

Non-invasive and *in-situ* investigation of panel paintings stratigraphy by portable micro-SORS

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Abstract

A non-invasive and *in-situ* investigation of the chemical make-up of the superimposed paint layers of two 16th century panel paintings has been carried out using, for the first time, portable micro-Spatially Offset Raman Spectroscopy (micro-SORS). In paintings, the identification of the chemical compounds within the stratigraphy allows achieving relevant information about the materials, the artist's technique and the decay processes. Nowadays the research in conservation science is focused on developing advanced portable analytical techniques able to achieve subsurface data *in-situ* and in a non-invasive way. Micro-SORS is an emerging analytical technique developed to address the need of retrieving the molecular composition of the sub-surface compounds in a non-invasive way; however, so far micro-SORS studies of artworks have been carried out only with benchtop Raman microscopes, precluding the non-invasive analysis of large objects and artworks *in-situ*. Here, the potential of portable micro-SORS is demonstrated through the

reconstruction of the layer sequences in selected areas of panel paintings, providing unequivocal information about the preparation layer spread over the panels and the pigments used in the painted layers.

Keywords: painting stratigraphy, micro-SORS, non-invasive, portable, in-situ analysis

Introduction

The current challenge in Cultural Heritage field is to develop an effective portable analytical technique for the non-invasive identification of the materials in art objects. An exhaustive characterization of these objects includes the study of both the surface and the subsurface essential for achieving relevant information about the materials, the artist's technique and the decay processes within the entire volume. This information should be collected in a non-invasive way to preserve the integrity of the artwork and to increase the statistical meaning of the data - ideally performed at multiple location to obtain holistic information about the makeup of the art object. To date, X-Rays, visible, infrared (and near-infrared) and terahertz-based methods¹⁻⁸, are used for the non-invasive investigations of multilayered materials such as painted stratigraphy.

In order to fully accomplish the direct and non-invasive retrieval of molecular composition through micro-stratified turbid organic, inorganic, crystalline and amorphous compounds, a Raman spectroscopy method (Micro-Spatially Offset Raman Spectroscopy, micro-SORS) has been recently developed⁹⁻¹¹. The technique permits the reconstruction of the molecular composition of superimposed layers by collecting a higher proportion of Raman photons originated from the inner part of the material compared to a conventional micro-Raman measurement. In micro-SORS spectra, the sub-surface layer signals emerge or alter their relative intensity compared to the surface contribution. The layered system

reconstruction is therefore possible, for example, by comparing the micro-SORS spectra with the Raman spectrum conventionally acquired¹².

Micro-SORS has been developed on conventional benchtop Raman microscopes and a large body of literature exists reporting on data from layered systems in biological materials¹¹, in micro-samples taken from art objects¹², in polymers and industrial paper¹¹ and in biomedical area¹³⁻¹⁵. Because of the importance of avoiding the invasive sampling and analyzing the artworks *in-situ* two portable micro-SORS prototypes, set-up according to the defocusing and full micro-SORS variants¹⁶⁻¹⁷, were developed and tested using laboratory mock-up samples. Defocusing, the simplest micro-SORS variant, relies on the collection of Raman spectral sequences at different distances between the surface and the microscope objective, starting from the imaged surface position. By enlarging the laser illumination and the Raman collection areas through the above defocusing, the Raman photons emerging from the depth are collected and through a simple spectral subtraction the contribution of different layers is reconstructed⁹.

Here, a micro-SORS defocusing portable device was applied, for the first time, to a study of layered makeup of artworks *in-situ*. Defocusing micro-SORS measurements were carried out on two 16th century panel paintings by Marco d'Oggiono permitting the non-invasive recovery of sublayer compositional information. The paintings have been previously investigated with non-invasive and micro-invasive techniques: macro X-Ray fluorescence spectroscopy (MA-XRF), visible and near infrared (VNIR) hyperspectral imaging (HIS) and IR-Reflectography were used *in-situ*, while Fourier transformed infrared spectroscopy (FT-IR) and Scanning Electron Microscopy coupled with Energy Dispersive X-rays spectroscopy (SEM-EDX) measurements, were performed on micro-samples with the aim of identifying the pigments, their layering sequence both in the original and in the re-painted areas^{5,18}. Micro-SORS supplements the information obtained by these

techniques providing an opportunity for integrating XRF, visible and near infrared imaging with molecular depth profiles.

The portable micro-SORS measurements were carried out, for the first time, at the near infrared excitation wavelength of 1064 nm enabling to also analyze fluorescent regions of the paintings.

Materials and Methods

The artwork consists of two panel paintings: *Saint Francis and Bona Bevilacqua Trivulzio (or Antonia Pallavicini)* (panel 1, Figure 1a) and *Saint Anthony from Padua and Giulia Trivulzio (or Lucia Bevilacqua)* (panel 2, Figure 1b). The panels belongs to the permanent collection of *Pinacoteca di Brera* (Milano), and the micro-SORS measurements were collected during their restoration work at the scientific laboratory of “*Centro Conservazione e Restauro (CCR) la Venaria Reale*” (Torino, Italy); here the results obtained from four selected areas (Figure 1) are reported.

A portable Xantus-2™ (Rigaku, Boston, USA) Raman spectrometer was modified for performing the defocusing micro-SORS analysis: the instrument collection lens attachment was removed and replaced with a standard microscope objective (20×, WD 1.3 mm, NA 0.4, Olympus), the device was mounted on a micro-positioning stage to enable the setting of defocusing distances with high accuracy and reproducibility and positioned on a tripod (Figure 2). The defocused micro-SORS spectra were collected by moving the entire instrument away from the paintings, starting from the surface imaged position, with defocusing steps ranging from 100 μm to 1500 μm.

The instrument was equipped with a thermoelectrically cooled CCD and enabled two excitation wavelengths to be deployed, 785 nm and 1064 nm. Most of the measurements were carried out using the 1064 nm excitation to mitigate fluorescence present otherwise with the 785 nm excitation. Preliminary tests allowed to observe that 1064 nm excitation is

more efficient in analyzing lighter areas, whereas darker portions, like the black dress of the panel 1 devotee (*Bona Bevilacqua Trivulzio - or Antonia Pallavicini*) and the dark brown hair of the panel 2 devotee (*Giulia Trivulzio - or Lucia Bevilacqua*), did not provide any useful Raman information due to high photons absorption, in line with expectations. Where fluorescence signal is low, 785 nm source was preferable due to its higher Raman scattering probability and better spectral resolution compared with 1064 nm.

For both wavelengths, the measurements were performed using laser power in the range between 80 to 150 mW and an acquisition time ranging between 5 and 20 s. Longer measurements could not be acquired due to the difficulties when dealing with portable *in-situ* analyses such as vibrations and the presence of variable ambient light.

Ratio values between two main peaks of selected compounds have been calculated for each measurement point to highlight the evolution of the intensities over the degree of defocusing. Spectra manipulation (baseline correction and normalization), plots construction and ratio calculations were performed using ORIGIN software.

Results and discussion

The non-invasive investigation of the composition of preparation layer was performed by selecting an area where a simple stratigraphy (only one layer applied over the preparation layer) was expected to be present. The light blue area of the sky in panel 1 (point A - Figure 3a) was analyzed with 1064 nm excitation wavelength and it provided the best micro-SORS results in terms of contrast between the top and the bottom layers. The Raman spectrum collected at the imaged position (conventional Raman spectrum) revealed the presence of white lead $[(\text{PbCO}_3)_2 \cdot \text{Pb}(\text{OH})_2]$ and gypsum ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$), identified by their main Raman bands, located at 1050 cm^{-1} (white lead) and 1008 cm^{-1} , 671 cm^{-1} and 492 cm^{-1} (gypsum). Unfortunately, no information about the blue pigment (azurite, $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ ¹⁸), was obtained, probably, due to its scarce quantity in this very

light area and the low Raman scattering cross-section of such pigment. The micro-SORS spectra (Figure 3b) show a progressive relative intensity increase of gypsum signal compared with white lead, as also highlighted by the lead white/gypsum ratios calculated for each defocusing steps (Figure 3c). This outcome reveals the presence of a gypsum-based layer under the surface, in line with the traditional artist's technique, that suggests the use of a mixture of gypsum and animal glue spread over the wood support. The presence of tiny gypsum signal at the imaged position is explained by potentially only thin top layer being used, as Raman scattering cross section for gypsum is high and low for white lead.

The micro-SORS sequences acquired with 1064 nm laser source on the light pink area of S. Francesco's hand light flash tones of panel 1 (point B - Figure 4a) provided further information about artist's technique. The imaged Raman spectra revealed the presence of vermilion (HgS , Raman bands at 255 cm^{-1} and 344 cm^{-1}) and white lead. The defocusing spectra (Figure 4b) show a progressive decrease of white lead Raman bands compared to vermilion, as confirmed by their relative intensity ratios (Figure 4c). Moreover, the relative increase of gypsum band at 1008 cm^{-1} is apparent. According to these outcomes and considering the gypsum-based preparation layer highlighted in the previous measurement, it is reasonable to suggest a relevant presence of white lead in the external part of the stratigraphy, followed by an increase of vermilion below the surface, and finally the presence of a preparation layer consisting of gypsum. Since the imaged spectrum shows the presence of both white lead and vermilion signals and considering that the external layer is pink colored, it is reasonable to deduce that the external layer, as well as the second layer, could contain both the pigments, but with different relative abundances (Figure 4d). This could suggest that the artist used a mixture of white lead and vermilion for the flash tones, adding, in the lighter areas, a layer of the same mixture which has a higher relative content of white lead. The persistence of white lead and vermilion Raman

signals even at large defocusing distances is ascribed to the nature of the defocusing micro-SORS Raman concept where only bias to certain depth is introduced by setting a certain defocusing distance and mixture of signals from various layers can be present, in principle, at any defocusing distance, including the imaged position⁹. Therefore, the signal of the surface does not necessarily disappear even at large defocusing distances.

A layer sequence was also non-invasively identified by micro-SORS in the grey pearl drop earring of the devotee in panel 2 (point C - Figure 5a) using the 1064 nm excitation line. The imaged spectra are dominated by the presence of white lead and vermilion. Micro-SORS analyses showed a progressive decrease of the white lead band with defocusing distance (Figure 5b); the noticeable change of relative intensity between these two pigments is highlighted in Figure 5c. This finding suggests the presence of two layers (Figure 5d): an external layer mainly consisting of white lead (the earring) and a bottom layer mainly made of vermilion; the gypsum based preparation layer is not visible at this point even at large defocusing distances. It is reasonable to assume that the bottom layer corresponds to the flash tones of the devotee's cheek, indicating potentially that the artist painted the earring after, and over, the devotee's ear. MA-XRF performed in the same area⁵ indicates the presence of a former hairstyle, underneath the presently visible one, where vermilion was used in the reddish tones. Therefore, the increase of vermilion signal from the subsurface could be also ascribed to the original (hidden) painting. The absence of the gypsum band is probably due to the thickness of the two upper layers which prevents the acquisition of any signal from the most internal part of the stratigraphy.

In the last measurement point (point D - Figure 6a), the vibrant red dress of the panel 2 devotee, the imaged position Raman spectra showed the presence of vermilion and red ochre (Fe_2O_3); the goal was to establish if they are located at two different positions of the stratigraphy or mixed together in the same external layer. In the micro-SORS spectra (Figure 6b) the intensity ratio between the main bands of vermilion at 255 cm^{-1} and red

ochre at 296 cm^{-1} is quite constant, without any significant variations, as confirmed by the ratios graph in Figure 6c, where the slight fluctuations among the values are ascribed to measurement noise. This data indicates that the vibrant red portions of the dress was made by mixing two pigments. Interestingly, macro-XRF and HIS highlighted the overlapping of red ochre on top of vermilion in the shadows of the dress⁵; therefore, the combination of the analytical data (macro-XRF, HIS and micro-SORS) permits to conclude that a pigments mixture was used for the vibrant red dress areas, whereas for the shadows a further external, darker, ochre layer was superimposed.

Measurement point D was collected with 785 nm excitation wavelength because fluorescence was not severe; the better spectral resolution provided by the 785 nm wavelength permitted more confident characterization of the red ochre and vermilion Raman bands. In this case the absence of gypsum signal of the preparation layer could be due to the presence of other painted layers below the external one. In fact, the overlapping of the devotee's red vest and the Saint's white vest emerges in the IR-Reflectography images¹⁸. To paint the Saint's vest, white lead was mainly used, as the MA-XRF maps showed high lead content in that area^{5,18}; in the micro-SORS measurements white lead signal is absent probably because of the relatively low scattering Raman cross-section of the pigment.

Conclusions

This study demonstrates the possibility of obtaining, in non-invasive way, the chemical make-up of paintings subsurface using portable micro-SORS optimized for *in-situ* measurements. Slight modifications to a conventional portable Raman were implemented to permit the collection of micro-SORS spectral sequences at different z-distances. This set-up allowed obtaining useful information about artist's technique in a non-invasive way, reconstructing the stratigraphy, up to the preparation layer. The 1064 nm line proved to be

effective in recovering deep Raman photons, avoiding the fluorescence phenomenon that typically limits the application of Raman spectroscopy in art field. This study paves the way for including portable micro-SORS in the range of the non-invasive techniques for Cultural Heritage investigations, providing a further effort towards a more powerful multi-analytical approach.

References

- [1] Vanmeert, F.; Hendriks, E.; Vander Snickt, G.; Monico, L.; Dik, J.; Janssens, K. *Angew. Chem. Int.* **2018**, *57*, 7418-7422
- [2] Possenti, E.; Colombo, C.; Conti, C.; Gigli, L.; Merlini, M.; Plaisier, J. R.; Realini, M.; Gatta G. D., *Analyst.* **2018**, *143*, 4290-4297
- [3] Farges, F.; Cotte, M. *X-Ray Absorption Spectroscopy and Cultural Heritage: Highlights and Perspectives* in J. A. Van Bokhoven, C. Lamberti, *X-Ray Absorption and X-Ray Emission Spectroscopy*, John Wiley & Sons, **2016**.
- [4] Bendada, A.; Sfarra, S.; Ibarra-Castanedo, C.; Akhloufi, M.; Caumes, J.P.; Pradere, C.; Batsale, J.C.; Maldague, X. *Opto-Electron. Rev.* **2015**, *23*, 88-99.
- [5] D'Elia, E.; Buscaglia, P.; Piccirillo, A.; Picollo, M.; Casini, A.; Cucci, C.; Stefani, L.; Romano, F. P.; Caliri, C.; Gulmini, M. *Microchem. J.* **2020**, *154*, 104541.
- [6] Mercuri, F.; Paoloni, S.; Cicero, C.; Zammit, U.; Orazi, N. *Infrared Physics & Technology.* **2018**, *89*, 223-230.
- [7] Gibson, A.; Piquette, K. E.; Bergmann, U.; Christens-Barry, W.; Davis, G.; Endrizzi, M.; Fan, S.; Farsiu, S.; Fitzgerald, A.; Griffiths, J.; Jones, C.; Li, G.; Manning, P. L.; Maughan Jones, C.; Mazza, R.; Mills, D.; Modregger, P.; Munro, P.R.T.; Olivo, A.; Stevenson, A.; Venugopal, B.; Wallace, V.; Wogelius, R. A.; Toth, M. B.; Terras, M. *Herit. Sci.* **2018**, *6*, No. 7.
- [8] Invernizzi, C.; Fiocco, G.; Iwanicka, M.; Kowalska, M.; Targowski, P.; Blumich, B.; Rehorn, C.; Gabrielli, V.; Bersani, D.; Licchelli, M.; Malagodi, M. *Microchem. J.* **2020**, *155*, 104754
- [9] Conti, C.; Colombo, C.; Realini, M.; Zerbi, G.; Matousek, P. *Appl. Spectrosc.* **2014**, *68*, 686-691.
- [10] Matousek, P.; Conti, C.; Realini, M.; Colombo, C. *Analyst.* **2016**, *141*, 731-739.
- [11] Conti, C.; Realini, M.; Colombo, C.; Sowoidnich, K.; Afseth, N.K.; Bertasa, M.; Botteon, A.; Matousek, P. *Anal.Chem.* **2015**, *87*, 5810-5815.
- [12] Conti, C.; Botteon, A.; Colombo, C.; Pinna, D.; Realini, M.; Matousek, P. *J. Cult. Herit.* **2019**, *in press*.
- [13] Buckley, K.; Atkins, C. G.; Chen, D.; Schulze, H. G.; Devine, D. V.; Blades, M. W.; Turner, R. F. B. *Analyst.* **2016**, *141*, 1678-1685.
- [14] Di, Z.; Hokr, B. H.; Cai, H.; Wang, K.; Yakovlev, V. V.; Sokolov, A. V.; Scully, M. O. *J. Modern Optics.* **2015**, *62*, 97-101.

[15] Khan, K.; M. Ghosh, N.; Majumder, S. K. *J. Opt.* **2016**, *18*, 095301.

[16] Realini, M.; Botteon, A.; Conti, C.; Colombo, C.; Matousek, P. *Analyst.* **2016**, *141*, 3012-3019.

[17] Realini, M.; Conti, C.; Botteon, A.; Colombo, C.; Matousek, P. *Analyst.* **2017**, *142*, 351-355.

[18] D'Elia, E. Two panel paintings by Marco D'Oggiono (Pinacoteca di Brera): Restoration and interdisciplinary study of the works of art. Master Thesis, University of Turin, A.Y. 2017/2018

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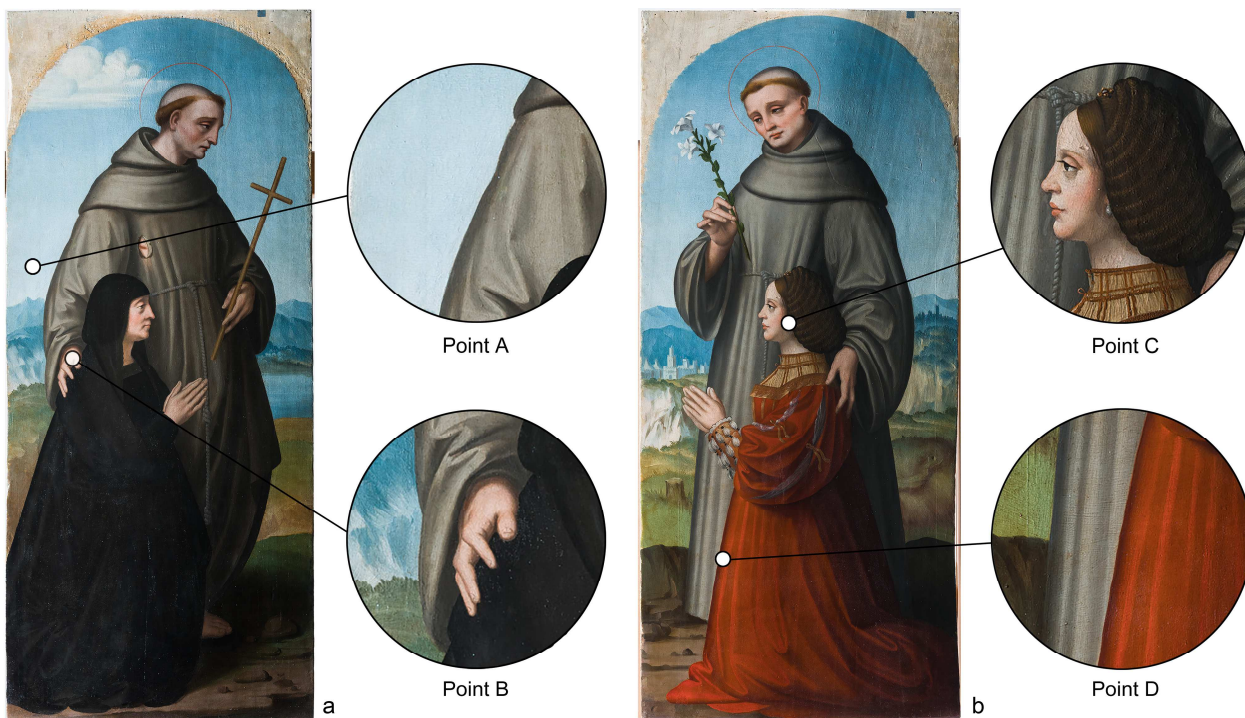


Figure 1: (a) panel painting 1 and (b) panel painting 2. The locations of the points A, B, C and D are indicated and their details reported in the circles.



Figure 2: (a) portable Raman device optimised for micro-SORS measurements; (b) detail of the microscope objective and its adapter.

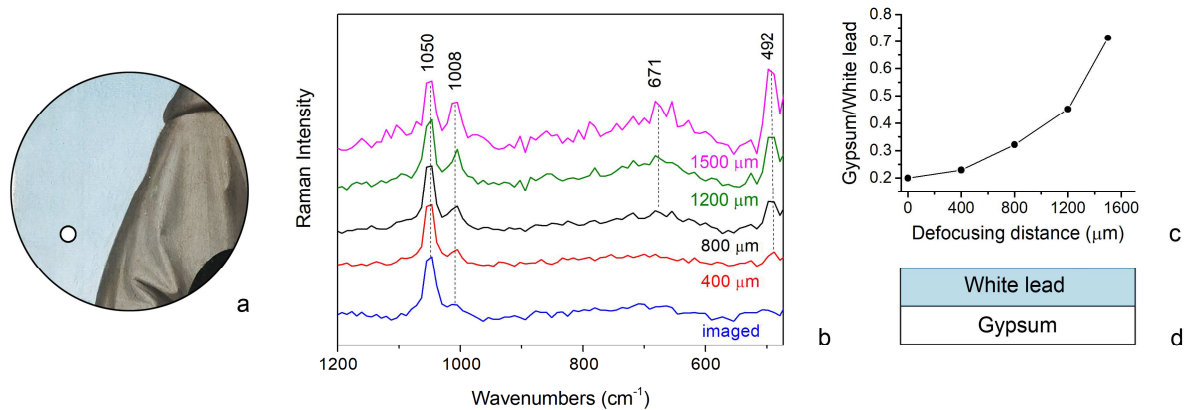


Figure 3: Point A – (a) detail of the analyzed area; (b) micro-SORS sequence from imaged position to 1500 μm of defocusing distances (indicated next to the spectra), normalized to the white lead band at 1050 cm^{-1} ; (c) gypsum/white lead Raman intensity ratios calculated for each defocusing step; (d) scheme of the suggested stratigraphy.

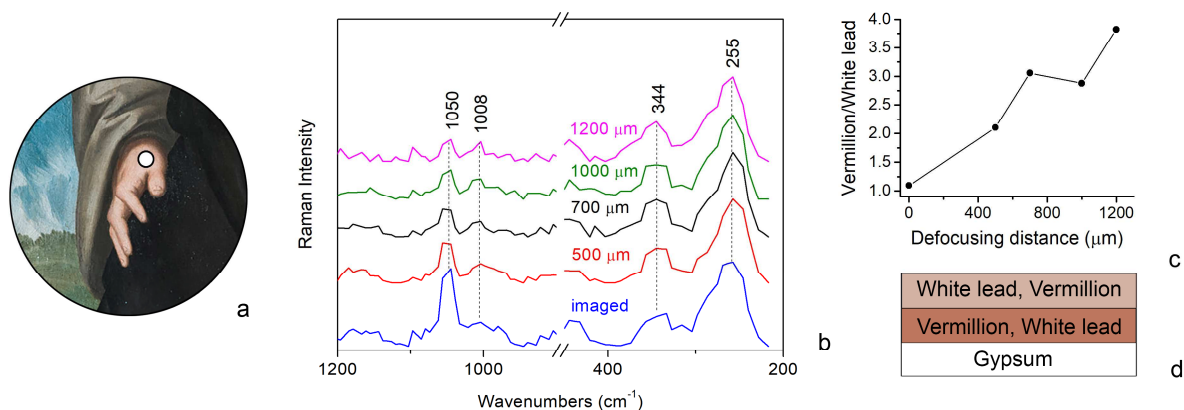


Figure 4: Point B – (a) detail of the analyzed area; (b) micro-SORS sequence from imaged position to 1200 μm of defocusing distances (indicated next to the spectra), normalized to the vermilion band at 255 cm^{-1} ; (c) vermilion/white lead ratios calculated for each defocusing step; (d) scheme of the suggested stratigraphy.

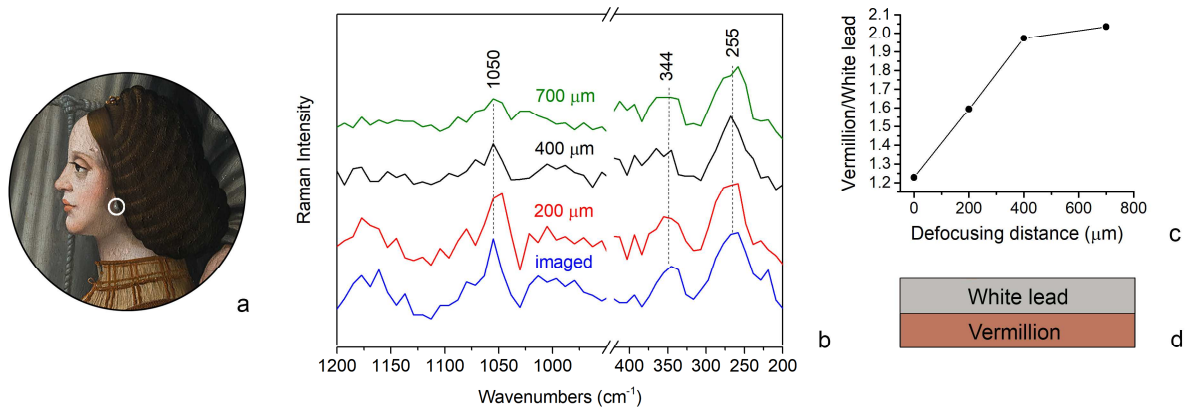


Figure 5: Point C – (a) detail of the analyzed area; (b) micro-SORS sequence from imaged position to 700 μm of defocusing distances (indicated next to the spectra), normalized to the vermilion band at 255 cm⁻¹; (c) vermilion/white lead ratios calculated for each defocusing step; (d) scheme of the suggested stratigraphy.

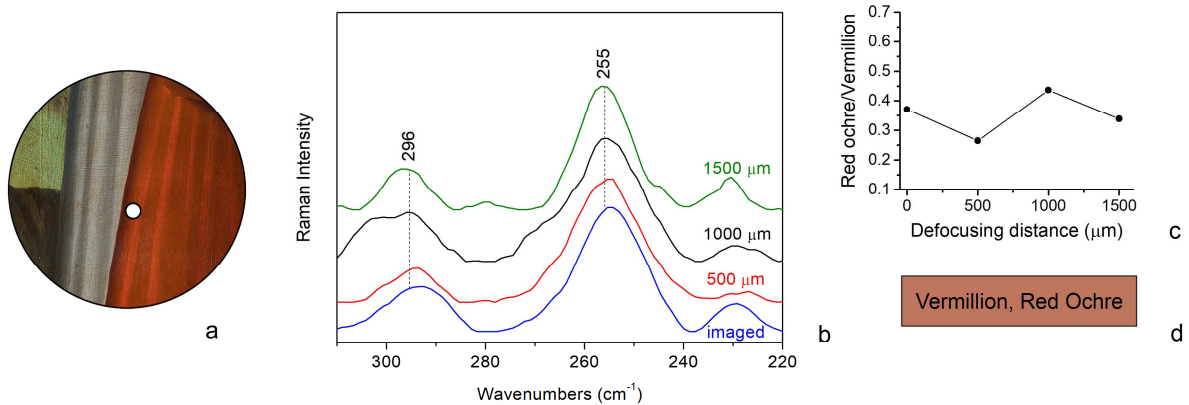


Figure 6: Point D – (a) detail of the analyzed area; (b) micro-SORS sequence from imaged position to 1500 μm of defocusing distances (indicated next to the spectra), normalized to the vermilion band at 255 cm⁻¹; (c) red ochre/vermilion ratios calculated for each defocusing step; (d) scheme of the suggested stratigraphy.