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Mini Review

Non-Invasive Spectroscopy for the Study and Conservation of Cultural Heritage. A Brief Review.

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Abstract

The scientific investigation of cultural heritage objects has a long history, dating back approximately 250 years. Early studies were often based on the collection and chemical analysis of material samples, sometimes involving irreversible damage to the artworks or archaeological objects. The progressive development of non-invasive analytical techniques has fundamentally changed this approach, making it possible to investigate the composition, condition, and evolution of works of art without sampling or otherwise altering their surfaces. Among these techniques, spectroscopy has played a particularly important role. The development of optical spectroscopy, color science, and fiber-optic technologies has progressively enabled the investigation of artworks directly in situ. In the field of cultural heritage, fiber-optic reflectance spectroscopy (FORS) has become a valuable tool for the identification of pigments, dyes, glasses, and alteration products, as well as for the monitoring of color changes over time and during restoration treatments. More recently, investigations have been extended to the near- and mid-infrared regions of the spectrum and to hyperspectral imaging. These approaches provide complementary information and can be integrated with other non-invasive techniques, such as X-ray fluorescence (XRF) and micro-Raman spectroscopy. The combination of these methods represents an increasingly effective strategy for the characterization, conservation, and monitoring of cultural heritage.

Keywords: Cultural Heritage; Spectroscopy; Non-Invasive Techniques; Fiber Optics; FORS; Hyperspectral Imaging; Pigments; Conservation; Restoration.

Introduction

The scientific analysis of archaeological materials and works of art has a history extending back approximately 250 years. The earliest investigations were frequently based on traditional chemical and physical methods that required the removal of fragments or small samples from the objects under study [1].

Although such approaches provided important information about the materials used by artists and craftsmen, they inevitably involved some degree of alteration to the original object. The development of increasingly sensitive and sophisticated analytical techniques has therefore been accompanied by a growing interest in methods capable of obtaining information without sampling.

This transition has been particularly significant in the field of cultural heritage, where the preservation of the integrity and authenticity of an object is a fundamental requirement. Non-invasive spectroscopy represents one of the most important results of this evolution.

From Destructive Analysis to Non-Invasive Methodologies

Some of the earliest scientific studies of artworks are due to Gmelin, a German chemist, who was primarily interested in the embalming process, but also turned his attention to the paintings inside sarcophagi. He scraped small fragments (blue, red and yellow) from the sarcophagus and analyzed them by traditional chemical and physical techniques [2,3].

Successively, the excavations of Herculaneum and Pompeii gave a strong impulse to the study of ancient pigments. The best

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scientists of the time such as Jean-Antoine Chaptal and Humphry Davy were involved in the investigations. Empress Josephine herself was interested in the problem and delivered 7 samples of Pompeian pigments to Chaptal, while it was Davy himself who personally chose different samples of pigments from Pompei and Bagni di Tito e di Livia, thanks to the friendship with the famous artist Antonio Canova. In fact, at that time Canova as Ispettore Generale per le Antichità was charged with the care of the works connected with ancient art in Rome [4,5].

The analytical procedures available at the time relied on traditional chemical reagents, including chlorine, hydrochloric acid, and ammonia. These methods, clearly not non-destructive, however made it possible to identify materials such as ochres, green earth, Egyptian blue, red lead, cinnabar, and aluminum red lakes.

During the nineteenth century and the first part of the twentieth century, researchers became increasingly aware of the need to avoid altering works of art. Fallen fragments or micro fragments were therefore preferentially selected whenever possible. Nevertheless, truly non-invasive analysis was still far from being achieved.

Color observation can be regarded as one of the earliest forms of non-invasive investigation. Although initially rudimentary and largely qualitative, visual examination provided information without physical sampling. However, because human vision integrates light's spectral components rather than distinguishing individual wavelengths, spectroscopic analysis became essential for studying materials, including works of art.

Following Newton's demonstration that white light consists of radiation at different wavelengths, optical spectroscopy advanced through the pioneering work of Joseph von Fraunhofer, who developed a diffraction-grating spectrometer, and Gustav Kirchhoff and Robert Bunsen, who built the first prism spectroscopes. Together, their work established key principles for understanding light–matter interactions and laid the foundations of spectroscopic analysis.

The development of spectroscopy led also to an advancement of color science and supplied a scientific basis for the knowledge of the dye/pigment's properties and their interactions with light. Indeed, following the use of artificial lighting in museums, particular concern arose regarding the effects of light on the colors of works of art and a wide-ranging and thorough investigation was published in 1888 by Russell and Abney [6]. During the twentieth century, research progressively focused on the optical properties of pigments and dyes. In 1905, Albert Henry Munsell developed a systematic approach to color based on the three parameters of hue, value, and chroma, that uniquely identified each color [7].

Continuing the path that will lead to the current spectroscopic investigations on works of art, the fundamental milestones are the following ones. In 1917, H. E. Merwin widely investigated the optical properties and color theory of pigments and paints [8]. During the 1930s, F. I. G. Rawling used a tintometer to measure the color of pigments and their variations due to the presence of varnish [9,10] and, in 1939, Norman F. Barnes measured the reflectance spectra of approximately fifty pigments and calculated corresponding colorimetric data (tristimulus values, trichromatic coefficients, dominant wavelength) [11,12].

Finally, an important step toward modern in situ analysis was made in 1978, when Linda Bullock carried out the first reflectance studies of color changes over time using homemade fiber-optic equipment [13].

Fiber Optics: From Physics to Cultural Heritage Applications

Nowadays, fiber optics are widely used in every aspect of daily life and are known to people especially in relation to internet connections. But what are fiber optics?

The term "fiber optics" was coined in 1960 by the Indian physicist Narinder Singh Kapany [14], who was said to have been able to bend light. The underlying principle is based on the physical phenomenon of total internal reflection, whereby when radiation passes from a medium with a higher refractive index to one with a lower refractive index, it is reflected into the first medium when the angle of incidence exceeds the so-called critical angle.

During the 1970s and 1980s, fiber optics became increasingly important in telecommunications and sensor technology and, as early as 1974, at the Institute of Applied Physics "Nello Carrara" of the Italian National Research Council (IFAC-CNR), formerly IROE-CNR, a device for spinning fiber optics was developed [15]. Afterwards at IFAC-CNR both fundamental and applied research was extended to telecommunications [16] and optical sensors [17,18].

These developments also opened new possibilities for spectroscopy. In fact, fiber optics, allowing radiation to be sent and received remotely from the spectrophotometer, made it possible to carry out in situ investigations without any sampling, allowing the spectrophotometer to be physically separated from the object being investigated.

The First in Situ Applications

It is on the basis of these premises that the first non-invasive in situ investigations were carried out in 1983 when, for the first time, the frescoes by Masaccio, Masolino and Filippino Lippi in the church of Carmine, Florence, were examined using a Perkin-Elmer 552 spectrophotometer equipped with an external integrating sphere [19]. The used integrating sphere was characterized by a hole 0.8 cm in diameter (area = 0.5 cm2), so only homogeneously colored spots were chosen. About one hundred spots were investigated before and after the restoration and their spectra compared to evaluate possible changes due to the cleaning and restoration process [20]. Color analysis revealed that the color change was mainly due to the increase of lightness, as is expected when the color is modified by a deposit of light-scattering particles; in addition, various pigments used by the artists were identified.

As noted above, the relatively large measurement area prompted the development of more spatially precise devices suitable for smaller paintings. Subsequent investigations therefore replaced the spectrophotometer with a fiber-optic spectrum analyzer. A fiber-optic bundle directs the instrument's radiation to the object and returns the reflected light to the detector for analysis. This configuration offers two main advantages: a higher signal-to-noise ratio and a smaller measurement area, while also allowing the overall instrument to be miniaturized.

In the early 2000s, a particular non-invasive in situ fiber-optic study was conducted on a painted glass window at the Certosa del Galluzzo in Florence. Because the transparent panels reflected too little light for conventional reflectance measurements, solar radiation replaced the instrument's halogen lamp. The sunlight transmitted through the window was collected by an optical-fiber bundle and directed to the spectrum analyzer detector. Light transmitted through an opaque white panel served as reference [21].

All previous investigations were performed using silica glass fiber optics. However, by modifying the fiber material, such as chalcogenide fiber optics, and, of course, the radiation source, it was possible to extend the investigation range from the ultraviolet to the mid-infrared [22,23]. In such a way it is possible to get information about the electronic and vibrational transitions of the material and its possible identification. However, particular attention is required in the interpretation of mid-infrared spectra due to the distortion of the spectral bands caused by the interplay of specular and diffuse radiation [23-26].

Some Applications

Since its earliest applications [19], FORS has been used to identify pigments in paintings. With its extension across the ultraviolet-to-mid-infrared range, the technique can also identify various dyes and organic materials such as glasses and plastics. Because it permits virtually unlimited measurements without damaging the artwork, FORS offers several valuable applications.

First, it enables preliminary investigations during the study of an artifact. One example is the examination of Leonardo's *The Madonna of the Yarn winder* at the Opificio delle Pietre Dure in Florence. Extensive spectral measurements of the blue sky revealed spectra characteristic of lapis lazuli, along with several slightly different spectra attributable to Thénard's blue. Because this pigment was not known during Leonardo's lifetime, its presence was likely the result of restoration work undertaken during the nineteenth and twentieth centuries [27]. The investigation was subsequently extended through hyperspectral imaging (see below), which made it possible to identify the restored area.

Furthermore, the large amount of data that can be acquired allows for statistical treatments such as principal component analysis (PCA), which allows for highlighting differences between different samples and identifying individual components in complex mixtures [28-30].

One of the major advantages of non-invasive spectroscopy is the possibility of repeating measurements over time. This allows researchers to monitor changes in the appearance and condition of an artwork without affecting the object.

Since its earliest applications [13,19], FORS has been used to monitor the color changes of a painting over time and/or following restoration. In this context, an important example concerns a predella by Luca Signorelli, housed in the Uffizi Gallery in Florence, which was examined before, during, and after restoration [31].

The monitoring campaign covered three main stages: the period from 1990 to 1995, during which the artwork was monitored before restoration; the period from 2000 to 2001, during which cleaning and restoration were carried out; and the period from 2001 to 2004, following restoration and the return of the artwork to public display.

The restoration itself took place between February 2000 and June 2001. Colorimetric FORS measurements were performed in June 2001 and subsequently in January 2003 and January 2004.

The comparison of spectra acquired at the same points over time made it possible to identify changes associated with the restoration process, namely the original varnish, the subsequent removal of the varnish and the new revarnishing. In particular, removing the old varnish caused substantial color changes, especially in the b* (yellowness) and L* (lightness) parameters. Color changes were also monitored for 30 months after the Predella was returned to display in the Gallery. Quite interestingly, a larger color variation, mainly due to the lightness, was found for the last 12 months that were monitored, than for the initial 18 months period. This fact could be attributed to a variation of the optical properties of the varnish due to the loss of the varnish solvent and natural ageing of the varnish itself [31].

Such measurements demonstrate the value of non-invasive spectroscopy not only as a diagnostic technique but also as a tool for documenting and evaluating conservation treatments.

Integration of Analytical Techniques

No single analytical technique can provide a complete description of the complex materials and processes involved in cultural heritage. For this reason, integrated non-invasive investigations are often required. FORS can be combined with hyperspectral imaging, X-ray fluorescence, and micro-Raman spectroscopy to obtain complementary information about the composition and condition of an artwork.

The combination of these techniques makes it possible to investigate both the chemical nature of materials and their spatial distribution, while maintaining a non-invasive approach.

Hyperspectral imaging represents a further development of spectroscopic investigation, combining spatially resolved imaging with spectral information [32].

The hyperspectral system first developed by the IFAC team

acquired approximately 10 points per millimeter, corresponding to about 254 pixels per inch, and approximately 500 spectral bands between 400 and 900 nm. The resulting data flow could reach approximately 10 MB/s, while a scan of a 1 × 1 m^2 surface could generate approximately 130 GB of data. A complete scan of an area of this size required approximately four hours. The system employed a prism-grating-prism line spectrograph, ImSpector V10 (Specim Ltd.), equipped with a 25 μm slit and a Hamamatsu ORCA-ERG CCD detector. The maximum investigated area was approximately 1 × 1 m^2, acquired through twenty vertical line-scan stripes at a scanning density of 10 points per millimeter Illumination was provided by a 3200 K, 150 W quartz-tungsten-halogen lamp and two Schott-Fostec fiber-optic line lights equipped with focusing lenses. The geometry consisted of symmetrical illumination at 45° and observation at 0°.

Improvement of the instrumentation for imaging were successively made [22,23,32] so that at the present hyperspectral imaging makes it possible to associate spectral information with each spatial location on the surface investigated, providing a detailed map of the distribution of materials and their optical properties.

Conclusions

The development of non-invasive spectroscopy has profoundly changed the scientific investigation of cultural heritage and requires a close collaboration between physicists, chemists, conservators, restorers, art historians, and other specialists.

The transition from traditional destructive sampling to optical and spectroscopic methods has made it possible to investigate artworks and archaeological objects while preserving their integrity. The introduction of fiber optics represented a crucial technological step, enabling spectroscopic measurements to be performed directly in situ and at locations that would otherwise be difficult to access.

Visible and near-infrared reflectance spectroscopy has proved particularly useful for the identification of pigments, dyes, glasses, and alteration products, as well as for the monitoring of color changes associated with conservation and restoration treatments.

The extension of these approaches to the mid-infrared region provides complementary molecular information, while hyperspectral imaging adds a spatial dimension to spectroscopic analysis.

Today, the most effective investigations increasingly rely on the integration of several non-invasive techniques. FORS, hyperspectral imaging, XRF, and micro-Raman spectroscopy can provide complementary information that contributes to a more complete understanding of the materials, techniques, alterations, and conservation of works of art [23,32,33].

Non-invasive spectroscopy should therefore be regarded not simply as an alternative to destructive analysis, but as a fundamental component of a modern, interdisciplinary approach to the study, conservation, and monitoring of cultural heritage.

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