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Application of analytical techniques for unveiling the glazing technology of medieval pottery from the Belgrade Fortress

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Abstract: Medieval glazed ceramics, dated to the early 15th century, excavated at the Belgrade Fortress, Serbia, was investigated combining optical microscopy, X-ray powder diffraction (XRPD), scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS), micro-Raman spectroscopy and multivariate statistical analysis. Decoration and style of investigated ceramics were characteristic of workshops from different areas of medieval Serbian state: Ras, Kruševac and Belgrade/Smederevo. Comparison was made with ceramic samples from the same period excavated at the Studenica Monastery, the earliest workshop discovered so far, which were used as reference material for Ras area. Ceramics from the Belgrade Fortress was covered with transparent, lead-based glaze. Majority of the glazes were produced by application of mixture of lead oxide and quartz to the clay body, whereas only two samples were glazed by application of lead oxide by itself. Brown colours of the glaze originate from Fe-based spinel, whereas copper and iron were responsible for the coloring of the green and yellow glazes. The obtained results revealed glazing technology taken from Byzantine tradition.

Keywords: Glazes, ceramics, XRPD, SEM-EDS, micro-Raman spectroscopy.

INTRODUCTION

Glazes are applied on ceramic vessels for protective as well as for decorative purposes. After production of transparent lead glaze, about the 1st century A.D.1, glazing became a widespread and important technological procedure. Between the 11th and 12th centuries, Byzantine glazed ceramics became recognizable by vessels produced combining glazing with painting and incisions to create products with specific decorations; the most famous products were slip-painted and sgraffito wares2. Numerous studies have been dedicated to Byzantine glazed ceramics from the point of view of decoration and style, identification of workshops, but also determination of materials and production technologies and sometimes provenience3-9. Medieval Balkan states, Bulgaria and Serbia, each in its own way,
inherited Byzantine decorative techniques and used them to develop their own design of tableware\textsuperscript{10,11}.

Several archaeometric studies of medieval glazed pottery from the most significant centers of medieval Serbian state have been performed: the first state capital Ras\textsuperscript{12}, the first monastery Studenica\textsuperscript{13,14} and the most important mining center Novo Brdo\textsuperscript{15}. Considering the raw materials and procedures employed in their manufacturing, the investigations confirmed the local pottery production and originality.

Belgrade was the capital of Serbian medieval state at the beginning of 15\textsuperscript{th} century. The focus of this study is the glazed pottery originating from that period excavated at the area of the Belgrade Fortress. The investigated samples have been classified by archaeologists in three groups based on decoration characteristics of workshops from the three different areas of medieval Serbian state: Ras, Kruševac and Belgrade/Smederevo. The aim of this work is to identify the materials used for pottery production as well as glazing technology. Multi-analytical approach has been employed to achieve this aim using optical microscopy, X-ray powder diffraction (XRPD), scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS), micro-Raman spectroscopy and multivariate statistical analysis.

The Belgrade Fortress is regularly used as an exhibition space and the partial archaeological excavation performed so far did not provide enough archeological (and ceramic) material which would be a solid starting point for consideration of ‘the Belgrade pottery workshop’, \textit{i.e.} the organization of ceramics production within the city area. Therefore it is difficult to determine the potential sources of raw materials for the pottery investigated in this work. However, the majority of medieval glazed pottery samples excavated at the Belgrade Fortress are related, based on decoration and style, to pottery produced in the Ras area\textsuperscript{10}. That is why in this work pottery samples from Ras area, well characterized in recent archaeometric studies, dated to the 14\textsuperscript{th} to early 15\textsuperscript{th} century and found in the Studenica Monastery, were used as material for comparison\textsuperscript{13,14}. The previous investigations have shown the use of local raw materials for preparation of clay body and local pottery production\textsuperscript{13,14}.

Archaeometric study of glazed pottery shards found at the Belgrade Fortress can contribute to the understanding of pottery production technology in Serbia in the late medieval phase and will be an addition to the existing archaeometric data on Serbian medieval ceramics.

**EXPERIMENTAL**

\textit{Description of samples:} Pottery fragments are usually the most numerous finds at excavation sites, but in this case only about 50 shards of glazed ceramic vessels have been discovered during archaeological excavations at the Belgrade Fortress. The main reasons for such a small number of finds are: 1) the partial exploration of the Belgrade Fortress and 2) the
GLAZED MEDIEVAL POTTERY FROM THE BELGRADE FORTRESS

atypical samples have been discarded in accordance with museum practice at the time. Some of excavated shards were used for complete reconstruction of five original vessels\textsuperscript{16}. Therefore, 16 glazed pottery shards that represent this collection were investigated, out of which 13 shards underwent minimal damage. All investigated pottery samples were shards of jugs formed using the fast-turning (foot) potter’s wheel. Photographs of investigated samples are given in Table S-I in Supplementary material. Investigated samples are classified in three groups (group I – 3 samples (BG-1, BG-2, BG-4), group II – 11 samples and group III – 2 samples (BG-12, BG-15)) based on the decoration techniques and colours (archaeological context and detailed description of samples are given in Supplementary material). Five pottery shards, which were part of large assemblage of 43 pottery shards excavated in Studenica Monastery and characterized by multi-analytical approach in earlier studies\textsuperscript{13,14}, have been used as reference material in this study.

Analytical methods: Cross sections of all investigated ceramic shards were recorded by Citoval 2 Binocular Stereo Microscope Carl Zeiss Jena, under magnification x16. The chemical composition of the body and the glaze of 13 samples from the Belgrade Fortress: BG-1, BG-2, BG-3, BG-4, BG-5, BG-6, BG-9, BG-10, BG-11, BG-12, BG-13, BG-14, BG-15 and five samples from the Studenica Monastery, S2.33, S2.34, S2.36, S2.37, S2.42, was obtained by scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS). The small fragments of investigated pottery shards were cut, polished and analyzed uncoated by the Phenom ProX desktop scanning electron microscope (SEM) equipped with a fully integrated Energy Dispersive Spectrometer (EDS) alongside an elemental identification software package. The analyses were performed under acceleration voltage of 15 kV. A minimum of five areas of 150×150 µm\textsuperscript{2} were analysed on each sample to obtain a representative composition; data were normalized to 100 wt% oxides.

With the aim to compare samples from two archaeological sites multivariate statistical analysis was performed on SEM-EDS data using PLS_ToolBox v. 8.7, MATLAB vR2017b. Hierarchical Cluster Analysis (HCA) was made using Ward’s method and Euclidean distance on ceramic body compositional data. The centred log-ratio transformation of the data was applied, which decreases the difference between magnitudes of major and minor oxide concentrations\textsuperscript{17}. This transformation consisted of dividing each individual variable value by its geometric mean, and logarithmic transformation to base 10. Dataset with 18 samples made of chemical composition of ceramic body with 18×8 matrix was analysed.

X-ray powder diffraction patterns were recorded at room temperature on a Rigaku Ultima IV diffractometer in Bragg–Brentano geometry, with Ni filtered CuK\textsubscript{α} radiation (\(\lambda = 1.54178\) Å), applied voltage \(U = 40\) kV and current intensity \(I = 40\) mA. Diffraction data were acquired over the scattering angle 2\(\theta\) from 2 to 50\(^{\circ}\) with a step of 0.020\(^{\circ}\) and acquisition rate of 1°/min.

Micro-Raman spectra of the glazes of all investigated samples were recorded directly on the glaze surface, at various points on each sample using DXR Raman Microscope (Thermo Scientific). Also, in order to identify particles in the clay paste micro-Raman spectra were recorded at different points of the cross sections of all investigated samples. The 532 nm line of a diode-pumped solid state high brightness laser was used as the exciting radiation and the power of illumination at the sample surface was 10 mW. The scattered light was collected through an Olympus microscope with infinity-corrected confocal optics, 50 µm pinhole aperture, standard working distance objective 10×, grating of 900 lines/mm, and resolution of 2 cm\textsuperscript{-1}. Acquisition time was 10 s with 10 scans. Thermo Scientific OMNIC software was used for spectra collection and manipulation. The Raman spectra from inhouse data base and literature\textsuperscript{18} were used for the identification of the pigments and minerals by comparison with the recorded spectra.
RESULTS AND DISCUSSION

Ceramic body

In order to understand the glazing production technology, it is also important to characterize the ceramic body of the investigated samples. Acquiring this information will lead to a better understanding of the knowledge transfer in that particular historical period.7

Microstructure. Optical micrographs of polished cross sections can provide information about pottery fabrics and consequently indications about pottery production. The cross sections, shown in Fig. 1, reveal differences in texture and colour of samples from group I (BG-4) compared to samples from the groups II (BG-5 and BG-8) and III (BG-15). Fine-grained fabric with small inclusions is characteristic of the samples from group I. Other samples (from groups II and III) have quite uniform medium-grained fabric, with rounded, medium-coarse inclusions with noticeable particles that have equant angular shape. Optical micrographs of cross sections of all investigated samples are given in Supplementary material (Table S-I).

Micro-Raman spectroscopy revealed that majority of inclusions originate from quartz, which can be present as sediment but also as temper19. Voids present at cross sections of all samples may indicate release of the air trapped in clay paste during the kneading and construction process or insufficient and improper drying of the vessels. Uniform matrix colours, red for BG-1 and BG-4 and yellowish red for BG-2, and presence of hematite identified by micro-Raman
spectroscopy indicate firing in oxidizing conditions for samples from group I\textsuperscript{14}. For the samples BG-3, BG-5, BG-11, BG-12, BG-13 outer parts are light red and inner parts are darker different shades of brown, which indicates rapid firing procedure. The pottery shards from the Belgrade Fortress, the groups II and III, have similar fabric and clay colour to the pottery shards from the Studenica Monastery. The samples from Studenica have medium-grained fabric, but particles are large and have different sizes contrary to samples from Belgrade Fortress which have uniform sizes of particles. The samples have either core darker than the edges (e.g. S2.37) or the bright outer edge and the dark inner edge (S2.42). Cross section of sample S2.34, dark grey core and orange-brown outer margin, indicate a short firing or hasty cooling in air when the vessel is still hot\textsuperscript{19}.

Chemical composition. The chemical composition of 13 pottery samples from the Belgrade Fortress and 5 pottery samples from the Studenica Monastery was determined by SEM-EDS (Table I). The samples BG-1, BG-4 and BG-15, based on low amount of lime (less than about 5 wt%), belong to the group of non-calcareous clay. Also, low content of calcium oxide classifies clay used for production of samples from Studenica as non-calcareous, as previous studies have shown\textsuperscript{13,14}.

Table I. The chemical composition of ceramic body of samples from the Belgrade Fortress and the Studenica Monastery determined by SEM-EDS; oxide concentration normalized to 100 wt%; standard deviation shown in brackets; n.d. – not detected

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO\textsubscript{2}</th>
<th>Al\textsubscript{2}O\textsubscript{3}</th>
<th>FeO</th>
<th>CaO</th>
<th>MgO</th>
<th>K\textsubscript{2}O</th>
<th>Na\textsubscript{2}O</th>
<th>TiO\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>BG-1</td>
<td>58.3 (4.9)</td>
<td>19.5 (0.1)</td>
<td>12.1 (4.1)</td>
<td>1.3 (0.2)</td>
<td>3.0 (0.4)</td>
<td>2.8 (0.1)</td>
<td>1.6 (0.3)</td>
<td>n.d.</td>
</tr>
<tr>
<td>BG-2</td>
<td>49.1 (2.5)</td>
<td>17.0 (0.1)</td>
<td>9.3 (0.8)</td>
<td>16.3 (0.9)</td>
<td>2.8 (0.1)</td>
<td>3.1 (0.2)</td>
<td>1.0 (0.3)</td>
<td>0.7 (0.1)</td>
</tr>
<tr>
<td>BG-3</td>
<td>70.1 (3.7)</td>
<td>12.0 (3.3)</td>
<td>6.6 (0.4)</td>
<td>6.2 (1.9)</td>
<td>2.0 (0.4)</td>
<td>1.9 (0.8)</td>
<td>0.8 (0.1)</td>
<td>0.4 (0.1)</td>
</tr>
<tr>
<td>BG-4</td>
<td>58.0 (6.1)</td>
<td>20.7 (3.2)</td>
<td>12.1 (1.7)</td>
<td>0.9 (0.1)</td>
<td>2.6 (0.4)</td>
<td>2.8 (0.5)</td>
<td>2.0 (0.4)</td>
<td>0.3 (0.1)</td>
</tr>
<tr>
<td>BG-5</td>
<td>62.2 (2.4)</td>
<td>17.6 (1.7)</td>
<td>6.1 (1.7)</td>
<td>7.9 (0.3)</td>
<td>2.7 (0.3)</td>
<td>2.3 (0.3)</td>
<td>1.3 (0.3)</td>
<td>n.d.</td>
</tr>
<tr>
<td>BG-6</td>
<td>54.7 (1.7)</td>
<td>22.2 (0.3)</td>
<td>7.4 (1.0)</td>
<td>6.9 (0.1)</td>
<td>3.6 (0.5)</td>
<td>2.8 (0.3)</td>
<td>1.8 (0.1)</td>
<td>0.5 (0.2)</td>
</tr>
<tr>
<td>BG-9</td>
<td>55.8 (3.6)</td>
<td>22.2 (1.6)</td>
<td>7.5 (0.5)</td>
<td>5.6 (0.7)</td>
<td>3.3 (0.2)</td>
<td>2.2 (0.2)</td>
<td>2.6 (0.4)</td>
<td>0.5 (0.1)</td>
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<tr>
<td>BG-10</td>
<td>57.2 (2.5)</td>
<td>17.2 (2.1)</td>
<td>11.4 (1.8)</td>
<td>7.2 (2.1)</td>
<td>2.8 (0.6)</td>
<td>1.4 (0.6)</td>
<td>1.3 (0.1)</td>
<td>0.6 (0.1)</td>
</tr>
<tr>
<td>BG-11</td>
<td>55.4 (1.1)</td>
<td>22.2 (0.9)</td>
<td>8.2 (3.7)</td>
<td>6.9 (1.2)</td>
<td>2.7 (0.2)</td>
<td>2.5 (0.3)</td>
<td>1.8 (1.4)</td>
<td>0.2 (0.1)</td>
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<tr>
<td>BG-12</td>
<td>49.7 (2.0)</td>
<td>20.8 (0.8)</td>
<td>8.9 (2.0)</td>
<td>13.3 (2.8)</td>
<td>2.9 (0.2)</td>
<td>2.8 (0.1)</td>
<td>2.3 (0.6)</td>
<td>n.d.</td>
</tr>
<tr>
<td>BG-13</td>
<td>63.9 (5.9)</td>
<td>16.1 (1.5)</td>
<td>7.9 (1.4)</td>
<td>5.2 (1.6)</td>
<td>2.2 (0.4)</td>
<td>2.2 (0.5)</td>
<td>2.4 (0.6)</td>
<td>0.5 (0.1)</td>
</tr>
<tr>
<td>BG-14</td>
<td>51.3 (2.0)</td>
<td>22.0 (0.1)</td>
<td>8.4 (1.1)</td>
<td>9.5 (0.4)</td>
<td>3.9 (0.1)</td>
<td>2.6 (0.1)</td>
<td>1.6 (0.1)</td>
<td>0.5 (0.1)</td>
</tr>
<tr>
<td>BG-15</td>
<td>62.1 (4.7)</td>
<td>19.6 (3.8)</td>
<td>9.7 (2.3)</td>
<td>2.5 (0.7)</td>
<td>2.5 (0.7)</td>
<td>2.4 (0.2)</td>
<td>1.3 (0.1)</td>
<td>n.d.</td>
</tr>
<tr>
<td>S2.33</td>
<td>53.4 (0.8)</td>
<td>21.1 (0.3)</td>
<td>15.4 (1.2)</td>
<td>1.3 (0.1)</td>
<td>3.8 (0.4)</td>
<td>2.9 (0.2)</td>
<td>0.8 (01)</td>
<td>1.0 (0.1)</td>
</tr>
<tr>
<td>S2.34</td>
<td>53.0 (1.0)</td>
<td>24.2 (1.1)</td>
<td>12.3 (1.3)</td>
<td>1.7 (0.3)</td>
<td>2.7 (0.2)</td>
<td>3.8 (0.9)</td>
<td>1.3 (0.1)</td>
<td>0.4 (0.1)</td>
</tr>
<tr>
<td>S2.36</td>
<td>56.9 (0.3)</td>
<td>22.0 (0.3)</td>
<td>11.2 (0.5)</td>
<td>2.2 (0.1)</td>
<td>2.4 (0.4)</td>
<td>2.9 (0.1)</td>
<td>2.3 (0.6)</td>
<td>n.d.</td>
</tr>
<tr>
<td>S2.37</td>
<td>64.7 (2.7)</td>
<td>18.1 (1.0)</td>
<td>4.6 (1.0)</td>
<td>2.4 (0.7)</td>
<td>1.7 (0.2)</td>
<td>4.4 (0.6)</td>
<td>3.5 (0.2)</td>
<td>0.3 (0.1)</td>
</tr>
<tr>
<td>S2.42</td>
<td>55.8 (1.4)</td>
<td>22.0 (0.9)</td>
<td>13.2 (0.5)</td>
<td>1.4 (0.8)</td>
<td>3.7 (0.8)</td>
<td>2.4 (0.2)</td>
<td>1.2 (0.4)</td>
<td>0.2 (0.1)</td>
</tr>
</tbody>
</table>
The other samples from the Belgrade Fortress contain higher amount of lime and samples BG-2 and BG-12 can be classified as calcareous clay having lime contents higher than about 10 wt%. The results obtained for all investigated samples show relatively high alumina (~20 wt%) and iron oxide (up to ~15 wt%) contents and relatively low content of alkali oxides. These findings are in good agreement with the results of chemical analysis of six glazed samples from the Belgrade Fortress, dated to different periods between 11th and 15th centuries published in 1970\(^2\). However, a detailed description of the studied samples is missing and it is not clear which vessels were subject of investigation. Consequently, it can only be considered as preliminary study.

The HCA result of chemical composition of ceramic body of all studied samples is shown in Fig. 2. As TiO\(_2\) was under the detection limits for certain samples, this variable was omitted from the statistical analysis.

Two clusters can be seen in dendrogram obtained by Ward's method and Euclidean distance (when cut at distance 1). The samples are distinguished based on both the calcium oxide and iron oxide content. The first cluster is composed of the samples from Belgrade Fortress which all have higher content of calcium oxide (above 5 wt %). The second cluster consists of the samples found in the Studenica Monastery and three samples found at the Belgrade Fortress (BG-1, BG-4 and BG-15). They all have low content of calcium oxide (under 2.5 wt %). Grouping of BG-1 and BG-4 within ‘cluster Studenica’ (in contrast to BG-2), as well as BG-12 within ‘cluster Belgrade’ (in contrast to BG-15) show two different ways of raw material preparation (clay and temper) among samples that belong to the same decorative circle.

![Hierarchical clustering dendrogram of the chemical composition of ceramic body of the samples from the Belgrade Fortress and the Studenica Monastery](image-url)
Mineralogical composition. XRPD patterns of representative samples from Belgrade Fortress are shown in Fig. 3. Characteristic reflections of quartz are dominant in the patterns of all investigated samples. Also, characteristic reflections of feldspar from plagioclase group are detected in all samples. The presence of phyllosilicates (illite/muscovite) is detected for samples BG-2, BG-3, BG-5, BG-12 and BG-15. Except sample BG-15, all other samples from groups II and III contain reflections of high temperature phases, diopside and gehlenite, which are not present in the samples BG-1 and BG-4 from group I. This finding is in agreement with CaO content detected by SEM-EDS analysis (Table I). The mineralogical composition of samples BG-1, BG-4 and BG-15 is very similar to mineralogical composition of samples from the Studenica Monastery determined by multiphase Rietveld analysis of high resolution diffraction patterns in an earlier study\textsuperscript{14}. This agrees with results obtained by EDS measurements in this work.

The mineralogical composition provides information about the firing process, such as estimation of the firing temperature or the atmosphere in the kiln used for the production of ceramics. Phyllosilicates disappear at temperatures between 900 °C and 950 °C\textsuperscript{12}, whereas gehlenite forms between 800 and 850 °C as a reaction between calcite and clay mineral illite\textsuperscript{21}. Therefore, identified minerals suggest firing temperature higher than 800-850 °C, but lower than 950 °C. Firing temperature for the samples from the Studenica Monastery has been estimated at 900 °C in previous study\textsuperscript{14}. Presence of hematite indicates oxidizing conditions during firing process and it is in agreement with reddish colour of the ceramic body.

![Fig. 3. XRPD patterns of representative samples from Belgrade Fortress. Abbreviations: II/M-illite/muscovite, Q-quartz, P-plagioclase, D-diopside, G-gehlenite, He-hematite.](onlinelink)
**Glaze**

The average thickness of the investigated glazes was in the range 60-300 µm. The thickness of glaze varies among samples but also from one part to another of particular sample. The glazes were well preserved; majority of the samples was covered on one side, whereas samples BG-5, BG-6, BG-8, BG-10, BG-14 and BG-15 were covered with glaze on both sides.

**Glazing method.** Chemical composition of glazes of pottery found at the Belgrade Fortress and the Studenica Monastery determined by SEM-EDS is shown in Table II. The content of lead oxide is high and varies from ~50 to ~75 wt%. The alkali contents (Na$_2$O + K$_2$O) are rather low, up to ~2 wt %. Consequently, glazes of all investigated samples can be classified as lead-rich glazes, with lead oxide as flux agent. Only two colorants have been detected: Cu and Fe.

Two glazing techniques, application of mixture of lead oxide and quartz or application of lead oxide by itself on the surface of the ceramic body, can be distinguished when the glaze compositions is renormalized after subtraction of the lead oxide as well as copper oxide and iron oxide (considered as colorants purposely added)$^{22}$. For the majority of the investigated samples, the concentrations obtained after the subtraction and renormalization did not match the composition of the body. The silica content in glaze, calculated in this way, was higher than in the body (Fig. S-2 is given in Supplementary material) and alumina content in glaze was lower than in the body indicating that glazing was performed applying mixture of lead oxide and quartz$^{22}$. Only for samples S2.37, BG-3 and BG-13 calculated concentrations matched the composition of the body (Fig. S-2) indicating that these samples were glazed by application of lead oxide by itself.

Additionally, glaze can be applied on unfired ceramic body or on biscuit-fired body. Investigation of the body-glaze interface leads to differentiation between these two methods$^{7,9,23}$. Formation of lead potassium feldspars in the body-glaze interface is a consequence of diffusion of elements from the body to glaze during firing and it is more pronounced if the glaze is applied on an unfired body (Fig. 4 left). These findings are indication that samples BG-1, BG-3, BG-4, BG-9, BG-10, BG-13, BG-14 and BG-15 were fired once only as well as samples from the Studenica Monastery. Absence of lead potassium feldspars in the body-glaze interface (Fig. 4 right) is an indication of biscuit-fired ceramic body before application of glaze which is the case for the rest of the investigated samples.

The typical, fluorescence corrected, Raman spectra of glazes of pottery samples from Belgrade Fortress and Studenica Monastery are shown in Fig. 5. Glazes are almost amorphous silicate networks with SiO$_4$ tetrahedra as the main building units. The Raman spectra of glazes of all investigated samples, both from Belgrade Fortress and Studenica Monastery, were very similar: two broad bands originating from Si-O stretching modes centered between 920 and 950 cm$^{-1}$ are more intense than Si-O bending modes centered at about 490 cm$^{-1}$.
Fig. 4. SEM photographs of body-glace interfaces of the samples BG-4 (left) and BG-5 (right)

Table II. Chemical composition of glazes of samples from the Belgrade Fortress and the Studenica Monastery determined by SEM-EDS; oxide concentration normalized to 100 wt%
When tetrahedral units are weakly connected the stretching modes are more intense than bending modes, because the relative intensity of these bands is very sensitive to the composition of glaze \(^{24,25}\). Higher intensity of stretching band and shift of its position towards lower wavenumber values is associated with high concentration of lead \(^{25}\), which is in agreement with results obtained by SEM-EDS analyses (Table II). Therefore, findings acquired by these two techniques confirm that applied glazes were lead-based.

The Raman spectra of glazes of all investigated pottery samples often showed additional narrow peaks originating from the crystalline phases like undissolved quartz (463 cm\(^{-1}\)) and feldspars (513 cm\(^{-1}\))\(^{26}\), as illustrated at Fig. 5a. Traces of gas bubbles on the surface of glazes have been detected at some samples from the Belgrade Fortress (BG-2, BG-5, BG-8, BG-9, BG-11, BG-13 and BG-15) and at five samples from the Studenica Monastery, similar to other samples from this excavation site as shown in an earlier study\(^{14}\). This can be a consequence of fast firing process or inappropriate maximum firing temperature which results in decomposition of the glaze and the body indicating that glaze was not matured properly\(^{27}\).
**Colorants.** The macroscopically observed colours of glazes are green (olive green), yellow and brown. The Raman spectra, recorded at different points of coloured glazes, exhibit signals of a glaze-pigment mixture or signals of the pure pigment. Fig. 6. shows representative Raman spectra of brown glazes of pottery samples from the Belgrade Fortress and the Studenica Monastery. As shown in an earlier study\(^{14}\), iron oxides were responsible for brown shades of glaze of pottery from Studenica Monastery because characteristic bands for hematite, Fe\(_2\)O\(_3\), (228, 248, 295, 410, 504, 619 and the strong mode at 1325 cm\(^{-1}\)) and magnetite, Fe\(_3\)O\(_4\), (~ 670 cm\(^{-1}\)), have been detected (Fig. 5). However, the Raman spectra of brown glazes of all pottery samples from Belgrade Fortress display intensive peak of spinel structure, commonly found in pigment systems, at about 700 cm\(^{-1}\) (Fig. 6).\(^{28}\) It is difficult to differentiate chemical composition of spinels by Raman spectroscopy\(^{28}\), but combining these results with SEM-EDS analysis indicates use of Fe-based spinels for dark brown colorations. Magnetite was identified only in the case of BG-3 sample. Broad Raman doublet at 1374 and 1590 cm\(^{-1}\) characteristic for amorphous black carbon was identified for samples BG-1, BG-6, BG-8, BG-12, BG-13 and BG-15 (Figs. 6. and 7.) at brown and dark green areas, indicating firing in a reducing atmosphere\(^{28}\).  

![Raman spectra of brown glazes](image)

Fig. 6. Raman spectra of brown glazes of the representative pottery samples from the Belgrade Fortress and the Studenica Monastery; abbreviations: He – hematite, M – magnetite, G – graphite, S – spinel, Glz – glaze.

The Raman spectra of green and yellow glazes did not show characteristic signals of any green or yellow pigments neither in the case of pottery from Belgrade Fortress nor in the case of pottery from the Studenica Monastery\(^{14}\). As illustrated at Fig. 7., only glassy Raman signature together with bands originated from crystalline precipitates were detected both for green and yellow glazes.
EDS analyses identified Fe in yellow glazes, whereas Cu is detected in majority of green glazes (Table II). When Raman spectra of glaze show only glassy signature, then color is achieved by dispersion of ions (Fe$^{3+}$ or Cu$^{2+}$) in glassy matrix\(^{29}\). Several samples, e.g., BG-1, BG-6, BG-11 (Table II), with green glaze did not contain any significant Cu content, but the amount of Fe$_2$O$_3$ was rather high and varied from 2 wt% to 7 wt%. Green color can be produced by Fe$^{2+}$ ions formed in reducing atmosphere even when there is no copper in the glaze\(^{30}\). Presence of amorphous carbon, detected in the Raman spectrum of green glaze of sample BG-1 (Fig. 7), supports this claim.

CONCLUSION

Glazed pottery samples from the archaeological site Belgrade Fortress, dated to the beginning of the 15\(^{th}\) century, were studied using optical microscopy, X-ray powder diffraction (XRPD), scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS), micro-Raman spectroscopy and multivariate statistical analysis. Combined results of SEM-EDS and micro-Raman spectroscopic analyses revealed that samples were covered with thin, lead-based glaze. Glazing was performed, for majority of samples, by applying a mixture of lead oxide and quartz on the clay body. Fe-based spinel was used for brown glazes, whereas copper and iron were responsible for the coloring of the green and yellow glazes.

The selected ceramic samples, all shards of decorated jugs, show characteristics of several “potter’s signatures”, i.e., decoration styles distinctive for workshops from the areas Ras, (represented by the material from the Studenica Monastery), Kruševac and Belgrade/Smederevo which have produced pottery from the mid-14\(^{th}\) to mid-15\(^{th}\) century. Considered together, the glazed pottery
from Belgrade and Studenica enable us to compare the characteristics of the glazes and to gather complementary information about the glazing technology. Using SEM-EDS and micro-Raman spectroscopy, it was shown that the chemical composition and glazing technology of the samples from Belgrade Fortress and the Studenica Monastery are similar regardless of their different workshops’ origin (which is manifested by different composition of clay paste used for ceramic body of vessels). In addition, the results of an earlier investigation of glazed pottery found at Novo Brdo are very similar to the results presented in this work. The great similarity between the samples investigated in this work and the typical material from Byzantine areas dated to an earlier period (12th-13th centuries), as well as from the same period (early 15th century) indicates that the glazing technology was in Byzantine tradition. A better understanding of the medieval pottery production in the Balkans could contribute to a comprehensive analysis of glazed ceramic of the Byzantine world.

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SUPPLEMENTARY MATERIAL TO
Application of analytical techniques for unveiling the glazing technology of medieval pottery from the Belgrade Fortress

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Serbian medieval glazed ceramics is group of products dated from the first half of the 13th century to the middle of the 15th century. Archaeological investigations distinguished several workshops on the territory of medieval Serbian state. The earliest workshop discovered so far was in the Studenica Monastery dated at the first half of 13th century. Also, there were workshops in Ras area during the 14th century and at the beginning of the 15th century, and in Kruševac, Smederevo and Novo Brdo in the first half of the 15th century1,2. The relevant locations in medieval Serbia are shown in Fig. S-1.

Fig. S-1. Map showing relevant locations in medieval Serbia (drawn by Uglješa Vojvodić)
Table S-I. Photographs and cross sections of the pottery samples (shards of jugs) from the Belgrade Fortress (denoted as BG) and the Studenica Monastery (denoted as S2); groups are based on decoration techniques and colours.

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<th>Sample photo exterior</th>
<th>Cross section</th>
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Archaeological context of pottery. The Belgrade Fortress is a multilayered archaeological site and monumental complex which has been changing for almost two millennia: from the first traces of settlements dated Late Stone Age (Neolithic) till the 18th century. Because of the very important geopolitical position, at the same location (hill above the confluence of the rivers Sava and Danube) a Roman castrum Singidunum (2nd century) and later Byzantine castle (12th century) were constructed. At the beginning of 15th century, during the reign of Despot Stefan Lazarević (1404-1427), Belgrade became capital of Serbia. It was a fortified town where Despot resided in the palace located in the thoroughly rebuilt Byzantine castel. Further changes in relief and more complex fortifications occurred during Austro-Turkish wars (17th-18th century). Fortress was reconstructed three times and became one of the strongest defence points in Europe.

The most significant growth of Belgrade was at the beginning of the 15th century, when it became the military, political, economic and cultural center of Serbia. The most important part of the town was the palace with court complex – Castle, protected in different ways by three separate fortifications: Upper Town, Western Suburb and Lower Town. Unfortunately, the parts of the walls and towers of this fortification, as well as the buildings located inside, were destroyed in the gun powder explosion in 1690.

Archaeological investigations of the Castle have been performed between 1963 and 1980, with occasional breaks. Extensive research related to late Middle Age and later periods are still unpublished. However, information about the condition, character and content of discovered archaeological unites can be obtained from the available field documentation. Archaeological layers from the
early 15th century were separated in all the investigated areas, but contained limited ceramic material. The most important layer where glazed vessels were found was located above the level of Palace’s courtyard. The shapes and decorations of ceramic vessels provide insight into furnishing of the Despot’s court.

Description of samples. Group I (BG-1, BG-2 and BG-4) is characterized by fine-grained fabric. The body colours are different shades of red, with uniformly colored cross sections. These samples are decorated in the same way: green, brown and yellow painted motives over white slip and transparent glaze. According to technological and decorative characteristics, this group of samples belongs to pottery produced at the north of the medieval Serbian Despotate at the beginning of 15th century, famous for jugs from nearby Smederevo Fortress.

Group II (BG-3, BG-5, BG-6, BG-7, BG-8, BG-9, BG-10, BG-11, BG-13, BG-14, BG-16) is characterized by medium-grained fabric. The body colours are brown, red and grey, uniform at cross sections or rarely with red boundary and brown core (BG-3, BG-5, BG-11). The shards were, contrary to group I samples, decorated by painted sgraffito technique. Characteristics of this technique are incisions of motives in white slip, green and yellow painting and, as the final step, application of transparent yellow or green (olive green) protective glaze. The samples from group II are related to pottery vessels produced in the Ras area during 14th and the first half of the 15th century.

Group III (BG-12 and BG-15) is characterized by medium-grained fabric. The body colour is red, uniform at the cross sections. The shards are decorated in painted sgraffito technique. The motives incised in the white slip are highlighted with green and brown colour, and surface is protected by yellow glaze. Even though by overall appearances these samples are similar to samples from group II, based on decoration and colour they are related to pottery produced in central Serbia to supply Kruševac the capital of Prince Lazar and neighboring town Stalač.

Archaeologically significant pottery material found at the Studenica Monastery, the oldest workshop in medieval Serbia, recently has been a subject of archaeometric investigations. Five representative pottery samples (S2.33, S2.34, S2.36, S2.37, S2.42) from this material were used in this work for comparison with pottery from the Belgrade Fortress in order to investigate similarities in pottery production. The samples from the Studenica Monastery were shards of painted and sgraffito jugs (Table S-I). They have the highest overall similarity with BG samples from group II, but pottery shards from Studenica have thicker walls compared to BG group II samples. This pottery is mostly of fine fabric and with uniform wall thickness. Regarding the petrography, it is the uniform group, made of local raw material. Compared to white painted olive-glazed jugs, which have brown and grayish brown body colour, the sgraffito vessels are red, in several nuances. Green, yellow and brown glazes were applied on the outer surfaces, over a white slip and sgraffito decoration.
Fig. S-2. Plot of adjusted glaze composition versus body composition for SiO₂

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