Application of micro-Raman spectroscopy for conservation projects in art and archaeology with a case study on Cappadocia rock-hewn wall paintings

By Pietro Baraldi, Cecilia Baraldi, Claudia Pelosi

Micro-Raman technique is today widely used in cultural heritage investigation both for inorganic and organic analysis. This paper would make a short review about possible applications of micro-Raman with a special focus on the results obtained on the wall painting materials of Cappadocia rupestrian churches.

An overview on Raman spectroscopy

Raman spectroscopy has been proposed as a reliable, sensitive, specific, non-destructive technique ideal in the examination of artwork materials [1-2]. Raman spectroscopy is a relevant technique for knowledge of the techniques in artworks [3-6], for conservative purposes [7-10], for authentication assessment [11-12].

Raman technique probes molecular and crystal lattice vibrations and therefore is sensitive to the composition, bonding, chemical environment, phase, and crystalline structure of the sample materials [2]. The technique is based on the effect of scattering process in a sample irradiated with a monochromatic photon beam. In particular, the inelastic scattering of the monochromatic radiation is at the base of the technique [13]. Raman spectroscopy had some intrinsic limitations that in the past prevented a wide use of this technique, especially in cultural heritage applications. In fact, the Raman scattering gives rise to weak signals, which sometimes are covered by broadband fluorescence emission from samples. These limitations, coupled with the high costs of instrumentations clearly limited the use of the technique in respect to other molecular spectroscopies such as FT-IR. The introduction of new optical configurations and CCD detectors improved a lot the sensitivity of modern Raman spectrometers also reducing the costs [14-15]. Moreover, the introduction of near-IR lasers together with dispersive or interferometric spectrometers further removed the limitations due to fluorescent materials samples [1, 16]. Furthermore, the coupling of a Raman spectrometer to an optical microscope further increased the versatility of the method making possible the analysis of components of heterogeneous samples on a micrometre scale and by reducing greatly the amount of sample required from precious materials [2, 17]. Further development in Raman spectroscopy derived from the use of portable instruments, particularly suited in art and archaeology applications, even if these spectrometers have several limitations mainly due to their low sensitivity in detecting low scattering materials [18], and in SERS (Surface-enhanced Raman scattering) a specific technique useful in enhancing weak Raman signals (from 10^8 to 10^{15} times) or decrease the fluorescence broad-bands [19].

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 be employed for identifying organic dyes, binders, resins, in textiles, paintings, ancient cosmetics, inks, with a quick detection of low concentrations of molecules, 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 mediaeval 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 1026 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

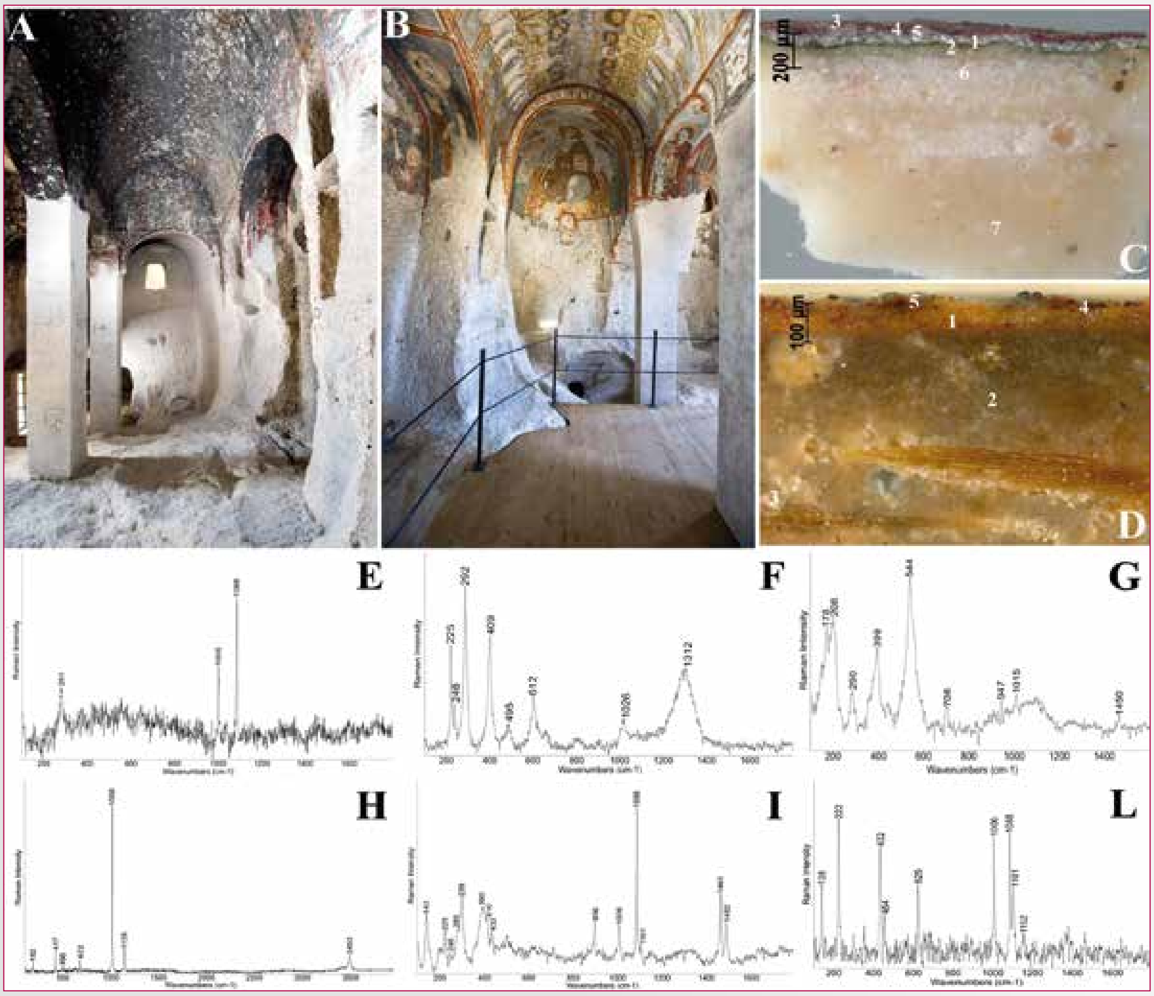

Fig. 1 - the Forty Martyrs church at Şahinefendi (Cappadocia, Turkey): A) a view of the interior of the church before the restoration; B) a view of the interior of the church after the restoration; C) cross section of a sample including three painting phases of the wall decoration with the points analysed by micro-Raman spectroscopy; D) cross section of the fourth phase (13th century) with the points analysed by micro-Raman spectroscopy; E) Raman spectrum of point 6 in C) showing calcite (band at 1088 cm^{-1} and 281 cm^{-1}) and gypsum (band at 1008 cm^{-1}); F) Raman spectrum of red layer, points 3 and 4 in C), showing all main bands of hematite (Fe2O3) and traces of anhydrite (band at 1026 cm^{-1}); G) Raman spectrum of green layer, point 2 in C), with the characteristic bands of green earth; H) Raman spectrum of point 5 in C) with the bands of high crystalline gypsum; I) Raman spectrum of point 5 in D) showing the presence of hematite (bands at cm^{-1}: 225, 246, 410), goethite (bands at cm^{-1}: 299, 390), lead oxide (band at 143 cm^{-1}), calcium oxalate (bands at cm^{-1}: 896, 1465, 1492), jarosite, $KFe_3(SO_4)_2(OH)_6$, (bands at cm-1: 432, 1006, 1101) calcite and gypsum; L) Raman spectrum of point 1 in D) showing the presence of all main bands of jarosite.

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.

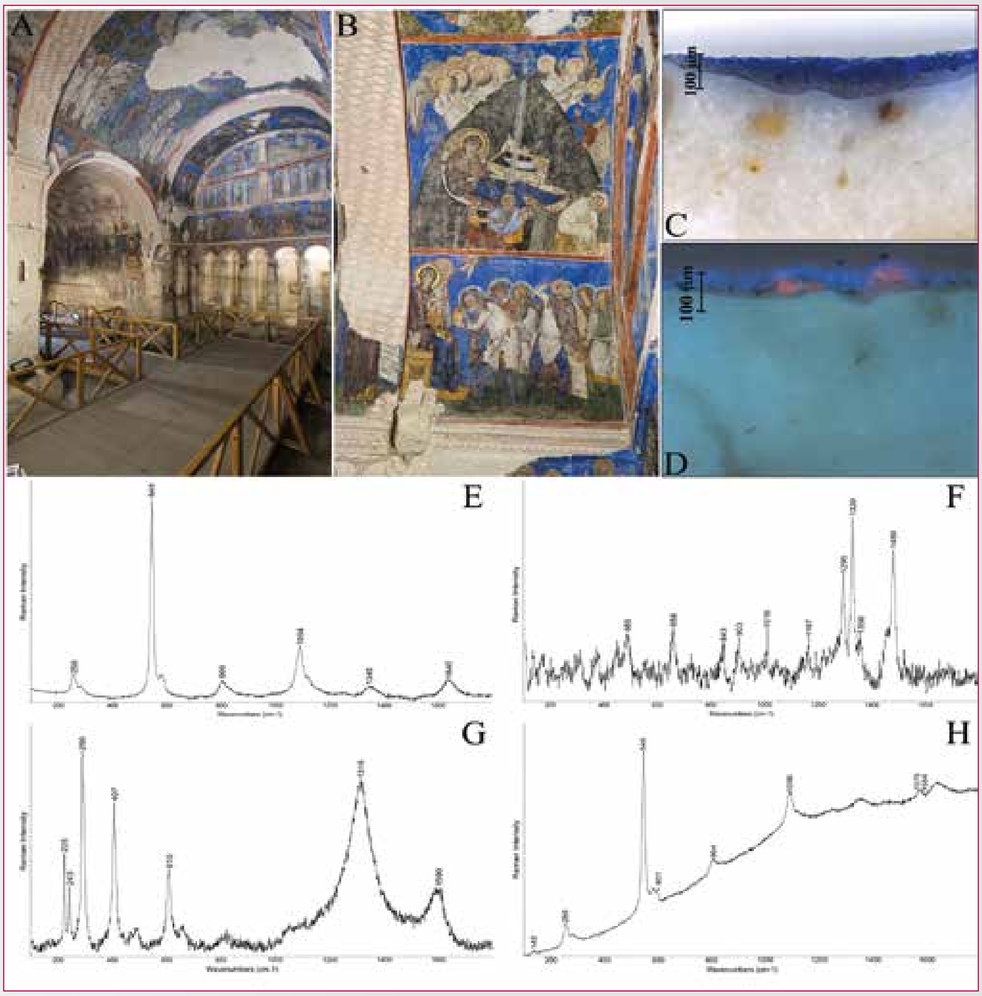

Fig. 2 - The Tokalı church at Göreme (Cappadocia, Turkey): A) a view of the interior of the church; B) a detail of the paintings showing the extraordinary use of ultramarine blue; C) cross section of a sample from the blue background in B) showing the presence of a grey setting under ultramarine blue; D) cross section of a sample from the north wall, visible in A), under ultraviolet radiation showing a red fluorescent organic dye; E) Raman spectrum a blue pigment showing the typical pattern of pure and crystalline ultramarine blue; F) Raman spectrum of the red organic dye, showing the bands of alizarin-type compound; G) Raman band of a dark red area showing the presence of hematite and carbon black bands. This last material has two broad bands at about 1340 and 1590 cm^{-1}, the first one partially overlapped with that of hematite at 1312 cm^{-1}; H) Raman spectrum of a dark blue area exhibiting the presence of the ultramarine bands associated to weak peaks due to indigo, a natural organic dye (cm^{-1}: 140, 601, 1575, 1584). Indigo was found also in other samples from the Tokalı church.

High purity ultramarine blue (Fig. 2) was widely used in the Tokalı 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 Tokalı 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 Karşibecak (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 base 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.

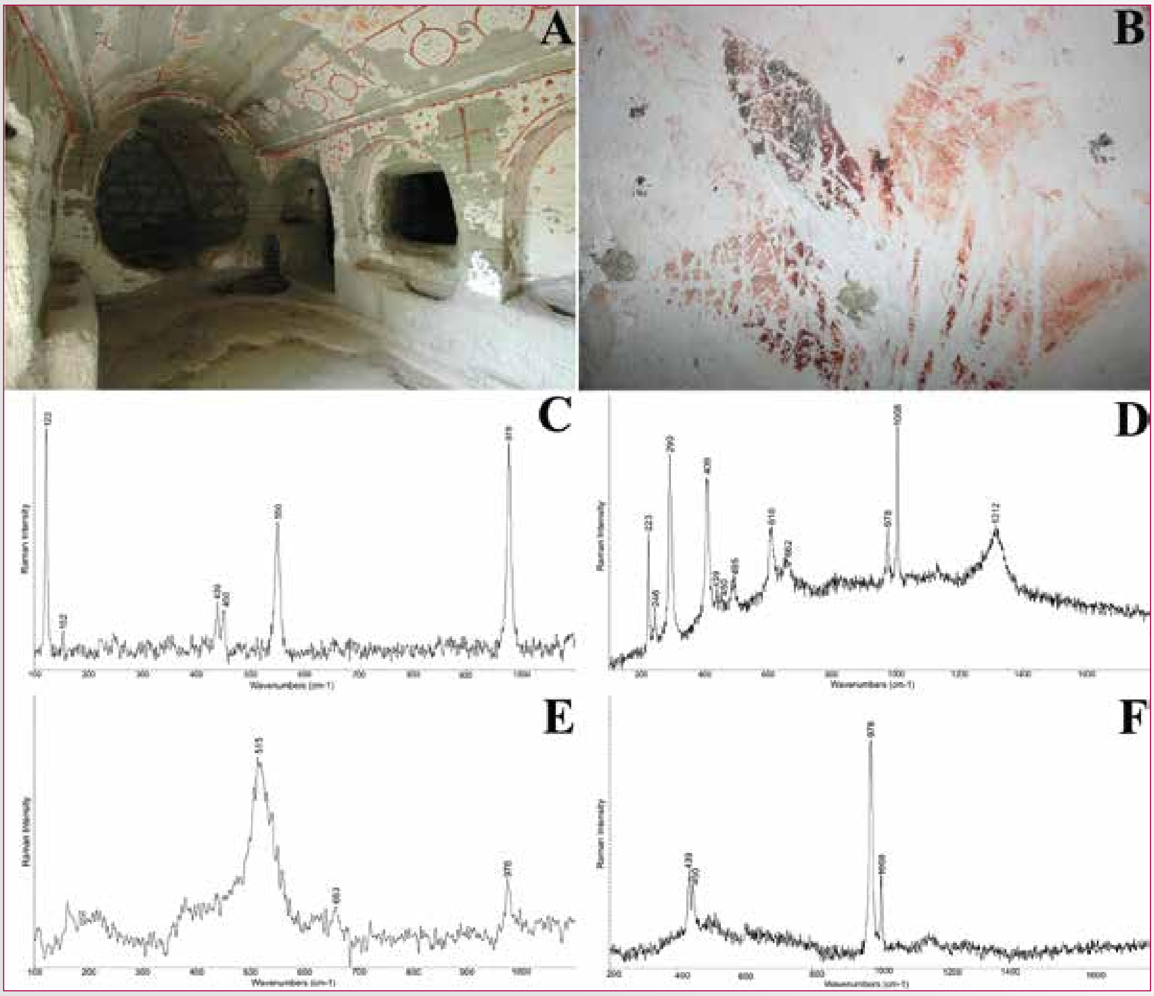

Fig. 3 - the Karşibecak church (Cappadocia, Turkey): A) a view of the interior of the church; B) a detail of the paintings with a clear darkened area; C) Raman spectrum of a red-orange grain in powder microsample taken from B) area showing the bands of red lead (Pb_3O_4, cm^{-1}: 122, 152, 550) and anglesite ($PbSO_4$, cm^{-1}: 439, 450, 978); D) Raman spectrum of a red grain in powder microsample taken from B) area showing the bands of hematite, magnetite (662 cm-1), gypsum and anglesite; E) Raman spectrum of a dark brown taken from B) area showing the bands of plattnerite (PbO_2) F) Raman spectrum of white grains in powder microsample taken from B) area showing the bands of gypsum and anglesite.

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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.

Keywords

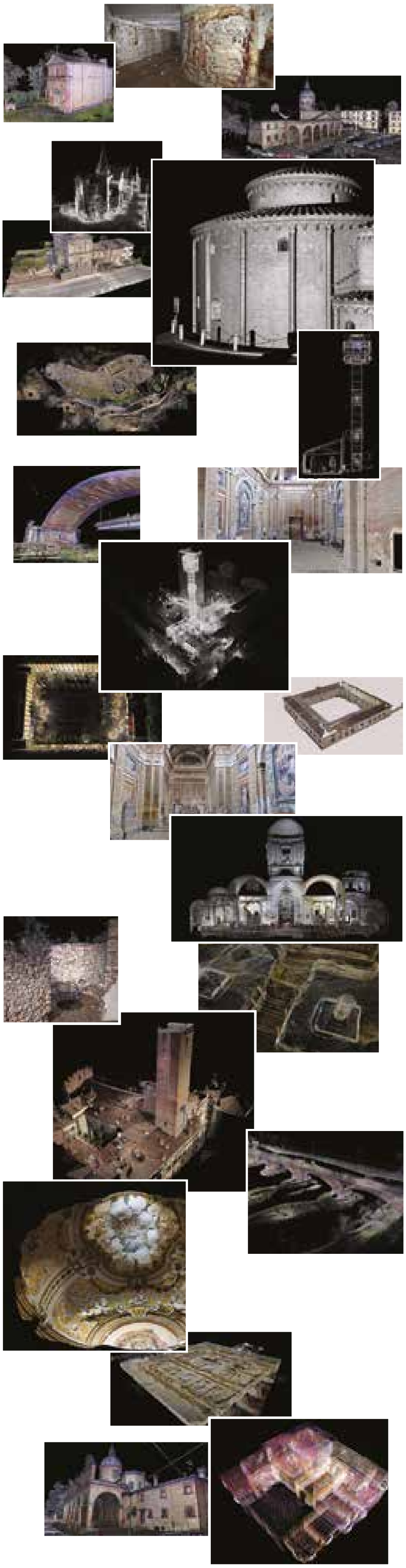
micro-Raman spectroscopy; Surface Enhanced Raman Spectroscopy; cultural heritage; pigments; conservation; Cappadocia wall paintings

Authors

Pietro Baraldi
pietro.baraldi@unimore.it
Università di Modena e Reggio Emilia, Dipartimento di Scienze Chimiche e Geologiche

Cecilia Baraldi
cecilia.baraldi@unimore.it
Università di Modena e Reggio Emilia, Dipartimento di Scienze della Vita

Claudia Pelosi
Diagnostica per la Conservazione e il Restauro, pelosi@unitus.it
Università degli Studi della Tuscia, Dipartimento di Economia, Ingegneria, Società e Impresa



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