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ABSTRACT BOOK

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ORAL SESSION 1



Terahertz Spectroscopy in Reflection Configuration for the Identification of Mineral Pigments

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This work proposes an experimental procedure to perform far-infrared vibrational study of inorganic and mineral pigments using terahertz time-domain spectroscopy in reflection configuration and a method to overcome the limitations due to scattering and absorption effects, which make the signals too weak to produce observable and detectable structures. Ten pigments used in ancient frescoes were chosen as samples for determining the pro and cons of the application of this technique on this class of materials. Specifically, Cu-based (Azurite, Malachite and Egyptian blue), Pb-based (Minium and Massicot), Fe-based (iron oxide yellow, dark ochre, hematite and Pompeii red) pigments and mercury sulphide (Cinnabar) were investigated. The spectroscopic characteristics of these samples set were investigated in the far- and mid-infrared frequencies, as well as the Raman active modes. Terahertz spectroscopy showed to be able to discriminate molecular phases of metal, detecting the absorption frequencies below 200 cm^{-1} of Azurite ($61.0, 74.7, 130.9, 137.71,$ and 144.3 cm^{-1}) but being blind to Malachite. In reflection geometry, Egyptian blue (69.0 cm^{-1}), Minium ($54.7, 62.8, 71.3,$ and 84.0 cm^{-1}) and Cinnabar ($39.0, 41.4,$ and 88.0 cm^{-1}) have absorption peaks in the far-infrared region, confirming the results performed in transmission configuration in other experimental works and the ones determined by theoretical ss-DFT calculations [1, 2]. Terahertz spectroscopy however failed in the detection of Fe-based pigments, because they absorb infrared radiation above 220 cm^{-1} , out of the investigated spectral range.

This work demonstrates the effectiveness of THz spectroscopy in reflection configuration for the characterization of these inorganic pigments and encourages the successful analysis of real samples, contributing to the creation of a database to guide the study of archaeological frescoes.

Key words: terahertz time-domain spectroscopy, reflection configuration, inorganic pigments

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Application of a new non-destructive and non-invasive sampling methodology based on SERS substrates for the detection of art materials

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Although Raman spectroscopy has long been used for the detection of art materials, its inherent disadvantages such as a large sample requirement, poor sensitivity, poor selectivity, and the inability to identify conclusively many compounds, strongly limited its potential and wider applicability. Further potentials of the technique are being explored through the development of surface-enhanced Raman spectroscopy (SERS), in which amplification of the signal mainly arises from the interaction of the Raman transition moment of the adsorbed molecules with the light-induced electromagnetic fields on the appropriate metal surface or nanostructured substrate. Additionally, SERS has the advantage of quenching the fluorescence, thus allowing to reach even lower limits of detection with respect to traditional Raman spectroscopy. In the cultural heritage field, micro-destructive methods are generally preferred to destructive ones, due to the limited amounts of material required and SERS-based methodologies are emerging as promising applications.

A novel non-destructive and non-invasive methodology, based on a recently developed nanostructured SERS substrate [1] was applied to solve differently analytical challenges, from the detection of degradation markers from the surface of plastic contemporary artworks [2], linseed oil films [3] or restored prehistoric dolmens to the identification of dyes in Japanese woodblock prints [4], pen drawings and other cultural heritage artifacts [5].

Independently on the analytical target, either an artistic polymer surface, an oil painting or a woodblock print, the first step of our procedure consists in the application of an appositely developed silicone strip sampler onto the surface of interest for a few seconds. Physisorbed target molecules are then dissolved in an adequate solvent and transferred onto novel SERS-active Al-coated 3D nanostructures (enhancement factor of 10^9 for a 514 nm excitation wavelength). The upper molecular weight limit of the extracted molecules is around 2 kDa, with a lower molecular weight cutoff of just few hundreds of Daltons. It was estimated that the detection limit is in the order of 1 picogram.

As an example, the sensitivity of the approach was demonstrated by analyzing oligomeric degradation markers resulting from the artificial photo-ageing of linseed oil and model polymers commonly used in artworks, and also from plastic-made contemporary artworks. The procedure was additionally applied on a Japanese woodblock print dated to the beginning of the XX century. No visible signs of material removal were reported after sampling, yet collected Raman spectra allowed discriminating the different coloring media. Azo dyes, Prussian blue and carbon black, as well as inorganic pigments, e.g. arsenic sulfide and mercury sulfide (vermilion), were easily detected. We finally show that the successful application of the procedure depends on the fine-tuning of an unconventional sampling approach, easily adaptable to the diverse analytical challenges usually faced in heritage science.

Key words: Raman spectroscopy, contemporary artworks, plastics, dyes, linseed oil

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Novel optical-photothermal infrared (O-PTIR) spectroscopy for the sub-micron molecular characterization of cultural heritage

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Optical-photothermal infrared (O-PTIR) spectroscopy is a recently developed molecular spectroscopy technique, which allows to obtain chemical information on organic and inorganic samples at a submicrometric scale. The high spatial resolution ($\approx 450\text{nm}$), potential lack of sample preparation and comparability of the spectral results to traditional FTIR spectroscopy, make it a promising candidate for application in heritage science.

This work presents the first use of O-PTIR for the study of cultural heritage, focusing on the identification of both original materials and degradation products. Two types of objects were considered: an extremely small fragment from a painting (*L'Arlésienne* by Van Gogh) and a series of small, degraded 16th-century brass and glass objects. Both cases presented intrinsic analytical challenges, linked to the limited size and/or chemical nature of the samples, or to the complex geometry of the objects. This made it impossible to answer crucial research questions on these unique pieces with traditional state-of-the-art speciation techniques (including SR- μ FTIR, μ Raman and MA-XRPD). O-PTIR, on the contrary, allowed to overcome these limitations, unraveling key chemical information which would have otherwise remained hidden. In particular, the results obtained on the paint fragment, include the sub-micrometric chemical imaging of the complete stratigraphy of the painting, and the detection of geranium lake pigments in the paint layers, failed with other high-end techniques [1]. The analysis of glass and metal objects further confirmed the great potential of O-PTIR, with the implementation of this technique in a multianalytical approach enabling the successful non-invasive characterization of original materials and degradation products. This ultimately uncovered markers of glass-induced metal corrosion processes on the surface of both glass and metal objects [2].

Building upon these striking results, advantages and disadvantages of this novel spectroscopic technique compared to other state-of-the-art methods currently employed in heritage science will be thoroughly discussed.

Key words: O-PTIR, molecular spectroscopy, Van Gogh, glass, metal

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