Temperature-controlled portable Raman spectroscopy of photothermally sensitive pigments

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ABSTRACT

In this work, an innovative NIR Raman device (excitation wavelength at 1064 nm) was developed in order to avoid thermal stress and consequent chemical alterations of the materials analyzed. In particular, we devised and tested for the first time a sensored Raman probe allowing for temperature-controlled measurements based on a thermoelectric sensor providing the feedback signal for suitably modulating the output power of the laser source and then limiting undesired heating effects within the irradiated volume. The experimentation was carried out on cinnabar, lead white and indigo pigments frequently used during the past centuries, which presents pronounced photothermal instability. The results achieved in a set of instrumental and analytical tests using different measurement control parameters allowed demonstrating the effectiveness and reliability of the present approach for preventing thermal alterations effects during Raman spectroscopy and speeding the measurements, as well as for monitoring spectral variations associated with the crystals anharmonicity over large temperature ranges. These features along with the portability of the novel device can make in situ Raman characterisation of valuable painted surfaces including photosensitive materials very safe and efficient.

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1. Introdution

Raman spectroscopy is routinely employed in various fields of applications and in particular those where high spatial and spectral resolution of the molecular components along with the non-destructiveness are required. Moreover, thanks to its intrinsic features, the technique has also been widely exploited in order to study dynamic systems such as those for investigating catalysis processes [1], photochemical reactions [2], chemically or thermally induced phase-transitions [3], and oxidation mechanisms [4]. In all these cases the direct heating of the irradiated volume due to the laser excitation should be controlled in order to avoid undesired phase changes contributions, as well as intensity variation peak broadening and shift due to the increase of the anharmonic components [5]. Thus for example, a shift of about 120 cm^{-1} was observed for the OH-stretching overtone under temperature changes between 20 and 95 °C [6], while for polymers and biological systems phase transitions are observed at relatively low temperatures, which produce significant spectral variations [7–10].

Laser heating represents a crucial feature whenever analyzing materials with a relatively high optical absorption at the excitation wavelength. This is a common situation when investigating pigments and polymeric materials with a pigment load using the typical laser wavelengths between 514 and 1064 nm. Undesired phase changes and discolorations induced by the laser excitation assume a peculiar relevance when considering the archaeometrical applications of the Raman spectroscopy, which are experiencing a significant growing along the last years also thank to the availability of portable devices. The non-destructiveness, which is achieved by properly selecting the irradiation parameters, represents the *conditio sine qua non* whenever investigating important painted artefacts (celebrated masterpieces and unique historical objects). However, in general the achievement of safe measurement conditions can be rather difficult because of the high photothermal sensitivity of some pigment mixtures, and of natural and synthetized binders, which can then easily undergo discolorations, reduction, phase changes, and combustion with unacceptable visible effects on the painted surface understudy [11–15] and spectral alterations. This risk represents a severe obstacle to the practicability and meaningfulness of the Raman compositional mapping of painted surfaces. Spot diameters of several hundred microns would be preferable in order to collect more representative spectra and speed up the measurement but the mentioned variability of the

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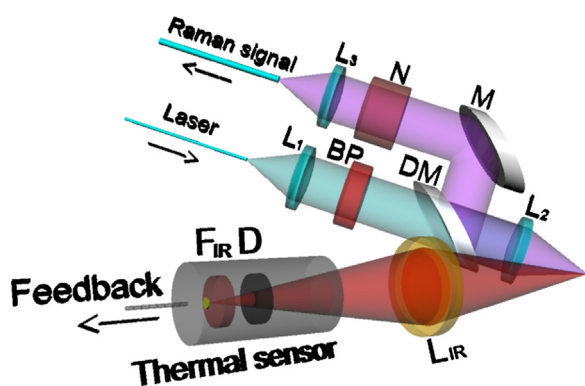
Fig. 1. Schematic view of the Raman probe setup employed for photothermal Raman measurements: L = lens; M = mirror; DM = dichroic mirror; N = notch filter; BP = band-pass filter; D = diaphragm; F_{IR} = IR filter; L_{IR} = ZnSe lens.

pictorial materials and the unpredictability of their photothermal properties make such an approach to the compositional mapping very harmful unless an accurate control of the laser induced temperature rise is achieved.

In the present work, a novel portable Raman device (excitation wavelength at 1064 nm) including an online temperature control has been developed and tested on cinnabar, lead white and indigo dye, which are notoriously photothermally sensitive pigments.

The temperature control has been achieved using a thermal sensor, which provided the feedback for suitably modulating the output power of the laser source and then limiting undesired photothermal effects within the irradiated volume. The experimentation carried out on samples of the mentioned pigments allowed showing the effectiveness and reliability of the present approach for preventing alterations during Raman spectroscopy and speeding up the molecular identification.

2. Instrumentation and method development

A portable Raman device (3.7 kg total weight) has been built by assembling a OEM spectrometer and Nd:YAG laser source (case sizes: $35 \times 25 \times 15$ cm), which was coupled to the homemade compact probe sketched in Fig. 1 ($6 \times 8 \times 10$ cm) through two optical fibers. The former (BaySpec Inc., CA, USA) was equipped with a 512-pixel deep-cooled ($-60\,^{\circ}$C) InGaAs array detector and a monochromator covering the spectral range between 165 and 1825 cm^{-1} with a resolution of 8 cm^{-1}. The exciting source was an ultra-narrow linewidth diode pumped CW Nd:YAG(1064 nm) laser with a maximum output power of 500 mW and a beam diameter of 700 μm (Innovative Photonic Solutions, NJ, USA). This laser system allows the external modulation of the output power, P(t), by means of a proportional signal $0\,V < V(t) < 1\,V$.

A thermal sensing line was conveniently designed, implemented and tested in order to collect temperature controlled Raman spectra of cinnabar, lead white, and indigo dye powders (Zecchi, Florence, Italy) flattened in small cells. They are deep red inorganic, white inorganic, and bluish organic pigments, respectively, commonly used in painting since ancient times. All of them exhibit high photothermal instability, which is cause of possible alterations during Raman characterization of paintings.

As shown in the schematic view of the probe of Fig. 1. The fiber-coupled Nd:YAG laser beam, collimated by the lens L_1, passes through a band-pass filter (BP, @ 1064 nm, FWHM 10 nm) and a dichroic mirror (DM), and is focused onto the target by the lens L_2. The Raman-scattered light, collected and collimated by the lens L_2, reflected by DM and M mirrors, filtered by means of a notch filter (N) in order to cut-off the elastic scattering contribution, is then focused by L_3 into a 200 μm core diameter optical fiber leading

to the spectrometer. The ZnSe lens, L_{IR}, collects and focuses onto the thermopile the IR radiation emitted by the irradiated area. The thermal sensor is equipped with a field diaphragm, D, in order to restrict the area imaged by the lens to the laser spot, and with a long pass filter (band 5.5–14 μm), F_{IR}, in order to shield the laser and ambient light.

A thermopile sensor with active area of about $750 \times 750\ \mu$m^2, angle of view of about 10°, response time of $t_R = 1.3$ s and an absolute accuracy at $25\,^{\circ}$C of $0.5\,^{\circ}$C was employed for thermal monitoring during Raman spectroscopy. The sensor was calibrated in order to provide the blackbody temperature, T_s, corresponding to the IR radiation collected and then used for estimating the temperature, T, of the laser heated spot. To this goal, the area of the material under laser excitation was imaged (1:1) on the active area of the sensor through the lens, L_{IR}, the IR filter (5.5–14 μm spectral band), F_{IR}, and the narrow field diaphragm, D (with a diameter of 1 mm) and the temperature was calculated by the following formula (in K) derived from Stefan-Boltzmann black body law:

$$T = \sqrt[4]{\frac{T_s{}^4 - (1-\varepsilon)R_A T_a{}^4 \theta - (1-R_A)T_a{}^4}{\varepsilon R_A \theta}} \qquad (1)$$

where ε is the emissivity of the sample under analysis, T_a the ambient temperature, R_A = laser spot area/sensor area (about 0.64 in the present condition) and θ the lens transmissivity (0.98 in the present setup). Eq. (1) is an adaptation to the present configuration of the correction formula for taking into account the reflected radiation [17]. In particular, it takes also into account the effect of the partial illumination of the active area of the sensor (R_A parameter).

The emissivity of the samples were achieved by heating them at a known temperature (as measured with a thermocouple) with an electrical resistance, imaging the heated surface using a thermocamera (PI 450, Optris), and eventually adjusting the emissivity in order to match the temperature measured by the latter with the known value.

In this way the sensor has been calibrated in order to measure an estimation of the real surface temperature at the target within the laser spot. However, in the present conditions, T still represents the average surface temperature within the imaged area, an underestimation of the real maximum temperature experienced by the material because of the inhomogeneous thermal distribution. Anyway, T is a usefully exploitable parameter in order to avoid undesired overheating and optimise the laser intensity release to the target.

The following time-dependent scaling law was assumed for suitably regulating the laser power:

$$P(t) = f(x) = \begin{cases} B\left[T_{exp} - T(t)\right]^{\frac{1}{4}} \tanh\left(\frac{t}{\tau}\right), & T_{exp} - T(t) > 0 \\ P_{min}, & T_{exp} - T(t) \leq 0 \end{cases} \qquad (2)$$

where B and τ are adjustable parameters, T_{exp} is the expected temperature set while $T(t)$ is the actual temperature measured by the sensor, and P_{min} was set to 20 mW (a reasonable low value in order to avoid to switch-off the laser). Eq. (2) represents a typical proportional control where the 4th root-dependence was preferred to the linear one in order to smooth the power variations associated to large temperature differences, $T_{exp} - T(t)$, while the factor $tanh(t/\tau)$ favours its gradual increase during the onset phase, being $\tanh(t/\tau) \sim 1$ for $t/\tau > 2$.

In practical applications, B has to be suitably selected in order to achieve the rapid convergence of the control process and, at the same time, to avoid strong power and temperature modulations. As better described in the following, when operating at T_{exp} close to a critical temperature the selection of B can become in turn rather critical.