MICRO-RAMAN SPECTROSCOPY FOR ANALYSIS OF MEDIEVAL PIGMENTS AND GLAZED CERAMICS – CASE STUDIES

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ABSTRACT

Micro-Raman spectroscopy was used for non-destructive identification of pigments in fragments of wall paintings found in a sacral building, built in the 14th century, on the archaeological site of *Skopsko Kale* (Skopje Fortress). The identified pigments in some of the wall paintings at *Skopsko Kale* could support the assumption of the art historians that the sacral building was repainted over the period of four centuries. Micro-Raman spectroscopy was also employed to characterize the materials and technological process used in manufacturing the glazed Byzantine ceramics found at two different archaeological sites in Republic of Macedonia: *Skopsko Kale* in Skopje and *Markovi Kuli* and *Sv. Atanas* church in Prilep. The study of the glazes and the ceramic body of 12 Byzantine glazed ceramics enlightened the technological process, i.e. firing temperature of the glazes and the mineralogical composition of the clays used for manufacturing the Byzantine glazed ceramics.

INTRODUCTION

Raman spectroscopy is an experimental technique for identification and analysis of molecular species. It enables the identification of both inorganic as well as organic compounds. By introducing the microscope to focus the laser on the sample, micro-Raman spectroscopy could be used to analyze a very small spot, with the diameter of 1 to 10 μm, depending on a selected laser wavelength and the focal length of the objective. This enables obtaining molecular information from a small particle, such as a pigment grain or a microcrystal of a mineral, but also a single fiber, gems, etc.

Nowadays, micro-Raman spectroscopy has been widely applied in analysis of numerous archaeological objects and has become an important analytical tool in conservation sciences and archaeometry. The number of scientific and professional papers dealing with micro-Raman spectroscopic analysis of various materials used in art and archaeology objects has increased enormously in the last decade [1, 2].

In this work, we present two examples (case studies) of application of micro-Raman spectroscopy on different artefacts from the Byzantine and post-Byzantine period, found in the archaeological excavations in Republic of Macedonia: (a) Micro-Raman pigment analyzes of wall paintings from a sacral building unearthed in *Skopsko Kale* and (b) micro-Raman studies of glazed ceramics finds from Skopje and Prilep.

EXPERIMENTAL

Micro-Raman spectrometer:

Micro-Raman measurements were performed with LabRam 300 (Horiba Jobin-Yvon) Raman spectrometer equipped with two lasers: He-Ne laser operating at 17 mW and 633 nm and frequency doubled Nd:YAG laser operating at 50 mW and 532 nm. An Olympus MPlanN microscope with x10, x50 and x100 magnification was used to focus the laser on the samples. The microscope was equipped with color video camera, allowing positioning the samples to a selected region of investigation. The backscattered light was dispersed by using the 1800 lines/mm grating and is detected on a multi-channel air cooled CCD detector. This allows recording the spectra with the spectral resolution of 3–4 cm^{-1}. The LabSpec software was used for data acquisition and GRAMS software was used for data manipulation.

Samples:

Pigments from wall paintings were provided by the archaeologists from the Museum of Macedonia and the Museum of the City of Skopje, directly involved in the 2007 excavations at the *Skopsko Kale* site. The small fresco fragments were placed directly under the microscope, while from some of the larger ones, the samples were collected with cotton buds. The obtained Raman spectra were compared to the reference data base of pigments [3]. Most of the pigments were analyzed with the 633 nm He-Ne laser and an average power of the laser on the sample of 13.7 mW.

Ceramic samples: The glazes and the ceramics body were analyzed using 532 nm laser line with the average power on the sample of 7 mW. The Raman spectra of the ceramics body were recorded from the pellets prepared from 250 mg scratched powder from the body of each fragment which were then placed under the microscope (*f*x100) and recorded on a mapping stage (10 x 10 point-to-point) on a 0.03 x 0.03 mm area.

RESULTS AND DISCUSSION

PIGMENT ANALYSIS

In the year 2007, an extensive excavation has been carried out on several sectors in the *Skopsko Kale* (Skopje Fortress), Republic of Macedonia (Fig. 1). The site is known to be inhabited since Neolithic times. In several layers, mostly dating from the Middle Ages, 1500 different archaeological objects were excavated. Remains of sacral and profane buildings were also unearthed, among them at least one church. According to the archaeological finds, it originated from the middle or the second half of the 14^{th} century, with evidences of reconstructions dateable to the 16th century, and more recent ones, from the 19th century, both of them made during the Ottoman rule in this region. Fragments of wall painting were uncovered in its vicinity [4] and their micro-Raman spectra were recorded [5].

Fig. 1. The foundation of the Medieval church – *Skopsko Kale* (Skopje Fortress) – Skopje

On Fig. 2.a, a detail of a conserved wall painting of a profane figure, most probably from the middle of 14th century, according to the stylistic features [4], is presented. The recorded micro-Raman spectra of some pigments from this wall painting and a fragment from the later redecorations are shown on Fig. 2.b and 2.c.

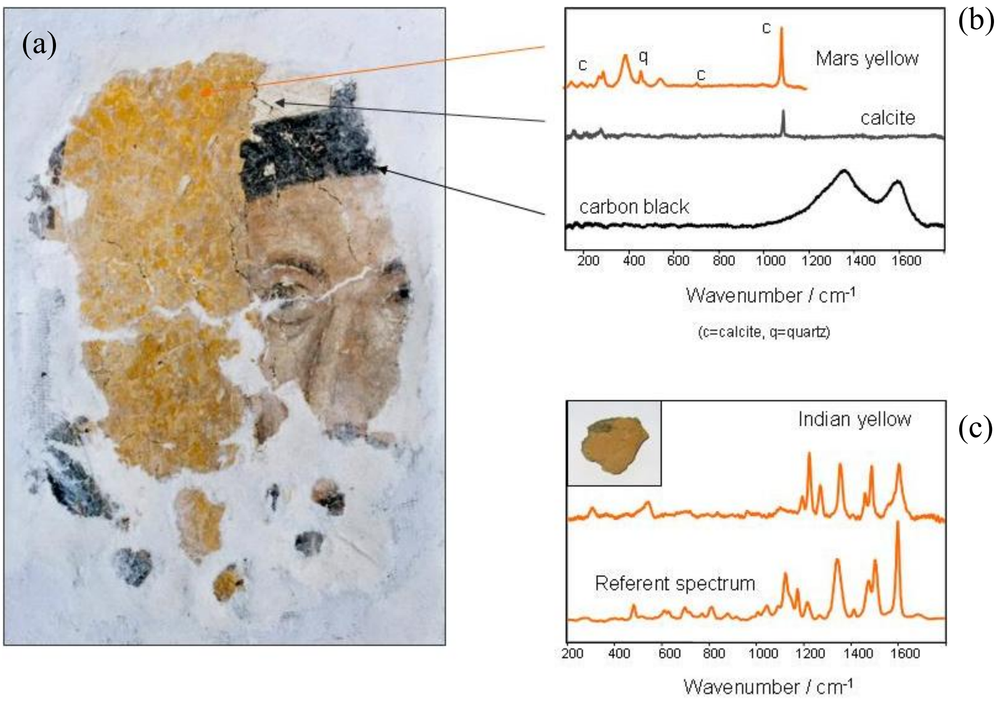


Fig. 2. (a) Fragment of conserved wall painting of a profane figure from the sacral building at S*kopsko Kale*, (b) Raman spectra of the pigments and (c) Raman spectra of a fragment from the later redecorated wall paintings.

All pigments identified by micro-Raman analyses are listed in Table 1. As it can be noticed, the palette is limited since most of the pigments are natural, mineral based, in use since Antiquity. However, in some fragments of the wall paintings, few pigments, dated from the 16th and 19th century were observed. The identification of pigments was made by comparison of their Raman spectra to the reference database of pigments [3]. As seen from Table 1, the red pigments were identified as vermilion, red earth and litharge and one of the red pigments was identified as Mars red (in use since 19th century) [3]. The blue pigments were detected as lazurite and smalt, black as carbon black and white as calcite (chalk). Two yellow/ochre pigments were identified as Indian yellow (in use from 15th until 19th century) [3] and Mars yellow (in use since 19th century) [3]. This could support the tentative dating of the redecoration of some parts of the wall paintings: it could have been made not earlier than beginning of the 15th century when Indian yellow was introduced as a pigment [3], most probably during the 16th century. Further evidence for this suggestion is the recorded Raman spectrum of the blue pigment, identified as smalt, in use since 16th century [3].

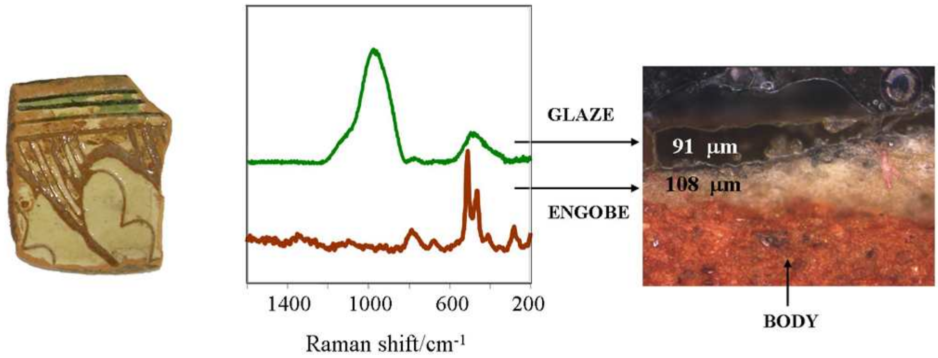
Table 1. Pigments identified in the fragments of the wall paintings from the sacral building at *Skopsko Kale*.

Colour	Minerals / *Antiquity*	Other pigments
red	red ochre, vermilion, hematite, *litharge*	Mars red (since 19th c.)
yellow / ochre		Indian yellow (15th–19th c.) Mars yellow (since 19th c)
blue	lazurite	smalt (since 16th c.)
black	magnetite, *carbon black*	
white	calcite	

The variety of pigments found and their allocation to different time periods confirms the assumption of the archaeologists that the sacral building has been most probably reconstructed/redecorated both in the 16th and 19th century [5].

CERAMICS

Twelve shreds of Byzantine glazed ceramic finds excavated in archaeological sites in Skopje and Prilep, Republic of Macedonia, all dated from the 12th –14th century were analyzed using micro-Raman spectroscopy. They are characterized with an under glaze engobe and sgraffito slip decoration. Although the glazes are coloured, the pigments gave no significant Raman signature, possibly, due to the dissolution of the metal oxides in the glass matrix. One of the Byzantine glazed ceramic shreds and its microscopic cross section is shown on Fig. 3.a and 3.b. Its corresponding Raman spectra of the glaze and under glaze engobe are shown on Fig. 3.c. The two broad bands, the strong one, at ~1000 cm^{-1} and the less intense one, at ~500 cm^{-1} (Fig. 3.c.) are characteristic for Si–O stretching and Si–O–Si bending modes from SiO_4, observed in any glassy network containing a large amount of fluxing PbO [6, 7].



(a) (b) (c)

Fig. 3. (a) Glazed ceramic shred from *Markovi Kuli* (Prilep); (b) its corresponding Raman spectra of the glaze and the engobe and (c) its cross section (from Ref. 2). The polished cross sections photographs were taken with a reflected light optical microscope - Leica MEF4 (magnification x100).

The recorded Raman spectra of the glazes were used for determining the ratio of the integrated areas of the Raman band envelopes, i.e. the polymerization index (I_p) [6–8]. The glazes of the twelve ceramic shreds have already been studied extensively with micro-Raman spectroscopy [2, 9–11]. They were classified according to their indexes of polymerization calculated from the ratio of the Raman band areas of the Si─O─Si bending and Si─O stretching modes (A_{500}/A_{1000}) [6–8]. Hence, the majority of the studied Byzantine ceramic glazes could be classified as lead-rich and fired below 700 ^{o}C, while only two samples are classified as lead-based and fired at around 800 ^{o}C [2, 10, 11].

Point-to-point micro-Raman spectroscopy [12] was used in assessment of the mineralogical composition of the ceramic bodies of the analyzed ceramic shreds. The pellets from the body of each ceramic shred were placed under the microscope (*f*x100) on a mapping stage covering an area of 0.03 x 0.03 mm (Fig. 4.), acquiring approximately 100 Raman spectra. Depending of the surface that has been recorded, some of the spectra represent a pure mineral (Fig. 4.a – 4.c), while others are mixtures of minerals (Fig. 4.d and 4.e). The results from the recorded point-to-point micro-Raman spectra of all studied ceramics bodies are summarized in Table 2. As presented on Table 2, fifteen different minerals were identified. According to the recorded Raman spectra, quartz, hematite, magnetite and feldspars have been detected in all the studied samples of the ceramics body. Four different feldspars could be identified: microcline, albite, sanidine and andradite and three different polymorphic forms of TiO_2: anatase, rutile and brukite could be distinguished from

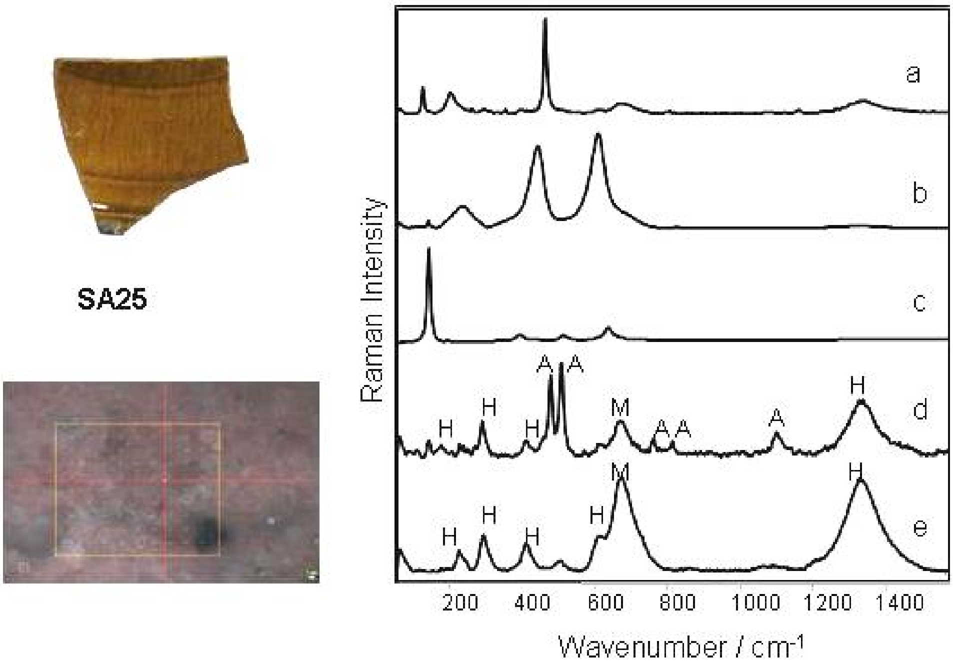


Fig. 4. Raman spectra of the obtained minerals from the mapping area (given on the left hand side). Spectrum **a** corresponds to Quartz; **b** to Rutile; **c** to Anatase; **d** to mixture of minerals: Albite(A)+Hematite(H)+Magnetite(M) and **e** to mixture of minerals: Hematite(H)+Magnetite(M).

Table 2. List of the obtained minerals by point-to-point micro-Raman spectroscopy from the ceramic samples. (F = Feldspars)

MINERALS	SA25	SA27	SA29	SK31	MK2	MK9	MK10	MK14	MK22
Quartz	√	√	√	√	√	√	√	√	√
Hematite	√	√	√	√	√	√	√	√	√
Magnetite	√	√	√	√	√	√	√	√	√
TiO_2 (rutil)	√		√						√
TiO_2 (anatase)	√		√	√			√	√	√
TiO_2 (brukite)			√						
F (microcline)		√	√	√		√	√	√	√
F (albite)	√						√		√
F (sanidine)					√				
F (andradite)						√			
Calcite					√			√	√
Apatite		√			√		√		
Forsterite							√	√	√
Enstatite		√				√			
Maghemite		√							

the Raman spectra in most of the samples studied. Calcite, apatite, forsterite (as olivine) and enstatite (as pyroxene) were also easily identified by micro-Raman spectroscopy in some of the samples. The Raman signature of maghemite from lepidocrocite has been observed in sample SA27.

A comparative study of the mineralogical composition of the ceramic shreds was made, using the well established techniques in this field, as XRD [12] and XRF [9, 10]. The obtained results from the three applied techniques are in good agreement, although in some cases Raman spectroscopy is more informative.

CONCLUSIONS

A spectroscopic analysis by micro-Raman spectroscopy on medieval pigments and glazed ceramics provides information on (a) the type of pigments used in wall paintings and (b) the technology of manufacturing of ceramics, i.e. the firing temperature of the ceramics glazes as well as the mineralogical composition of the ceramics body.

(a) The characterization and identification of the pigments used in the wall paintings remains one of the most important analytical tasks in characterization of the art objects. It provides artistic, historical and technological information and enables correct and appropriate approach during conservation and restorations procedures.

(b) Non-destructive Raman analysis offers considerable data and information about the technological and manufacturing processes of medieval glazed ceramics. The data recaptured from the polymerization indexes (I_p) of the studied glazes provide information on their manufacturing processes, such as firing temperatures. On the other hand, the mineralogical composition of the ceramics body can be easily studied by point-to-point micro-Raman spectroscopy, by mapping the ceramics body in a chosen area, which leads to identification of numerous minerals in ceramics. The mineralogical data obtained by XRD [12] and XRF [9, 10] techniques on the same samples were compared with the data obtained by micro-Raman spectroscopy. Although time consuming, micro-Raman spectroscopy was proven to be accurate and precise and could be used in mineralogical assessment of ceramics.

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