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Raman study of a work of art fragment

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ABSTRACT

The purpose of the present report was the study and identification of an unspecified sample from a work of art by means only of a microscope coupled to a Raman spectrometer. The origin of the fragment was obscure. The Raman spectra on the virgin sample were giving no results because of a deteriorated surface treatment, in spite of the evident blue color identified by microscopic visual inspection. The sample fragmentation and the preparation of a KBr pellet allowed the distribution of the painting layers of the different components on a flat substrate reducing surface effects. Selecting the areas of different color and focusing there it was possible to identify the pigments from their Raman spectra locally acquired by selective excitation. Raman spectra were assigned by comparison with published databases. It was possible to connect Carbon Black and Orange iron oxide, as documented historically, as constituents of Azurite preparatory layer - "Morellone", according to a technique generally employed to allow the use of Azurite blue pigment on frescos, consequently the identification of typology of work of art was deducted and attributed to a fresco.

1. Introduction

The context of this work is the field of compositional identification of a work of art that should be performed before any restoration and conservation intervention. Research Institutions, Universities, museums Research Sections are interested in the scientific study of work of arts. In Italy they may perform independent work or collaborate with peripheral Organs ("Soprintendenza ai Beni Culturali"), with a regional character, of the Ministry of Cultural Heritage and Activities (the Culture Ministry of Italian Republic). Among the activities of "Soprintendenze ai beni Culturali" are the identification of work of arts, their finding, investigation and successive command of binding for their protection and control by means of specific permits on works of restoration. Moreover "Soprintendenze" make rules on work of arts transfers, exports and on projects of landscape interest. Therefore each conservation intervention, particularly on "bonded" historical artifacts including buildings, must respect specific rules established by "Soprintendenze" and the specific protocol applied in the intervention need their approval. The work of restoration must respect rules, according to the best scientific acquired knowledge and technological progresses. Works of arts periodically need conservation and restoration intervention especially if they are exposed to the natural environment and are not in a museum under strictly controlled climatic and illumination condition: materials degrade over time, and once identified, over their characteristic time. Each intervention should be reversible as a criterion, and documented. A conservation and restoration intervention first of all requires a scientific identification of materials and their assembling methods, because the respect of the original formulation and of its expressive value must be preserved as a cultural value. The new materials should match at the best the original ones chosen by the artist since they are part of the historical value of an artifact: they can tell us about the socio-economic context, the technical and philosophical evolution of an artist or of an era.

Scientific studies on work of arts are necessary preliminary steps of any action of restoration aims at the reestablishment of the original status of the elements constituting the artwork. Now days it is praxis to document the steps of any restoration intervention aiming at the conservation and repair of cultural heritage items. Conservation actions are known to be necessary over time and a good documentation of prior actions are useful and sometimes crucial. Identifications on materials are routinely required in the area of conservation, especially when past actions are not documented.

The sample examined in this paper was not from a famous masterpiece, where the techniques and materials used by the artist deserves to be revealed to reconstruct an artist's historical path for example, but it is constituted instead an unspecified deteriorated fragment.

This papers deals with the problem of identification and deserves some interest because it reports about one of such cases where the sample under study needs a destructive manipulation for a successful analysis. It will be shown how in a first attempt a straightforward

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application of the technique was unsuitable for the identification of the artefact composition since it was a really deteriorated sample.

The technique chosen for the identification was the Raman Microscopy. It uses a laser beam coupled to a microscope to obtain spatial resolution, thus selectivity in studying the sample. The focused laser beam impinged the sample and excited the Raman vibrations of the components (in general pigments and other materials constituting the layer of interest) with a spatial resolution here of about 20 μm (the beam spot size). The collected scattered light from the sample carried the spectral information about the vibrations and was analysed with a spectrometer. The outputs were Raman vibrational spectra that compared with published databases [1–4] on reference materials maight allow in general identifying the painting layer components, the pigments and their assembling.

The main results of the work were the identifications of employed pigments and the reconstruction of their stratigraphic assembly, which allowed the artefact identification typology. Specifically it could be identified that the fragment was from a fresco, from the use of the pigments stratigraphic sequence, historically reconstructed: the external layer was recognized as Azurite, the inner layers as orange iron oxide and carbon black which applied on a calcite substratum are known as components of “Morellone”, a mixture that allows the use of Azurite on frescos [5]. In absence of Morellone layer the Azurite must have been substituted with the more expensive Lapislazuli [5,6].

2. Results

In this section results from the “path analysis” are reported. First of all the virgin sample was inspected with the microscope, then given the results from the spectroscopic analysis was then destructively manipulated to obtain spectra suitable for the Raman identification.

2.1. Microscopic visual inspection of the virgin fragment and analysis

Images of the fragment under the Raman microscope are presented in Fig. 1. As can be observed in Fig. 1 (a) the surface of the sample presented blue crystallites over a finer black crust, which indicates deterioration due to external agents, which may be chemical from the atmosphere, biological or even both together.

In Fig. 1 (b) the fragment was tilted and the image, in spite out of focus regions appeared in a cross sectional way: starting from the left, a white-yellowish deep inner layer, a out of focus dark zone then the surface painted layer where bigger blue crystals of pigment were dispersed over a finer dark crust. It is possible to notice an orange spot over the blue crystallites. While it was possible to spectroscopically analyze the surface, the interesting cross section, due to instability of sample position was just taken into consideration for reference, since its image told about the layers different qualitative composition. In Fig. 2 the sample was inspected and spectra were acquired in correspondence of the laser spot (Fig. 2 a), which was translated to select different zones: the black finer crusts and the blue bigger crystallites. It is possible to notice that a 20-μm laser spot size allowed picking different portions of the surface quite selectively.

In Fig. 2 (b) it is possible to observe three different Raman spectra, labeled E, F, G. The E spectrum presented a couple of bands in the low wavenumber region and few broad bands superimposed on a curved luminescence background, the latter gives indication a possible surface treatment. In F and G spectra the same two bands can be noticed: it is a too poor result to proceed to a Raman identification, in spite the qualitatively evident blue big crystallites over the back dark crust were selectively impinged by the laser. This indicates that the surface was not virgin but deteriorated and possibly treated, for example by varnishes or oils from a previous conservative intervention, in an attempt to protect it from deterioration [5,6].

2.2. Resin embedded cross section and analysis

In the field of cultural heritage research practice it is quite common to embed fragments in a resin matrix to obtain cross sections of the different painted layers. Here in Fig. 3 (a) it is shown an example of this sampling technique: it was possible to distinguish a channel into which the sample is confined. The laser beam, about 20 μm in diameter was scanned along the channel in an attempt to collect data about the different layers. Comparing this image with the one of Fig. 1 (b) it is imaginable to understand easily that the channel was too thin (Fig. 1 (b)) for a visual inspection and for the collection of selective spectra with a beam spot size of about 20 μm. Anyway a trial is shown in Fig. 3 (b), where the obtained spectra are reported: H spectrum was relative to the polyester matrix [7], I, L, M, N where acquired along the channel and essentially present a fluorescent background with weak signals from the matrix, therefore no information for a performable Raman identification was present also in this situation.

2.3. KBr pellet technique and analysis

Given that the above-described sampling techniques gave no useful results the sample was destructively manipulated. The sample was crushed into a mortar and mixed with KBr then pressed to obtain a pellet, shown in Fig. 4 (a).

As evident from the image in Fig. 4 (a) the different layers components were dispersed and pressed and this gave the possibility to select points different in color: A where white was prevalent, B representative of the dark area, C of the orange one and D for the blue zone. The laser beam was then shined over these selected spots to analyze them. In Fig. 4 (b) are presented the results obtained on the selectively excited zones presented in Fig. 4 (a): the spectra this time are rich in peaks and the Raman identification resulted possible, taking also advantage of the recognizable colors from the microscopic image. Spectrum A (Fig. 4 (b)), relative to the white spot A (Fig. 4 (a)) allowed to identify $CaCO_3$ in calcite phase [1–4]; calcite bands are marked with asterisks of the same cyan color of the spectrum. Other two bands as contaminants, marked with black asterisks come from carbon

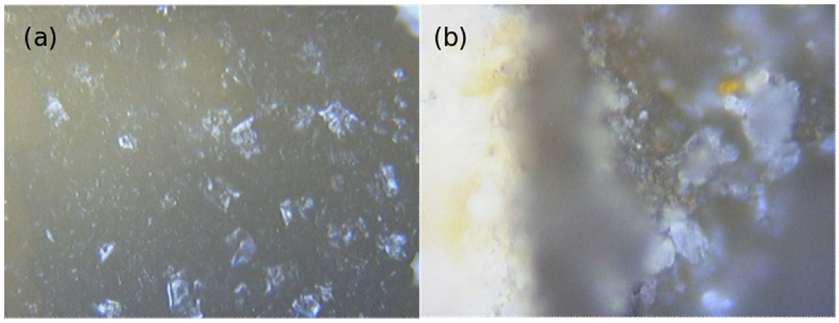

Fig. 1. (**a**) Surface image of the sample. (**b**) Cross section acquired with a tilted sample position.