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Spectroscopic and Micro-Elemental Analysis of some 20th-Century Paintings: Identifying Diagnostic Pigments

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Abstract – **This study addresses the challenges of authenticating early 20th-century paintings, a period marked by the introduction of new artistic materials and techniques. Non-destructive and micro-destructive analytical methods were employed to identify possible forgeries, including Raman Spectroscopy, Diffuse Reflectance Spectroscopy, and SEM-EDX, by analyzing the molecular and elemental composition of artworks. These techniques helped to determine whether the materials used were consistent with those historically available. The results of some investigations highlighted the presence of phthalocyanine pigments, commercially introduced only after the 1930s, casting doubt on the authenticity of the artworks. In contrast, other paintings contained materials typical of the early 20th century, suggesting their authenticity. Overall, the study underscores the importance of an integrated scientific approach in combating art forgery, particularly in modern and contemporary works.**

I. INTRODUCTION

Authenticating paintings from the early 20th century is a significant challenge, especially due to the increasing number of fakes entering the art market. This complexity arises not only from the presence of counterfeit materials, but also from the need to evaluate artists’ techniques, stylistic features, and provenance documentation. During this period, artists began using innovative materials and new techniques, driven by scientists' discoveries and synthesis of new molecules [1]. Therefore, scientific and chemical analyses are increasingly essential for the identification of pigments, binders, supports, and other constituent materials.

This study illustrates the application of both non-destructive and micro-destructive analytical techniques, such as Raman spectroscopy and Diffuse Reflectance Spectroscopy, for molecular identification, as well as Scanning Electron Microscopy combined with Energy-Dispersive X-ray Spectroscopy (SEM-EDX) for elemental composition analysis. The use of these techniques provides a scientific basis for detecting fakes by identifying materials associated with specific historical periods.

Several artworks from the early 20th century, coming from private collections and painted by well-known painters (such as Umberto Boccioni, Giacomo Balla and Julius Evola) were studied to verify whether the materials used were consistent with those documented at the time. A key finding was the detection, primarily through Raman spectroscopy, of phthalocyanine-based pigments [2], used as green and blue pigments in some of the analyzed works.

Their presence was confirmed through colorimetric measurements, comparing the spectra with those obtained from standard samples. It’s important to note that these synthetic pigments were commercially introduced only after the 1930s, making their use in authentic early 20th-century paintings unlikely. SEM-EDX further supported this conclusion by highlighting the absence of chromophores and elements typical of inorganic pigments commonly associated with that period. Conversely, some of the analyzed works displayed pigments consistent with the first decades of the 20th century, suggesting they could be authentic.

In conclusion, this study highlights the importance of combining various analytical techniques to address issues related to the identification of fake artworks, a problem that is widespread also in modern and contemporary art.

II. EXPERIMENTAL

Instrumentation

Visible Diffuse Reflectance Spectroscopy (Vis-DRS) analyses were performed using of a Konica Minolta CM 2300d portable spectrophotometer in the range 360–740 nm. Color detection was set at 1.5 seconds, and the instrument was suitably calibrated using a 100% reflective white standard.

SEM-EDX analyses were performed on micro shards taken from the painting surfaces using a small scalpel. The fragments were placed directly on the sample holder of the instrument, which consisted of an aluminum plate covered with a strip of double-sided graphite tape.

A Hitachi TM-4000 instrument equipped with backscattered electron (BSE) and secondary electron (SE) detectors and an Oxford-Aztec One EDX microprobe were employed. The analyses were carried out under low vacuum conditions in charge reduction mode, which enabled image acquisition without the need for sample metallization. Thanks to its high spatial resolution, the instrument allowed detailed investigation of surface morphology and the acquisition of false-color EDX elemental maps.

Raman measurements were conducted with a portable modular spectrophotometer from B&W Tek equipped with a microscope and an in-situ spectra acquisition system. A 785 nm excitation laser was used with a nominal power of 450 mW. However, signal attenuation from the fiber and probe resulted in less power reaching the sample (1-5% of the nominal power). Moreover, a silicon detector was used and the working range was selected between 56 cm^{-1} and 3350 cm^{-1}. Finally, the probe (d = 9.42 mm) was operated at a working distance of 5.5 mm, resulting in a 85 µm diameter of the laser spot in the focal plane.

Analyzed paintings

All the paintings that were investigated (Fig. 1, 2 and 3) belonged to private collections. Umberto Boccioni, Giacomo Balla and Julius Evola were important figures of early 20th century Italian culture linked to Futurism, an artistic and cultural movement born in Italy in 1909 that emphasized modernity, dynamism and speed.

Umberto Boccioni was among the main exponents of this movement. However, the painting that was studied (Fig. 1) precedes the artist's Futurist period and belongs to his formative phase, influenced by Impressionism and Symbolism. At this time, Boccioni was approaching the themes and styles he would later develop in Futurism. The painting dates to 1911, a year in which the artist was starting to break away from his Divisionist painting beginnings to embrace a more spontaneous, fast-paced style of rapid, almost impulsive brushstrokes [3].

Moving on, Giacomo Balla's works entitled “Forze nuove” (Fig. 2) is part of his extensive research on force lines, one of the founding elements of Futurism. In general, the title refers more generally to a conceptual series centered on dynamism and energy regeneration, in line with Futurist aesthetics and philosophy [4]. In particular, the paintings analyzed in this study belongs to the “Forze Nuove” series and dates back to 1919.

Instead, Julius Evola’s artistic production was mainly concentrated in the years between the two world wars, especially in the 1920s and 1930s. During this period he joined the Dada movement, still keeping a strong personal and philosophical bias. The investigated painting (Fig. 3) belongs to this period.

Fig. 1. Umberto Boccioni, Portrait of a young woman, 1911

Fig. 2. Julius Evola, untitled work, 1923

Fig. 3. Giacomo Balla, Forze Nuove, 1919

III. RESULTS

Diagnostic investigations were carried out into the paintings under investigation to identify the nature of the pigments by means of both Raman spectroscopy and Diffuse Reflectance Spectroscopy. In addition, some micro-fragments were taken for chemical composition analysis using SEM-EDX instrumentation. The synergic use of different analytical methodologies allowed to obtain useful information on the chemical nature of the pigments employed [5-9].

Figure 4 shows the Raman spectra acquired on Boccioni's "Portrait of a young woman" relating to a point corresponding to the blue pigment used in the painting. It was possible to assign the signal at around 548 cm^{-1} to ultramarine blue, essentially a sodium aluminum sulfosilicate used since the first half of the 19th century [10]. It is worth noting that EDX microanalysis evidenced the characteristic element diagnostic for this pigment (Al, Si, Na and S) but the presence of cobalt was also highlighted (Fig. 5A) also suggesting the use of cobalt blue, also in use at the time the painting was executed.

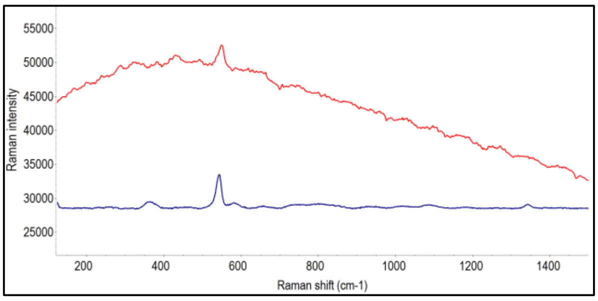

Fig. 4. Raman spectra of a blue spots on Boccioni's painting (red line) together with a spectrum acquired on a reference standard of ultramarine (blue line).

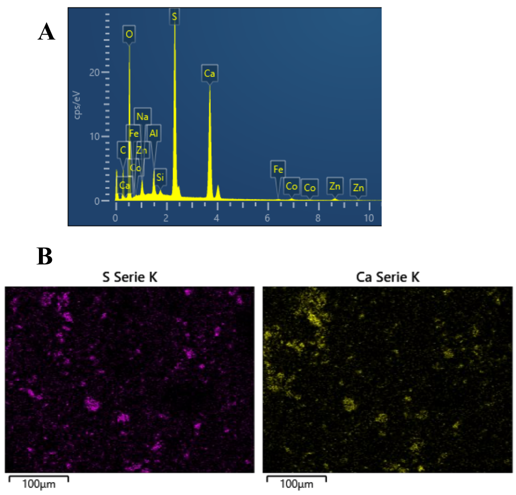

Fig. 5. A) EDX spectrum acquired on a micro-shard taken from a blue area of Boccioni's painting. Energy values on the x-axis are reported in keV. B) Elemental distribution of Ca and S on the micro-shard taken from a blue area of Boccioni's painting.

The EDX maps obtained on the same blue micro samples revealed the presence of calcium sulfate, as shown in Fig. 5B. These maps show the same elemental distribution of calcium and sulfur in the sample, indicating that gypsum was used by the artist to lighten the blue color.

SEM-EDX analyses were also used to investigate white pigments. The results highlighted the presence of zinc oxide and possibly lithopone (a mixture of barium sulphate and zinc sulfide), both consistent with the historical period in which the work was created.

Overall, the investigations into Boccioni's painting did not reveal inconsistencies with the period in which the artwork was created, suggesting that it is indeed genuine.

With regards to Evola's painting, a pigment was identified via Raman spectroscopy in the various green areas that are not compatible with the year the work was executed. This is the green pigment PG7, a copper-containing phthalocyanine, synthesized from the 1930s onwards [2]. The presence of the PG7 pigment was also confirmed by diffuse reflectance spectroscopy. No other green pigments were identified.

Moreover, a polymorph of titanium dioxide, i.e. rutile, was detected in the Raman spectra obtained on the white pigments of the painting (signals at around 238, 440 and 609 cm^{-1} in Fig. 6). Titanium was not yet commonly used at the time the work was created; its widespread adoption came later [11]. The peak at around 1010 cm^{-1} is instead due to the presence of gypsum.

Thus, pigments that were not in use at the time are present in Evola's work and this argues against the authenticity of the painting. It is also possible that a later repainting was carried out on the original.

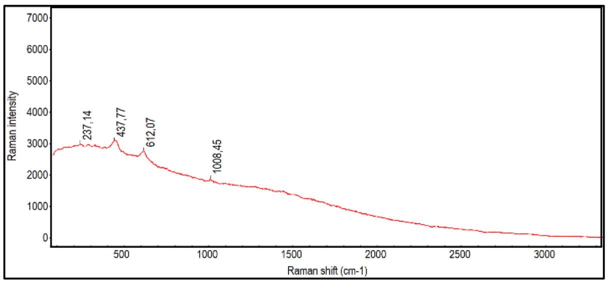

Fig. 6. Raman spectra acquired on a white point Evola's painting.

Finally, in the case of Balla's artwork, it was not possible to obtain satisfactory Raman spectra because of a very intense fluorescence background. However, by comparison with the spectra of standard reference samples, it was possible to establish the nature of the green pigment through diffuse reflectance spectroscopy, which turned out to be chromium oxide. This compound is indeed compatible with the period in which the artwork was created.

Moreover, a white micro-fragment was taken from an area underneath the painting where the canvas was fixed and analyzed by SEM-EDX (Fig. 7). The results show that both lead (probably white lead, basic lead carbonate) and zinc (i.e. zinc oxide) were present in the white pigment (Fig. 8).

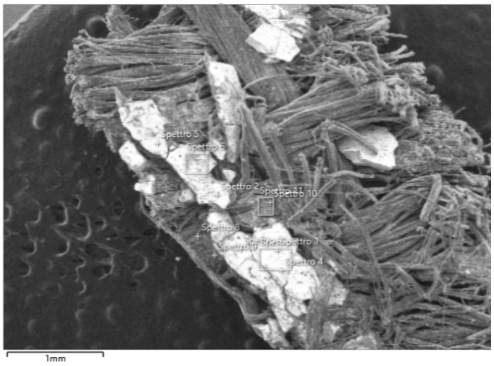

Fig. 7. SEM image of a micro shard taken from an area *underneath the canvas painted by Balla.*

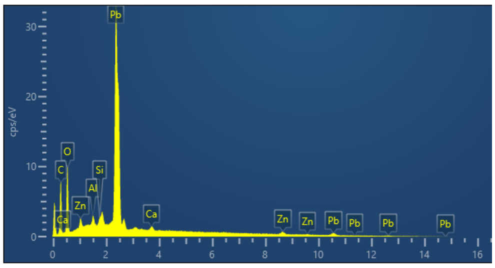

Fig. 8. EDX spectrum acquired on a micro-shard taken from a white area of Balla's painting. Energy values on the x-axis are reported in keV.

To confirm the nature of the white pigment also in the white backgrounds of the canvas (and thus not only on the border), a second micro-sample was retrieved and analyzed via SEM-EDX (Fig. 9, 10).

The results show the presence once again of zinc, but the absence of lead, suggesting that the latter comes from the preparatory layer and may not have been used as the white pigment. On the other hand, this confirms the use of a white zinc-based pigment, such as zinc oxide, which is compatible with the date of creation of the work, i.e. 1919.

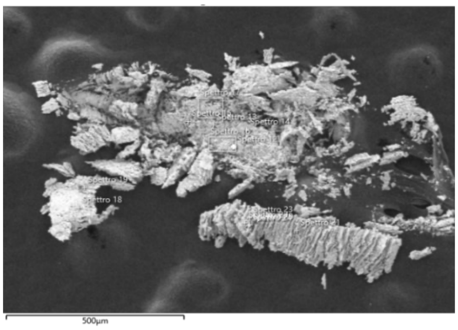

Fig. 9. SEM image of a micro shard taken from Balla's painting.

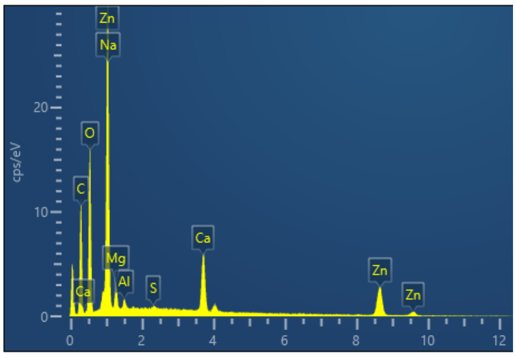

Fig. 10. EDX spectrum acquired on a micro-shard taken from a white area of Balla's painting. Energy values on the x-axis are reported in keV.

In conclusion, the analyses carried out on the painting "Forze Nuove" showed that the chemical nature of the pigments detected is completely compatible with the date of execution of the work.

The synergetic use of non-destructive spectroscopic and elemental micro-destructive analysis thus made it possible to confirm possible attributions of important 20th century paintings as well as to identify cases of non-authenticity.

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