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An innovative Raman scanner for rapid and controlled molecular mapping of painted surfaces

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***Abstract* – In this work, a novel Raman scanner capable of performing point-to-point mapping of relatively large surface of paintings is presented. This device employs an excitation wavelength of 1064 nm and it is equipped with a high efficiency probe in order to collect the back-scattered light from each point of analysis. The use of long depth-of-field optics as well as an auto focus system allowed maintaining the best conditions for the Raman signal acquisition during the scanning, regardless of the surface irregularities. The small dimension of the optical components and the reasonable size of mechanical parts made this instrumentation particularly suitable for on-site measurements. Finally, the Raman scanner was also equipped with an online temperature control using a thermal sensor, which allows modulating automatically the output power of the laser source in order to prevent overheating and alteration effects during the scanning process.**

I. INTRODUCTION

Raman spectroscopy is a widely used technique for molecular analysis of a variety of materials. In the field of cultural heritage, it has been proven to be suitable for the identification of pigments in different paint layers and substrates, for the recognition of alteration products [1,2] as well as for the characterization of organic materials as binding media, varnishes, and dyes [3,4]. However, especially in the case of the analysis of paintings, often, single Raman spectra do not provide sufficient information and a more complete molecular characterization of the materials is required. In the nineties several authors, focused their attention on the development of new technologies capable to collect more exhaustive analytical information by performing, for example, sequential acquisitions of many spectra on different areas of interest. Through this approach the acquisition of both spatial and spectral information (hyperspectral) of the scattered light was achieved. In practice, image profiles were reconstructed by sequential single-point acquisitions (point mapping) at each x, y position. Optimal-, under- and over-sampling were respectively achieved when the scansion step size is equal, larger and smaller than the laser spot. Whereas, another approach consists in focusing the laser to a line (line mapping) providing spectra at several points along a line thus reducing the acquisition time. In mapping, spatial resolution (both lateral and depth) depends on many parameters as laser spot size, collection optics, spectrometer, and detector. Raman mapping systems are nowadays commonly used in many applications as for example in pharmacology and medicine as well as geology, nanotechnology, and polymer science. Anyway, when considering the chemical heterogeneity of painting materials and their distribution over the surface, mapping is the most preferable approach as it provides an exhaustive material characterization. Published works prove that Raman mapping in the micro-scale dimension represent a well-established practice for the characterization of materials of different nature. However, the use of a microscope stage for moving the object implies limitations of the size and the impossibility to extend this approach to on-site campaigns. On the other hand, as highlighted above, the necessity of developing portable devices for *in situ* molecular mapping of the surface of works of art was underlined in several papers available in literature [5,6].

In the present work, we try to address this need by presenting a novel efficient Raman scanner capable of performing rapid point-to-point mapping of relatively large surfaces (on the order of square meter). Here, the technological features of the instrument along with its validation are discussed in some details.

II. INSTRUMENT

The instrumentation (Fig. 1) is made of two parts, the probe and the scanner, to placing the probe close to the sample, besides a portable PC. The excitation wavelength selected for painting characterization was 1064 nm. This choice arises from the purpose to minimize the fluorescence background and then increase the Raman signal/background. In this respect, despite the reduced efficiency at 1064 nm, besides the identification of the pigments, the system also allowed recognizing of some organic compounds used in paintings as colorants (i.e lakes), binding media (*i.e.* oils and proteins) and protectives (resins).

The Raman probe

The Raman system was equipped with a probe designed in order to optimize the collection of the back-scattered light from each point of analysis, as detailed in [7]. A feature of primary importance when scanning painted surfaces is to prevent undesired overheating and alteration of the material under analysis. Moreover, a relatively large laser spot was selected (∅ 450 µm) and a suitable optical collection coupling to the spectrometer characterized by a sufficient spatial resolution, high numerical aperture (0.4), and around 1 mm long depth-of-field optics was implemented. This last feature proved to be crucial for the analysis of objects with very uneven surfaces. The Raman probe was also equipped with a thermal control line, in order to prevent undesired overheating and alteration of the material under analysis and a USB endoscope camera, as described in [7,8]. Furthermore, in order to maintain the system focused over large surface scans an auto focus servo-mechanism was implemented in order to guarantee the reproduction of the best measurement condition during the scanning, regardless of the surface irregularities.

The scanning system

The scanning system consists of a 3-perpendicular-axes structure holding the Raman probe, essentially. The length of travel along any of the two axes perpendicular to the optical axis (z), the vertical (y) and the transversal (x) one is about 1 m. The length of travel of the linear stage along the z-axis is 100 mm. Such a system was designed with the aim to investigate quasi-planar surfaces; the correct placement of the structure in front of the square-meter addressable surface must keep the probe head within less than 100 mm distance from any point of the surface itself. Practical considerations on the ease of transportability and of placement of the system on-site suggested us to keep on-board all the necessary components excluding the portable PC. Such a solution allowed limiting the external connections of the system to a couple of USB links to the PC and to the outlet of a UPS for power supply.

To this purpose, the y axis has been implemented by means of a robust stand (System 800 IFF), provided with a dc motor, capable of lifting several tens of kg at speed of several m/min. The lighter x and z-axes mechanics as well as the platform carrying all the necessary devices and accessories are loaded onto the carriage of the stand. The travel along the y-axis is top- and bottom- limited by two end-of-travel mechanical switches. A 2 m long draw wire encoder (Phidgets P/N ENC4105_0) is used to control the carriage y-position in a SW-implemented feedback-loop with the PWM motor controller (Phidgets, P/N 1065_0, 24 V).

Fig. 1: The Raman scanner.

The x-axis mechanics was realized by a metallic structure, fixed to the carriage of the stand, to which a linear slide table (Igus P/N SHT-12-AWM-1000) is fixed. A dc gear motor with encoder (Phidgets P/N 3262E_0; 12V/0.9Kg-cm/285RPM 14:1) was directly connected to the slide shaft. Similarly to y-axis, the travel of the carriage along the x-axis is left- and right- limited by two end-of-travel mechanical switches. The maximum speed is about 1 m/min. The x-positioning is obtained in a SW-implemented feedback-loop with a second PWM motor controller (Phidgets, P/N 1065_0, 12 V).

Finally, the z-axis mechanics has been realized by means of an iron linear guide and relative carriage (Bosch Rexroth, P/N R987261834 and R044289401), which is moved by a RC Linear Actuator (Phidgets, P/N 3450_0), 100 mm length of travel. For such axis, a Servo Motor Driver was used (Phidgets, P/N 1061_1, capable of driving up to 8 servo-motors for possible implementation of two or more rotation axes). The above mentioned autofocus equipment includes a couple of IR Reflective Sensors (Phidgets P/N 1146_0), suitably placed in proximity of the spotted area. The IR sensor is capable of detecting an object placed 0.2 – 9 mm far away and measures accurately (better than 0.1 mm) its distance when placed within 1 – 4 mm. When activated, the feedback loop is able to accurately position the probe head in front of the "pixel" to be analyzed, at the optimal working distance.

The Raman probe was then fixed onto the carriage of z-axis. The bundle of optical and electrical connections between the probe and the devices fixed on the platform was inserted in a zipped cable chain (Igus, P/N 15.1.075.0); the mobile end (x-direction) is fixed to the x-axis carriage while the other end is fixed to the y-axis carriage. For ease of transportation purpose, the whole x-z system can be rotated by 90° about the z-axis, and thus fixed to the main platform, so that the amount of space required is reduced. The Nd:YAG laser, the relative driver unit, the spectrometer, and the electronic control boards along with the relative power supplies were mounted on the lifting platform, and here enclosed all around. Such an enclosure is necessary for out-of-lab use of the scanner, with consequent inner temperature increase. To overcome such a problem, especially in order to keep stable the background level of the IR spectrometer, very sensitive to case temperature, the two main parts (spectrograph and electronics) of the spectrometer itself were thermally stabilized using two independent sets of Peltier cells, heatsinks and fans, suitably placed.

The software, developed under National Instruments LabVIew^{TM}, allows full control of the operating conditions (laser thermal control, spectra acquisition, scanner control, data acquisition and display, and many others).

III. VALIDATION

The Raman scanner was preliminarily tested on a set of prepared paint samples, in order to determine the optimized measurement conditions, and collect information on the variation range of the emissivity, which was needed in order to calibrate the temperature monitoring. For this purpose, traditional pigments and an egg-tempera binding medium commercialized by Zecchi (Florence) were used for the reconstruction of mock-ups simulating Middle Ages panel paintings. According to historical recipes, multiple coats of gesso, a mixture of gypsum and hot animal glue (p/b=90/10 wt%), were applied on wood panels as preparation layer, thus to create an extremely flat and durable surface suited for the tempera painting technique. Afterwards, dry pigments including cinnabar, lead white, lapislazuli, azurite (dark), malachite (light), burnt Sienna, red ochre and yellow ochre were finely grinded and then added by mixing to egg-tempera using a pigment/binder ratio of 1:1 wt%. Once thoroughly blended, each paint formulations was evenly spread by brush on the primed wooden panels and all the samples were left to dry under laboratory conditions (T = 20 °C, R.H = 40-45%) protected from dust and direct sunlight radiation. After this preliminary optimization carried out on mock-ups, the Raman scanner was finally validated on a valuable painting attributed to Ambrogio Lorenzetti.

This was a painting on wood depicting the Madonnna with the Child dating from the fourteen century. The painting dimensions were circa 60X100 cm^2 and the identification of the color palette was required in order to help the restoration operations. Despite the whole painting was scanned by the Raman device, for image copyright reasons figure 2 shows the position of only a few points of analysis together with the correlated spectra

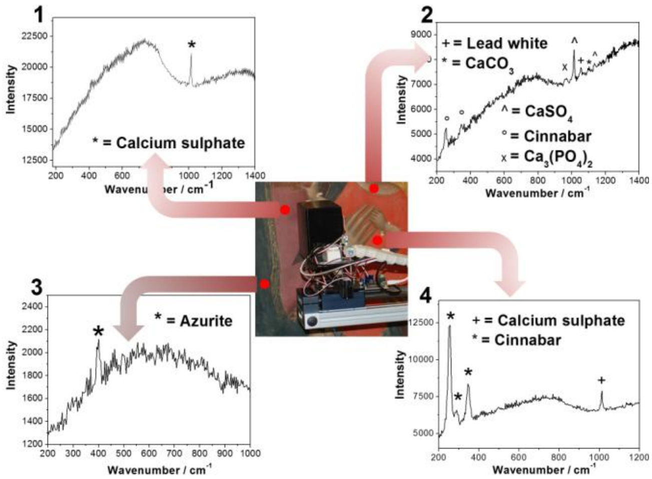

Fig. 2: A detailed view of four points of analysis performed using the Raman scanner. Several pigments were identified in the areas scanned.

In particular, the Raman analysis performed in the Lorenzetti's painting identified the presence of the following pigments:

1) a mixture of cinnabar, lead white and calcium sulphate and calcium carbonate in the flesh of Mary and Jesus child (spectrum n.2 of Fig.2)

2) azurite in the dark dress of Mary (spectrum n.3 of Fig.2).

3) Cinnabar was also used for red decoration of Mary's

headdress.

4) Irises of the baby Jesus's eyes were painted using lead white and calcium sulphate.

5) The red garment of the baby Jesus is composed of cinnabar and calcium sulphate (see spectrum n.4 of Fig.2).

6) The dark red color of the robe of Mary is made of lacquers. This was supposed on the base of the presence of a high fluorescent background in the Raman spectra acquired in that area (spectrum n.1 of Fig.2). However, this fluorescent component in the spectra did not allow identifying the type of lacquer used.

7) The fact that calcium sulphate was found everywhere (with the exception of Mary's garment) suggests it was probably used as a preparation layer.

IV. CONCLUSIONS

The Raman scanner described in this work was tested on real and valuable works of art by Sienese painters of the fourteen century as Duccio and Ambrogio Lorenzetti. Thanks to the online temperature control system, it revealed to be particularly suitable and safe for the molecular characterization of the large part of the color palettes. In this respect, despite the less Raman efficiency at 1064 nm, the identification of some organic compounds used in paintings as colorants (i.e lakes), binding media (i.e oils and proteins) and protectives (resins) was possible in some cases. Furthermore, all the implemented servo-motors, the use of compact components, along with the autofocus system and related engineering proved to be essential parts of the instrument both in terms of safety analysis and scanning time. Finally, the Raman scanner developed may be definetely considered an intelligent system for safe and on-site Raman characterization of paintings

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