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Editorial

Focus point on advances in photonics for heritage science: developments, applications and case studies

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Photonics is considered the flagship technology that will power innovation in the twenty-first century, just as electronics did in the twentieth century. The impact of Photonics in European economy is stated by the Photonics21 platform [1] that aims to establish Europe as a leader in the development and deployment of photonics technologies.

Photonics is the science of light and is considered one of the key enabling technologies for future innovation in all industries. New photonic applications are emerging in various fields, such as environmental monitoring and medicine. The same technological innovation is being adopted in the field of heritage science, where photonics is the foundation for the application of a range of non-invasive, non-contact, and often portable devices for studying works of art and artistic materials.

In this Focus Point, we have selected seventeen papers that present a range of optical and photonics-based techniques, highlighting their advantages and limitations, as well as current and future applications to study our heritage.

1 Photonics-based techniques

Daffara and coauthors [2] discuss the use of optical profilometry, based on conoscopic holography scanning, to study the surface roughness of highly reflective metal samples. Authors demonstrate how the method enables the collection of a high-resolution and high-accuracy dataset (with 0.1 µm depth and 5 µm lateral resolution) that is representative of the micro-surface structure of samples. In heritage science the method has interesting applications for the monitoring of cleaning treatments on metal artworks.

Hyperspectral imaging is a powerful tool to document, monitor and investigate the surfaces of works of art. In this Focus Point two papers discuss the use of an innovative hyperspectral camera that employs an ultra-stable interferometer to achieve high spectral accuracy. In a first paper, Candeo and coauthors [3] describe its use for diffuse reflectance imaging of paintings and discuss the advantages and drawbacks of the method with respect to the commonly used line- and spectral-scanning approaches, also suggesting strategies to increase the dynamic range of cameras and to achieve a balanced responsivity in the spectral range of interest. In a second paper, Ghirardello and coauthors [4] employ the same interferometer to perform hyperspectral imaging of the optical emission from artistic surfaces and samples. By coupling the interferometer with a time-gated camera or with variable fluence excitation authors demonstrate how multiple emitting species in paints can be better separated and identified based on their different emission lifetime and spectral features.

Optical techniques are optimally applied in artwork analysis to obtain structural, morphological, and compositional information in a non-invasive way. However, the multilayered structure of a painting hampers the penetration of light, making the non-invasive sectioning particularly challenging. Photo-acoustic imaging, originally developed for biomedical applications, can overcome the above-described detection limit as disclosed by Dal Fovo and coauthors [5]. For the first time, the method has been tested on a nineteenth-century painting to disclosure hidden features of the painting and of its canvas support.

The possibility of obtaining information from inner layers is studied in a further paper [6], where defocusing light in micro-spatially offset Raman spectroscopy (micro-SORS) is employed to study the diffusion processes of an agent into an opaque material. Authors demonstrate how the method, under certain conditions, can provide information on the depth of penetration of added materials. This application could pave the way for the non-invasive monitoring of the penetration effectiveness of conservation treatments in works of art.

Another paper focuses on the Raman spectroscopy combined with a novel extraction method to improve the detection of red lakes in paintings [7]. The identification of lake pigments using in situ techniques is an ongoing challenge, as these pictorial materials are usually present in low concentrations and mixed with other organic and inorganic compounds. Currently, the identification of

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the dye present in lake pigments can be achieved through its extraction from the sample matrix and subsequent chromatographic or surface-enhanced Raman spectroscopy measurements. In this paper, the authors propose a novel extraction method that exploits the solubility of red lakes and their subsequent recrystallization in a hydrogel. The method, tested on naturally aged mock-up panels and on a historical painting, is of considerable interest because, in addition to the dye identification, it provides information about the matrix to which the dye is bound.

Kokkinaki and coauthors [8] demonstrate applications of laser-induced fluorescence spectroscopy for the monitoring in real time of the thinning of a varnish layer during laser cleaning. The method exploits a simple spectral indicator extracted from fluorescence data. From a physical point of view, the spectral indicator reveals the percentage of fluorescence intensity loss as a consequence of varnish thinning. A graphical representation of this parameter versus the number of ablation pulses can indicate when the critical point has been reached in cleaning, after which the laser beam will interact with underlying paint layers.

2 Data analysis protocols

The study and identification of the palette used by an artist in a painting is often approached by combining X-ray fluorescence mapping (MA-XRF) and diffuse reflectance hyperspectral imaging measurements. In this context, Galli and coauthors [9] present a new data analysis protocol aimed at improving the synergy among the two collected datasets. First, elemental compositional maps, retrieved through MA-XRF, are exploited to classify hyperspectral imaging data. Starting from this classification, diffuse reflectance spectral endmembers are extracted, providing a good description of the palette used by the painter.

Two papers of this collection discuss how to analyze diffuse reflectance spectral data collected in the VIS–NIR spectral range (400–1000 nm) from textile artworks. In one paper [10], authors discuss how the high-dimensionality of spectra collected through fiber optics reflectance spectroscopy can be approached. In detail, they discuss two different multivariate classification methods, based on principal component analysis with linear discrimination analysis (PCA–LDA) and on soft independent modeling of class analogy (SIMCA), to distinguish between cotton, wool and silk and mixtures of these three elements. In another paper [11], authors show the study of eighteenth-century French tapestries through hyperspectral imaging and discuss the performance of two data analysis methods for identifying the materials used in tapestry manufacture and for mapping their spatial distribution. The first method exploits the use of external reference samples and maps their distribution on tapestries through the Spectral Angle Mapping algorithm, while the second method creates an internal database made of endmembers directly extracted from datasets recorded on the tapestry.

Melada and coauthors [12] discuss the possibility of automatically identifying pigments through reflectance spectroscopy measurements in the VIS–NIR spectral range (400–1000 nm). For this purpose, they evaluate high-order derivative approximation pre-processing and feature extraction methods. The study shows how spectral pre-processing of reflectance data strongly impacts the possibility of achieving correct pigment identification, where no or little data elaboration causes a wrong classification, as does the use of higher derivative spectra.

3 Case studies on artist materials and their degradation

Monico and coauthors [13] study the photochemical reactivity of cadmium red in oil paintings using a combination of non-invasive and non-destructive analytical techniques. The study shows that the degradation of cadmium red is triggered by the oil-binding medium and moisture levels, and also depends on selenium content. In another paper, Philippidis and coauthors [14] thoroughly investigate the laser irradiance conditions under which the pigment vermilion (HgS) is irreversibly damaged by laser-induced effects during Raman microscopy measurements. The study, performed on pigment particles, foresees the quantitative establishment of an appropriate regime of laser irradiation, capable of yielding reliable Raman spectra while ensuring no pigment damage. The study further suggests that laser-induced heating is the dominant phenomenon that drives the alteration of the pigment, which occurs with the transformation of the red α phase of HgS to the thermodynamically more stable β phase (commonly referred to as metacinnabar and known to be black in color) and/or to amorphous HgS.

Oujja and coauthors [15] focus on the study of alteration layers of model medieval-like glasses. To achieve a morphological and compositional characterization of the altered layers they propose the combination of laser spectroscopies and microscopy techniques, namely laser-induced breakdown spectroscopy, laser-induced fluorescence, FT-Raman, and multiphoton fluorescence microscopy. Osticioli and coauthors [16] focus on the study of pigments and gemstones present on complex decorative artifacts. To gather compositional and manufacturing information on a French folding fan, they combine Raman spectroscopy, particle-induced X-ray emission and Rutherford backscattering spectrometry and portable laser-induced breakdown spectroscopy. Albano and coauthors [17] propose an innovative protocol to chemically characterize the finishing layers of historical violins through the study of stratigraphic micro-samples by hyperspectral photoluminescence micro-imaging, μFTIR-ATR mapping and SEM–EDX analysis. Rousaki and coauthors [18] investigated street art using portable Raman spectroscopy at different excitation wavelengths combined with micro-Raman spectroscopy on selected samples achieving information on the use of paints containing dyes employed by street artists and on the degradation mechanism affecting the colored layers of the murals.

It is expected that in the future photonics-based techniques will continue to develop and will play an important role in the analysis, conservation and access to our cultural heritage. This collection of articles is a valuable reference source on the state of the art of photonic techniques for the study of cultural heritage. We hope that it will be a source of inspiration for readers to carry out new and significant research studies in this fascinating field of research.

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