The SERS effect is mainly due to the enhancing of the electromagnetic field in correspondence of a surface that has been made appropriately nano-rough or of metal nano-structured systems (nanoparticles of Au, Ag, Pt, Cu, etc.). The different kinds of supports for this technique are called SERS substrates. In the last fifteen years, several substrates have been developed thanks to the nanotechnologies [20-21].

In the field of cultural heritage the most used substrates are silver colloids prepared according to various techniques [22-24]. SERS technique have been employed for identifying organic dyes, binders, resins, in textiles, paintings, ancient cosmetics, inks, with a quick detection of low concentrations until $10^{-5}$ M [25-26]. The method is based on the application of few microliters of colloid suspension to the surface to be analysed or otherwise the sample solution could be mixed with the colloid sometimes with the addition of aggregating agents improving the contact between the analyte and the Ag nanoparticles [25, 27]. In case of complex matrices, a pre-treatment of the samples could be useful such as the extraction of the dye compound from the sample mixture [24]. So, SERS can be considered a micro-invasive and micro-destructive technique.

In this contribution, a case study about rock-hewn wall paintings in Cappadocia (Turkey) will be presented, as relevant example of application of Raman spectroscopy to investigate in depth the constituent materials and their change in use during the medieval centuries for knowledge and for conservative purposes.

**EXPERIMENTAL**

The Raman analysis were performed by a Labram Model spectrometer of the Horiba JobinYvon with a spatial resolution of 1 µm and the possibility of fast detection owing to the use of a CCD detector with 1024 x 256 pixels cooled to -70°C by the Peltier effect. The spectral resolution was 1 cm⁻¹. The exiting wavelength was the 632.8 nm red line of a He-Ne laser. Integration times varied between 10 and 20 s with 5 accumulations. The output power for the He-Ne laser was 5 mW.

Identification of pigments, minerals, and others was performed by comparing the experimental spectrum with
those found in the main database available on-line [28-31] or with spectra obtained in our laboratories during the years of work on different artefacts.

RESULTS - ROCK-HEWN WALL PAINTINGS IN CAPPADOCIA

Since 2006, an Italian group has been entangled in a project on “Rupestrian art and habitat in Cappadocia (Turkey)” and in central and southern Italy. Rock, excavated architecture, painting: between knowledge, preservation and enhancement”, directed by Prof. Maria Andaloro. The project has been developed thanks to the funding of Italian Ministry of Education, University and Research (PRIN 2010) and the permission granted by the Turkish Ministry for Culture.

Within this project, an important part was devoted to the study of the materials and techniques in Cappadocia’s churches, both of the support rock and paintings [6, 32-33] with different aims: at knowing these never studied materials, at understanding their degradation phenomena, at finding the most appropriate methodologies to preserve them as extraordinary heritage (UNESCO heritage).

In this regards, micro-Raman spectroscopy was widely used as powerful technique to study pigments, mortar binders, degradation products. More than fifty churches were studied starting from 2006 until today so gathering a deep knowledge of the materials and techniques of the rock hewn wall paintings of Cappadocia region through the Middle Ages centuries.

An interesting characteristic of Cappadocia paintings is the use of gypsum rich mortars or of gypsum as setting layer for paintings (Fig. 1). This was supposed due to the use of a so-called “sweet plasters” by adding lime to that rock containing calcium sulphate [34]. Gypsum or gypsum rich mortars are well preserved in Cappadocia due to the quite dry climate that prevents the solubilization of calcium sulphate. Sometimes, anhydrite was also found in the wall paintings to testify the dry environmental conditions (Fig. 1F). A mapping of gypsum was made by using micro-Raman spectroscopy directly on the cross-sections resulting in a clearly presence of this compound associated to calcite (Fig. 1E) or as high crystalline material (Fig. 1H).

Micro-Raman spectroscopy was particularly useful to characterize pigments allowing defining the palette employed in Cappadocia rupestrian paintings. A wide use of ochre and earth based pigments was found. These materials are often constituted by very pure crystalline compounds, such as hematite, goethite and jarosite (Figs. 1F, I, L). A peculiarity of goethite based pigments from Cappadocia is their extreme stability to laser irradiation during Raman analysis. In fact, usually goethite undergoes transformation into hematite due to laser irradiation. Also green earths in Cappadocia paintings give well defined Raman spectra even if the red line of He-Ne laser has been used (Fig. 1G).

Apart traditional pigments of medieval wall paintings, in Cappadocia also other compounds were found such as lead-based pigments, especially in the oldest churches, indigo, ultramarine blue, red lakes, often applied by a secco technique.
High purity ultramarine blue (Fig. 2) was widely used in the Tokali church (10th century) for backgrounds, garments, haloes giving extraordinary wall paintings. In the backgrounds ultramarine was used on a grey setting layer made of gypsum and carbon black (see Fig. 2C). Often, pigments are found to be mixed with carbon black in order to obtain darker hue (Fig. 2G). In the Tokali church organic dye were also found such as indigo and red lake (Figs. 2F, H). Indigo was found in mixture with ultramarine in dark blue areas (Fig. 2H).

Lead-based pigments are used especially in the archaic churches in different forms: lead white (basic lead carbonate), red lead (lead tetra-oxide) and litharge (lead oxide). For example, in the church of Karşıbebek (6th-7th century) the red aniconic decoration are made of red lead and hematite on a gypsum setting layer (Fig. 3). The careful micro-Raman investigation on pigment powders sampled from a blackened area (Fig. 3B), allowed for discovering the presence of different compounds: red lead associated with anglesite (Fig. 3C); hematite associated with magnetite, anglesite and gypsum (Fig. 3D); plattnerite, a dark brown compound generally produced by alteration of lead based pigments (Fig. 3E); anglesite associated to gypsum (Fig. 3F). Plattnerite is a very low Raman scattering compound giving a quite noisy spectrum.

**CONCLUSIONS**

This paper tried to outline the principles of Raman spectroscopy with a general presentation on the main methods used in investigating cultural heritage materials, on the basis of authors’ experience in the specific field. The case study proposed offers a clear evidence of how micro-Raman spectroscopy is a powerful technique able to study pigments, binders, minerals etc. both on powders and cross sections so giving valuable information on the constituent materials, on the execution techniques and on the conservation state of the artefact.

The project in Cappadocia was a great opportunity to apply a work methodology based on a multidisciplinary approach to deepen the knowledge of the rupestrian habitats and, specifically concerning Raman analysis, to create a database of spectra for materials never investigated before by this technique.
ACKNOWLEDGMENTS
The Raman analysis was performed within the project PRIN 2010 “Rupestral art and habitat in Cappadocia (Turkey) and in central and southern Italy. Rock, excavated architecture, and painting: between knowledge, preservation and enhancement” directed by Prof. Maria Andaloro. The project could not have been carried out without the kind permission granted by the Turkish Ministry for Culture. The photographs of the churches shown in Figures 1-3 were taken by Gaetano Alfano.

ABSTRACT
This paper aims at reporting an overview of the principles and applications of micro-Raman spectroscopy in cultural heritage. Micro-Raman was used for characterizing painting pigments, inorganic binders, degradation materials in artworks with different goals: to know the materials and so the execution technique, to investigate the state of preservation, to establish the authenticity of the artefacts. The micro-Raman analyses were often performed on the occasion of conservative projects and they were able to supply valid and useful information to the conservators during their work. As case study, the project on the investigation of rock-hewn wall paintings in Cappadocia (Turkey) will be shortly presented as exemplificative of application of Raman techniques for the knowledge of the constituent materials, for supporting the conservation work and for detecting degradation products. The analysis was performed in the Interdepartmental Instrument Center of Modena and Reggio Emilia University by a bench top system equipped with a microscope allowing for studying in non-destructive way different kinds of samples: powders, cross and thin sections, pre-treated samples.
References


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