

Report on Raman spectroscopy analysis of frescos fragments from the "Villa della Piscina" (Centocelle, Roma)

Marco Sbroscia, Ludovica Ruggiero, Armida Sodo, Maria Antonietta Ricci
Dipartimento di Scienze
Universita' Roma TRE

The color palette used for the frescos fragments has been characterized, with the aim of pointing out differences between elements belonging to different locations or different historical periods. Here we briefly introduce the Raman effect, describe the experimental conditions and finally report the results.

Raman spectroscopy is widely used in Cultural Heritage studies, because of its high sensitivity and spatial resolution, and for the short time usually required for data acquisition. Moreover, this technique in most cases does not require sampling and does not entails sample damage. It is used for chemical analysis of the artifacts (e.g. molecular identification of pigments and degradation products), in order to study ageing mechanisms, production technologies and surface treatments, degradation state and corrosion of exposed surfaces.

Raman spectroscopy is based on the inelastic diffusion of light from an illuminated portion of the sample, being the frequency shift of the diffused light with respect to the incident one a characteristic of the investigated material. The success of this technique has been boosted by the advent and rapid availability of lasers. Its success in diagnostics is due to the observation that each chemical species has its characteristic Raman spectrum, which can be used for chemical identification of materials. Importantly excitation of Raman spectra does not perturbs the chemical equilibrium between molecular species. Moreover, the spectral intensity depends on the concentration of the chemical species, allowing, at least in principle, a semi-quantitative analysis of the sample composition.

Experimental set-up

Raman spectra have been acquired by using a Labram micro-spectrometer (Horiba), equipped with three different laser sources: namely, a He-Ne a 633 nm (18 mW power), a diode laser at 532 nm (10 mW power), a diode laser at 785 nm (300 mW power). The Raman diffused light has been dispersed by a 1800 l/mm grating and collected at a Peltier cooled CCD (1024 X 256 pixel). The spanned spectral range, the acquisition time (of the order of seconds) and the number of scans have been adapted to the investigated point, in order to optimize the signal/noise ratio. In the majority of the cases of interest here, we have investigated the 200-3500 cm^{-1} spectral range, by averaging 3 scans (10 s each) and using 100X, 50X and 20X objectivs, depending on the quality of the investigated fragment. Spectra have been analyzed by using the LabSpec and Origin softwares.

Investigated samples

This report shows the analysis performed on 13 fresco fragments from different locations within the "Villa della Piscina". Sample's pictures and labels are reported in Table I.

Results

The color palette does not vary very much from one fragment to the other and consists of pigments of mineral origin, as expected for this kind of artifacts and for the assigned dating. In particular the following pigments have been identified:

- All red pigments are cinnabar (HgS).
- All dark brown and red purple colors are made of hematite (Fe_2O_3) and magnetite (Fe_3O_4).
- All yellow pigments are made of goethite (FeOOH).
- All green pigments are based on celadonite ($\text{K}(\text{Mg},\text{Fe}^{+2})(\text{Fe}_3+\text{Al})\text{Si}_4\text{O}_{10}(\text{OH})_2$). On sample "Campione 13-parete ghirlande" we have observed the presence of a mixture of celadonite and malachite (CuCO_3), while on sample "Campione 9 - cassetta fiore" grains of Egypt blue ($\text{CaCuSi}_4\text{O}_{10}$) are mixed with celadonite.
- All blue pigments consist of Egypt blue.
- All grey pigments are mixtures of red and yellow ochre with Egypt blue and carbon black.
- The white color is usually obtained by using calcite ($\text{CaCO}_3(\text{OH})_2$), but on sample "Campione 11 - parete cassone" we have observed the presence of dolomite (MgCaCO_3).
- The violet color on sample "Campione 9 - cassetta fiore" is a mixture of cinnabar and celadonite.
- The black pigment is carbon black.
- On sample "Campione 11 - parete cassone" we have found the finger print of anatase (TiO_2), which could be due to the presence of a white clay (kaolin), not easily detectable by Raman spectroscopy, which contains anatase as an impurity, or to a recent conservative intervention, since anatase is often used as a whitener.

TABLE I

<p>Gruppo 1</p> 	<p>Gruppo 2</p> 	<p>Gruppo 3A</p> 	<p>Gruppo 3B</p> 
<p>Gruppo 4</p> 	<p>Campione 6 - Cassetta $\alpha 1$</p> 	<p>Campione 7 - Cassetta $\alpha 1$</p> 	<p>Campione 8 - Cassetta fiore</p> 
<p>Campione 9 - Cassetta fiore</p> 	<p>Campione 10 - Parete cassone</p> 	<p>Campione 11 - Parete cassone</p> 	<p>Campione 12 - Soffitto cassettoni</p> 
<p>Campione 13 - Parete ghirlande</p> 			

Conclusions

The color palette of the fragments available at this time has been identified by Raman spectroscopy. On some yellow, green and white samples we have identified differences, which could be significant of a different provenance or dating, or request for different clues. This suggestion needs to be checked by increasing the sample statistics. Another issue deserving attention is the presence of anatase.