FTIR nano-spectroscopy at SISSI-Bio Beamline:
Recent insights in the field of Cultural Heritage

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Introduction

At SISSI-Bio beamline of Elettra Sincrotrone Trieste (Italy), the advantage offered by the infrared scattering-type Scanning Near-field Optical Microscopy (**IR s-SNOM**) to reach spatial resolutions down to tens of nanometers has been exploited for the first time in field of Cultural Heritage.
The following two cases of study show the exiting results obtained on complex samples from both a morphological and chemical point view.

Infrared s-SNOM

scattering-type Scanning Near-Field Optical Microscopy

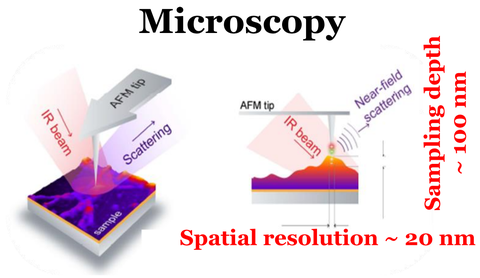

Image adapted from **Freitas, R.O. et al, Cells 2021, 10, 2559**.

Atomic Force Microscope (AFM) ↔ **3D topography**

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Infrared Interferometer ↔ **optical amplitude and phase (reflectivity and absorption)**

Stradivari's Violins

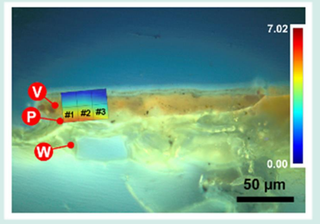
Revealing **new secrets** about **Stradivari**'s craftmanship.

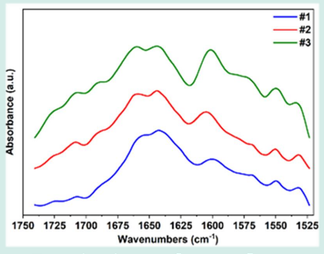
A long-debated question: was a proteinaceous preparation layer used?

from micro- to nano-scale

San Lorenzo 1718

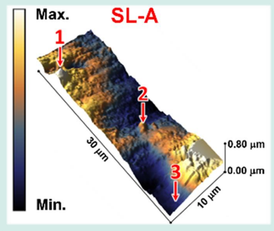
SR µ-FTIR

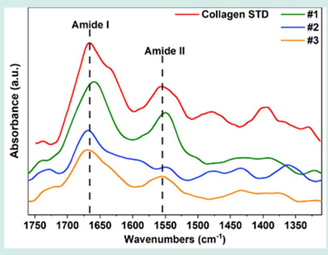




- Deviations from the typical shapes and proportions of Amide bands
- Not fully-recognizable proteins

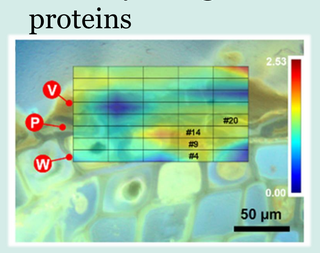
nano-FTIR

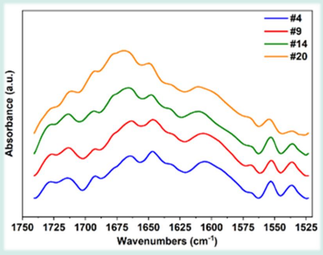


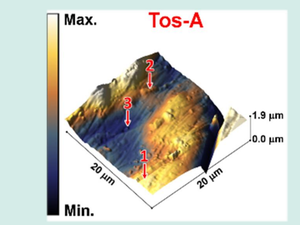


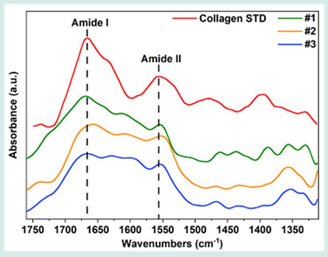
✓ Clear Amide I and II features
✓ Additional spectral contribution, possible degradation products

Toscano 1690





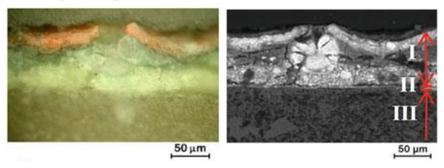




Stani et al., 2022, Analytical Chemistry

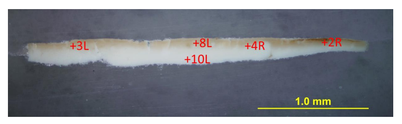
Zinc carboxylates

Image adapted from **Salvadò et al., 2019**



Translucent protrusions causing the cracking of the painting layers.
One of the most studied degradation products in oil and tempera paintings.

Morphological and spectroscopic characterisation at the nano-scale

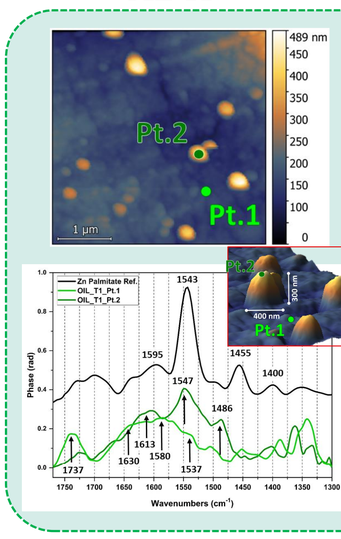


Zinc white (ZnO) painting models

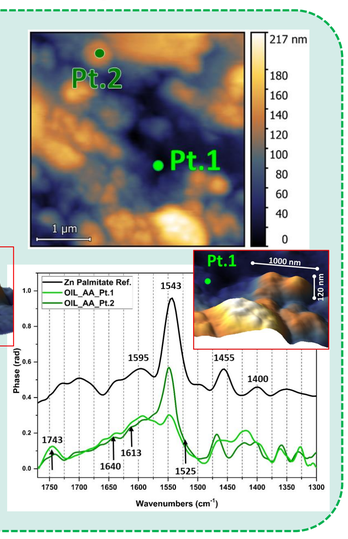
T1 → Unaged → measured after 2 months from preparation
AA → Artificially aged → 30 weeks at 40 °C, RH 99%

Zn white + linseed oil

OIL-T1

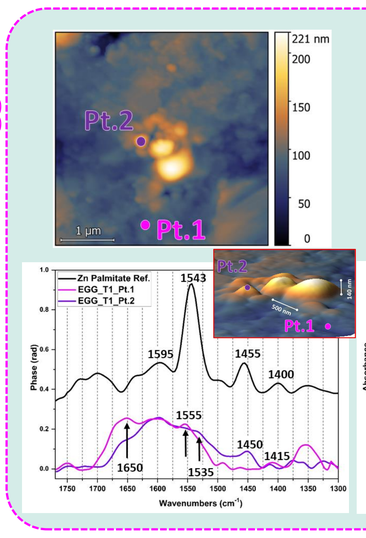


OIL-AA

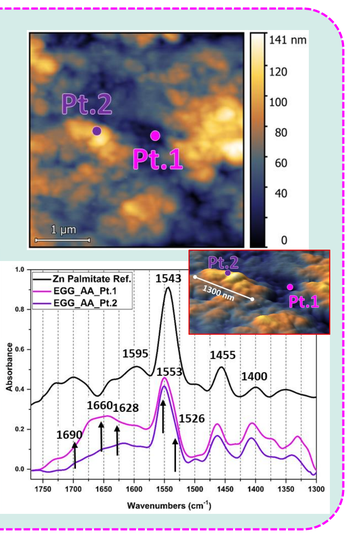


Zn white + whole egg

EGG-T1



EGG-AA



- ❖ Formation of conical objects
- ❖ Increased number of conical formations upon ageing
- ❖ Tendency to form aggregates
- ❖ OIL and EGG T1 → first step of transformation from amorphous to crystalline carboxylates
- ❖ Crystallisation has been clearly revealed by nano-FTIR spectra
- ❖ Higher number of small formations and aggregates in egg model
- ❖ Lower number of bigger formations and aggregates in oil model
- ❖ Proteins aggregation in egg model play a role in the different morphology of crystalline carboxylates

Stani et al.,in preparation

Conclusions

- ➢ At SISSI-Bio beamline of Elettra Sincrotrone Trieste (Italy), the IR s-SNOM has been used for the first time for studying complex cross-sectioned samples from the field of Cultural Heritage.
- ➢ The achievable wavelength independent lateral resolution of a few tens of nanometres allowed to enhance the level of attainable details, from both morphological and spectroscopic point of view.
- ➢ The technique provided fundamental chemical information on molecules strongly diluted in the surrounding matrix and/or degraded by time and aging.

Perspectives

New challenging materials such as roman glasses, ancient parchments and paintings are under investigation at the nano-scale at SISSI-Bio beamline.

From the end of 2023 the beamline will be equipped with an O-PTIR system covering the sub-micrometric lateral resolution and providing further complementary results to FTIR spectroscopy thanks to the coupling with Raman Spectroscopy and UV fluorescence.

O-PTIR

https://www.elettra.eu/elettra-beamlines/sissi.html

https://www.ceric-eric.eu/