Micro-Raman pigment analysis of wall paintings from a church in the Skopje Fortress, Republic of Macedonia

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Introduction

The Mediaeval fortification Skopsko Kale (Skopje Fortress) is situated in the heart of the modern capital of the Republic of Macedonia, Skopje, performing the role of a strategic centre of the Central Balkan Peninsula, mainly since the 6th until the end of the 19th century. This Fortress served as one of the most important military and administrative sites of the competing military powers of the Middle Ages: Byzantium; the II Bulgarian Kingdom; the Kingdom of Samuel and the Serbian Kingdom, when it became the capital of Tsar Dushan, and later the seat of the Ottoman rulers.

After the extensive field research conducted in 1967, a major excavation campaign was performed during 2007 within the circumference of the mediaeval Skopje Fortress [1]. Among the finds, the most unique discovery of the excavation campaign are the remains of a church (Fig. 1.a), located at the hilltop position within the fortification. This is so far the only church unearthed within the walls of the Skopje fortification. The existence of the church is documented in primary literary data from 1573 by the traveler Philippe du Fresne-Canaye. In his descriptions, he witnessed the existence of the ruins of an old fortress visible once you entered the town and the existence of an Orthodox church inside its remains [2].

Research based on stratigraphic methods of archaeological excavations and the consecutively performed analysis of finds, mainly pottery, suggested that the construction of the church was in the second half of the 14th century. However, the remains revealed the existence of two phases of renovation poorly supported by stratigraphic data due to interruption of cultural layers by recent interventions, mainly clearance of ruins from 19th and 20th century buildings after the major demolition caused by the 1963 earthquake in Skopje. While a second intervention was documented in historic photography and may be reliably dated to the 19th century, the earlier one was attributed to the unclear times of the early Ottoman rule. During the ruling of the Ottoman Empire, it was difficult to assume a major renovation phase of an Orthodox church within the imperial and military seat in the strategic center of the Central Balkan, at the Skopje Fortress. Still, stratigraphic finds suggest interventions on the mediaeval church sometime in the 16th century, probably after the major earthquake in 1555 [3].

Chronological support was obtained by a depot of scrapped fresco painting walls (Fig. 1.b), used as fillers for the terrain elevation against accumulation of rainwater. Fragments carrying similar motifs and colours were also detected within the architectural remains, but broken down to small bits, pointing to their common origin [3].



(a)





Fig. 1 - (a) The foundation of the Mediaeval church - Skopsko Kale (Skopje Fortress) (b) A detail of an unearthed wall painting of a profane figure, later conserved and analysed by micro-Raman spectroscopy

Results

The micro-Raman measurements were performed using LabRAM Raman instrument. The fresco fragments were placed directly under the microscope and anlyzed with the He-Ne laser operating at 17 mW 633 nm. The pigments were analysed prior to the conservation of the fresco fragments and selected Raman spectra are presented on Fig. 2.a-d. The results of the identified pigments by micro-Raman analyses are summarized in Table 1.



Fig. 2 - Raman spectra of the analysed pigments of small fragments of wall paintings: (a) red pigments; (b) yellow pigments; (c) blue pigment; (d) black pigment (c = calcite)

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Table 1 - Pigments identified in the fragments of the wall paintings from the sacral building at Skopsko Kale (Skopje Fortress).

Colour	Pigments in use since Antiquity	Other pigment
red	vermilion, haematite, litharge	
yellow / ochre	goethite	Indian yellow (15 th - 19 th c.)
blue	lazurite	
black	magnetite, carbon black	
white	calcite	

As seen in Table 1, the red pigments were identified as vermilion, haematite (and magnetite) and litharge [4-6]. The blue pigment was detected as lazurite, black as carbon black and white as calcite (chalk). Two yellow/ochre pigments were identified as goethite and Indian yellow, the latter in use from 15th until 19th century [4].

Indian yellow is an organic magnesium pigment, magnesium euxanthate (C19H16O11Mg • 5H2O) [7]. It was probably introduced in India in the 15th century from Persia (modern Iran) and is often found in Indian paintings of the Mughal period (late 16th to 19th centuries) [8]. The color was known in Europe as early as 1780 and was rarely used throughout the 19th century, mostly in watermedia paints [8]. It was brought in this region (today's Republic of Macedonia) most probably from Persia during the Ottoman rule.



Fig. 3 - Wall painting fragment with Indian yellow pigment

An example of the analysed wall painting fragment with Indian yellow pigment is shown on Fig. 3. The occurrence of Indian yellow in the wall paintings of the sacral building of Skopsko Kale (Skopje Fortress) could support the tentative dating of the interventions on some parts of the wall paintings: they could have been made not earlier than the beginning of the 15th century when Indian yellow was introduced as a pigment [4,7-9].

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The present study of mediaeval pigments using micro-Raman spectroscopy provides important information on the inorganic and organic type of pigments used in the wall paintings in the remains of the church in Skopsko Kale (Skopje Fortress). In general, the variety of pigments found and their allocation to different time periods confirms the assumption of the archaeologists that the sacral building has been reconstructed in the 19th century [10]. Most rewarding was the analysis of the yellow pigments: Indian yellow, in use in 15th-19th century [4,7-9].

All this information documented an important stage in the life of the Skopje Fortress. Despite the fully applied political and military power of the Ottoman Empire, the renovation confirms a subtle coexistence of the two communities, Muslim and Christian, in the city.

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