in cases where the optical properties of the soap agglomerate is sufficiently different from its surrounding materials. In two cases of sample cross-sections from real artworks (the mural painting from the Assisi Church with lead soaps and the polychrome statue with copper soaps), the metal soap aggregates (appeared in light microscopy as a whitish opaque agglomerate) were not distinguishable from the other materials composing the paint stratigraphy. On the other hand, in the sample cross-section "Bottino" from the ceiling of the Moncalieri Castle, the copper metal soap that had a translucent aspect, was visible in the 810 nm UHR OCT images. In addition, the results of the malachite and azurite mock-up samples showed that features resembling metal soaps detected with OCT need to be carefully examined as these could potentially be related to the pigment itself and not to the crystallization of metal soaps. The results of this preliminary research demonstrate that in order to confirm the presence of metal soaps in real objects and paintings, it is still required to combine OCT with other techniques, such as FTIR spectroscopy and mapping and/or SEM-EDX, depending on the case/object requirements. Nevertheless, the advantages of OCT imaging are rapid scanning of a much larger area than FTIR mapping and potentially detecting metal soaps below the paint surface without the need of sampling or time-consuming sample preparation protocol. A future protocol might be to use FTIR mapping on a micro-sample cross-section to help understand how the metal soaps might look like in an OCT image in the artwork under examination and then use the OCT to scan larger areas for the presence of metal soaps.

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