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Application of analytical techniques to the unveiling of 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, were investigated by combining optical microscopy, X-ray powder diffraction (XRPD), scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS), micro-Raman spectroscopy and multivariate statistical analysis. The decoration and style of the investigated ceramics were characteristic of workshops from different areas of the medieval Serbian State: Ras, Kruševac and Belgrade/Smederevo. Comparison was made with ceramic samples from the same period excavated at the Studenica Monastery, the hitherto earliest workshop discovered, which were used as reference material for the Ras area. Ceramics from the Belgrade Fortress were covered with a transparent, lead-based glaze. The 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. The brown colours of the glaze originated from Fe-based spinel, whereas copper and iron were responsible for the colouring 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 pro-

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ducts with specific decorations; the most famous products were slip-painted and sgraffito wares.[2] 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 provenience.[3–9] 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.[10,11]

Several archaeometric studies of medieval glazed pottery from the most significant centres of the medieval Serbian State have been performed: the first state capital Ras,[12] the first monastery Studenica[13,14] and the most important mining centre Novo Brdo.[15] Considering the raw materials and procedures employed in their manufacture, the investigations confirmed the local pottery production and originality.

Belgrade was the capital of the Serbian medieval state at the beginning of 15th century. The focus of this study is glazed pottery originating from that period excavated from the area of the Belgrade Fortress. The investigated samples have been classified by archaeologists in three groups based on decoration characteristics of the workshops from the three different areas of the 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 the glazing technology. The multi-analytical approach was 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 but the partial archaeological excavation performed so far did not provide enough archaeological (and ceramic) material to be a solid starting point for consideration of "the Belgrade pottery workshop", *i.e.*, the organization of ceramics production within the city area. Therefore it was 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.[10] For this reason, pottery samples from the Ras area, well characterized in recent archaeometric studies, dated to the 14th to early 15th century and found in the Studenica Monastery, were used in this work as material for comparison.[13,14] Previous investigations showed the use of local raw materials for the preparation of the clay body and local pottery production.[13,14]

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

EXPERIMENTAL

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 were 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) atypical samples were discarded in accordance with museum practice at the time. Some of the excavated shards were used for complete reconstruction of five original vessels.[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 a fast-turning (foot) potter's wheel. Photographs of the investigated samples are given in Table S-I of the Supplementary material to this paper. The investigated samples were classified into 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 the samples are given in the 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,[13,14] were used as reference material in this study.

Analytical methods. Cross sections of all investigated ceramic shards were recorded by a Citoval 2 binocular stereo microscope, Carl Zeiss, Jena, under magnification ×16.

The chemical compositions 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, were obtained by scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS). Small fragments of the investigated pottery shards were cut, polished and analyzed uncoated by a 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 an acceleration voltage of 15 kV. A minimum of five areas of 150×150 μm^2 were analysed on each sample to obtain a representative composition; the data were normalized to 100 wt. % oxides.

With the aim of comparing samples from the 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 the Ward method and Euclidean distance on the compositional data of the ceramic body. Centred log-ratio transformation of the data was applied, which decreases the difference between the magnitudes of the major and minor oxide concentrations.[17] This transformation consisted of dividing each individual variable value by its geometric mean, and logarithmic transformation to base 10. A dataset with 18 samples consisting of the chemical composition of the 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 CuKα radiation (λ = 1.54178 Å), applied voltage U = 40 kV and current I = 40 mA. The diffraction data were acquired over the scattering angle 2θ from 2 to 50° with a step of 0.020° at an acquisition rate of 1° min^{-1}.

Micro-Raman spectra of the glazes of all investigated samples were recorded directly on the glaze surface, at various points on each sample using a DXR Raman microscope (Thermo Scientific). In addition, 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^{-1}, and a resolution of 2 cm^{-1}. The acquisition time was 10 s with 10 scans. Thermo Scientific OMNIC software was used for spectra collection and manipulation. The Raman spectra from in-house data base and the literature[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 would 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 the 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. The other samples (from groups II and III) have a quite uniform medium-grained fabric, with rounded, medium–coarse inclusions with noticeable particles that have an equant angular shape. Optical micrographs of cross sections of all investigated samples are given in Supplementary material (Table S-I).

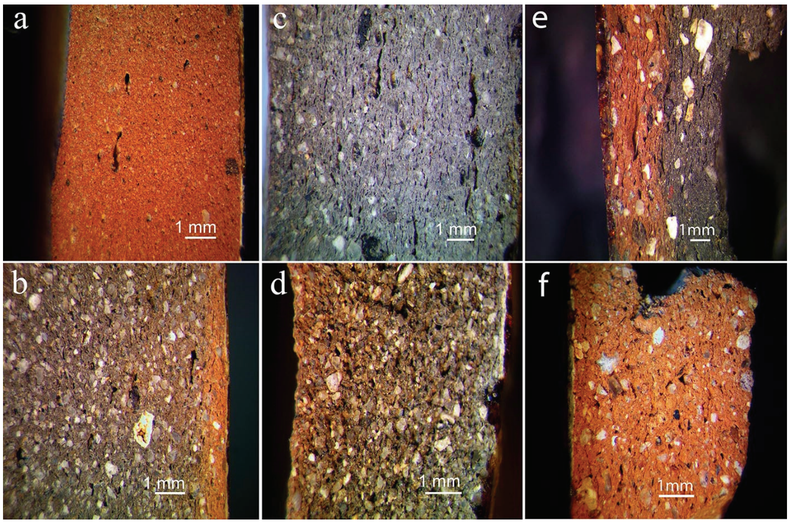

Fig. 1. Cross sections of typical samples from the investigated groups, the Belgrade Fortress and the Studenica Monastery: a) BG-4; b) BG-5; c) BG-8; d) BG-15; e) S2.33; f) S2.36.

The micro-Raman spectroscopy revealed that the majority of the inclusions originate from quartz, which could be present as sediment but also as temper.[19] Voids present in the cross sections of all samples may indicate the release of air trapped in the clay paste during the kneading and construction processes 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.[14] For the samples BG-3, BG-5, BG-11, BG-12, BG-13, the outer parts are light red and the inner parts are darker different shades of brown, which indicates a rapid firing procedure. The pottery shards from the Belgrade Fortress, 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 the particles are large and have different sizes contrary to the samples from Belgrade Fortress that have uniform-sized particles. The samples have either the core darker than the edges (*e.g.*, S2.37) or a bright outer edge and a 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 was still hot.[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. In addition, a low content of calcium oxide classifies the clay used for the production of samples from Studenica as non-calcareous, as previous studies have shown.[13,14]

The other samples from the Belgrade Fortress contained higher amounts of lime and samples BG-2 and BG-12 could 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 contents 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.[20] 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 a preliminary study.

The HCA results of the chemical composition of the ceramic body of all studied samples are 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 the Ward 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 that all have a 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 a low content of calcium oxide (under 2.5 wt. %). The grouping of BG-1 and BG-4 within the "cluster Studenica" (in contrast to BG-2), as well as BG-12 within the "cluster Belgrade" (in contrast to BG-15) show two different ways of raw material preparation (clay and temper) among samples belonging to the same decorative circle.

TABLE I. The chemical composition (Content (standard deviation), wt. %) 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

Sample	Component							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2
BG-1	58.3 (4.9)	19.5 (0.1)	12.1 (4.1)	1.3 (0.2)	3.0 (0.4)	2.8 (0.1)	1.6 (0.3)	n.d.
BG-2	49.1 (2.5)	17.0 (0.1)	9.3 (0.8)	16.3 (0.9)	2.8 (0.1)	3.1 (0.2)	1.0 (0.3)	0.7 (0.1)
BG-3	70.1 (3.7)	12.0 (3.3)	6.6 (0.4)	6.2 (1.9)	2.0 (0.4)	1.9 (0.8)	0.8 (0.1)	0.4 (0.1)
BG-4	58.0 (6.1)	20.7 (3.2)	12.1 (1.7)	0.9 (0.1)	2.6 (0.4)	2.8 (0.5)	2.0 (0.4)	0.3 (0.1)
BG-5	62.2 (2.4)	17.6 (1.7)	6.1 (1.7)	7.9 (0.3)	2.7 (0.3)	2.3 (0.3)	1.3 (0.3)	n.d.
BG-6	54.7 (1.7)	22.2 (0.3)	7.4 (1.0)	6.9 (0.1)	3.6 (0.5)	2.8 (0.3)	1.8 (0.1)	0.5 (0.2)
BG-9	55.8 (3.6)	22.2 (1.6)	7.5 (0.5)	5.6 (0.7)	3.3 (0.2)	2.2 (0.2)	2.6 (0.4)	0.5 (0.1)
BG-10	57.7 (2.5)	17.2 (2.1)	11.4 (1.8)	7.2 (2.1)	2.8 (0.6)	1.4 (0.6)	1.3 (0.1)	0.6 (0.1)
BG-11	55.4 (1.1)	22.2 (0.9)	8.2 (3.7)	6.9 (1.2)	2.7 (0.2)	2.5 (0.3)	1.8 (1.4)	0.2 (0.1)
BG-12	49.7 (2.0)	20.8 (0.8)	8.9 (2.0)	13.3 (2.8)	2.9 (0.2)	2.8 (0.1)	2.3 (0.6)	n.d.
BG-13	63.9 (5.9)	16.1 (1.5)	7.9 (1.4)	5.2 (1.6)	2.2 (0.4)	2.2 (0.5)	2.4 (0.6)	0.5 (0.1)
BG-14	51.3 (2.0)	22.0 (0.1)	8.4 (1.1)	9.5 (0.4)	3.9 (0.1)	2.6 (0.1)	1.6 (0.1)	0.5 (0.1)
BG-15	62.1 (4.7)	19.6 (3.8)	9.7 (2.3)	2.5 (0.7)	2.5 (0.7)	2.4 (0.2)	1.3 (0.1)	n.d.
S2.33	53.4 (0.8)	21.1 (0.3)	15.4 (1.2)	1.3 (0.1)	3.8 (0.4)	2.9 (0.2)	0.8 (01)	1.0 (0.1)
S2.34	53.0 (1.0)	24.2 (1.1)	12.3 (1.3)	1.7 (0.3)	2.7 (0.2)	3.8 (0.9)	1.3 (0.1)	0.4 (0.1)
S2.36	56.9 (0.3)	22.0 (0.3)	11.2 (0.5)	2.2 (0.1)	2.4 (0.4)	2.9 (0.1)	2.3 (0.6)	n.d.
S2.37	64.7 (2.7)	18.1 (1.0)	4.6 (1.0)	2.4 (0.7)	1.7 (0.2)	4.4 (0.6)	3.5 (0.2)	0.3 (0.1)
S2.42	55.8 (1.4)	22.0 (0.9)	13.2 (0.5)	1.4 (0.8)	3.7 (0.8)	2.4 (0.2)	1.2 (0.4)	0.2 (0.1)

Mineralogical composition. The XRPD patterns of representative samples from Belgrade Fortress are shown in Fig. 3. Characteristic reflections of quartz are dominant in the patterns of all the investigated samples. Moreover, characteristic reflections of feldspar from the plagioclase group were detected in all samples. The presence of phyllosilicates (illite/muscovite) were 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 contained reflections of high temperature phases, diopside and gehlenite, which were not present in the samples BG-1 and BG-4 from group I. This finding is in agreement with the CaO content detected by SEM-EDS analysis (Table I). The mineralogical composition of samples BG-1, BG-4 and BG-15 were very similar to the mineralogical composition of samples from the Studenica Monastery determined by multiphase Rietveld analysis of high resolution diffraction patterns in an earlier study.[14] This agrees with results obtained from the EDS measurements in this work.

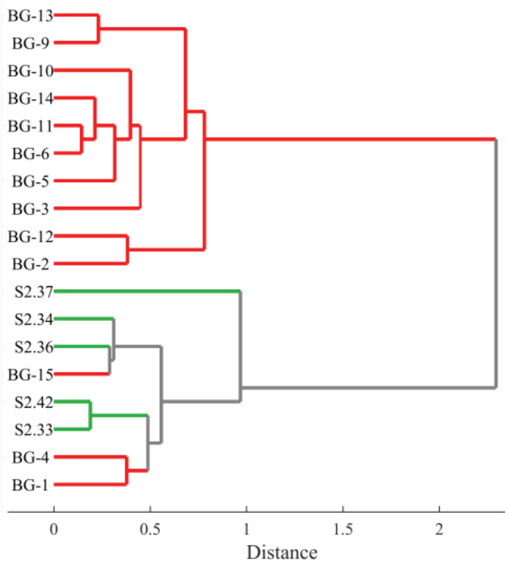

Fig. 2. Hierarchical clustering dendrogram of the chemical composition of ceramic body of the samples from the Belgrade Fortress and the Studenica Monastery.

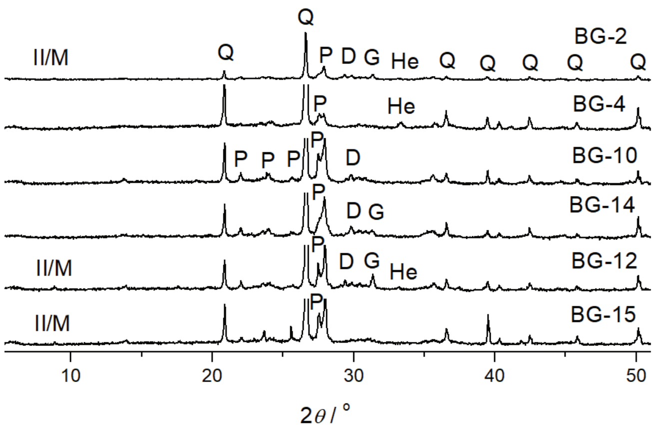

Fig. 3. XRPD patterns of representative samples from the Belgrade Fortress. Abbreviations: Il/M-illite/muscovite, Q-quartz, P-plagioclase, D-diopside, G-gehlenite, He-hematite.

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 the ceramics. Phyllosilicates disappear at temperatures between 900 and 950 °C,[12] whereas gehlenite forms between 800 and 850 °C in a reaction between calcite and the clay mineral illite.[21] Therefore, the identified minerals suggest firing temperatures higher than 800–850 °C, but lower than 950 °C. The firing temperature for the samples from the Studenica Monastery was estimated at 900 °C in a previous study.[14] The presence of hematite indicates oxidizing conditions during the firing process, which is in agreement with the reddish colour of the ceramic body.

Glaze

The average thickness of the investigated glazes was in the range 60–300 μm. The thickness of the glaze varies among samples but also from one part to another of a particular sample. The glazes were well preserved; the majority of the samples were 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 are shown in Table II. The content of lead oxide was high and varied from ≈50 to ≈75 wt. %. The alkali contents (Na_2O + K_2O) were rather low, up to ≈2 wt %. Consequently, the glazes of all investigated samples could be classified as lead-rich glazes, with lead oxide as flux agent. Only two colorants were detected: Cu and Fe.

Two glazing techniques, *i.e.*, application of a mixture of lead oxide and quartz or application of lead oxide alone on the surface of the ceramic body, could be distinguished when the glaze compositions was renormalized after subtraction of the lead oxide as well as copper oxide and iron oxide (considered as purposely added colorants).[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 the glaze, calculated in this way, was higher than in the body (Fig. S-2, Supplementary material) and the 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 did the calculated concentrations match the composition of the body (Fig. S-2), indicating that these samples were glazed by application of lead oxide alone.

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

TABLE II. Chemical composition (Content (standard deviation), wt. %) of glazes of samples from the Belgrade Fortress and the Studenica Monastery determined by SEM-EDS; oxide concentration normalized to 100 wt. %

Sample	Glaze colour	Component									
		PbO	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	CuO	TiO_2
BG-1	Green	53.5	27.4	7.5	6.9	1.7	0.6	2.0	0.3	0.2	n.d.
		(1.5)	(1.1)	(0.1)	(1.4)	(0.1)	(0.5)	(0.2)	(0.1)	(0.1)	
BG-2	Green–	64.3	23.9	3.6	4.0	1.1	0.6	0.2	0.2	1.8	0.2
	brown	(2.5)	(3.5)	(0.6)	(0.7)	(0.3)	(0.1)	(0.1)	(0.1)	(0.8)	(0.1)
BG-3	Light	71.1	18.8	5.5	0.9	0.9	0.6	0.9	0.4	0.7	0.3
	green	(1.9)	(0.2)	(0.5)	(0.3)	(0.1)	(0.1)	(0.2)	(0.2)	(0.3)	(0.1)
BG-4	Honey	55.3	31.8	6.5	2.1	1.1	1.1	0.7	0.6	0.6	0.2
	brown	(0.7)	(0.1)	(0.6)	(0.7)	(0.7)	(0.1)	(0.1)	(0.1)	(0.2)	(0.1)
BG-5	Honey	64.6	23.7	4.7	2.0	2.4	1.0	0.4	0.7	0.3	0.2
	brown	(3.0)	(2.2)	(0.7)	(0.2)	(1.9)	(0.3)	(0.2)	(0.3)	(0.1)	(0.1)
BG-6	Green	70.6	19.9	4.3	2.8	0.7	0.7	0.3	0.5	n.d.	0.1
		(3.0)	(1.3)	(0.1)	(0.8)	(0.1)	(0.1)	(0.1)	(0.1)		(0.01)
BG-9	Olive	53.3	28.8	8.3	3.0	1.1	1.6	0.9	1.5	1.2	0.3
	green	(5.2)	(2.6)	(1.0)	(0.8)	(0.3)	(0.5)	(0.4)	(0.6)	(0.5)	(0.1)
BG-10	Light	64.3	24.3	5.5	1.1	0.9	0.7	0.7	0.5	1.6	0.3
	green	(0.5)	(0.5)	(0.4)	(0.1)	(0.1)	(0.2)	(0.2)	(0.1)	(0.1)	(0.04)
BG-11	Olive	54.0	26.9	7.8	3.8	3.6	2.2	1.0	0.4	0.1	0.3
	green	(2.9)	(1.7)	(0.4)	(0.4)	(0.3)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)
BG-12	Yellow–	68.7	20.9	3.7	0.8	3.7	1.0	0.5	0.8	n.d.	n.d.
	green	(2.6)	(3.0)	(0.6)	(0.2)	(1.3)	(0.2)	(0.1)	(0.2)		
BG-13	Olive	58.9	21.6	8.9	4.2	2.5	1.1	1.1	0.5	1.0	0.3
	green	(2.4)	(0.1)	(1.4)	(0.9)	(0.1)	(0.1)	(0.1)	(0.1)	(0.5)	(0.1)
BG-14	Light	62.7	20.1	7.1	3.4	2.0	1.0	1.2	0.8	0.8	0.2
	green	(0.4)	(0.1)	(0.1)	(1.0)	(0.2)	(0.1)	(0.1)	(0.2)	(0.7)	(0.1)
BG-15	Yellow	50.6	38.2	7.8	0.3	0.5	0.5	1.5	0.9	n.d.	n.d.
		(2.8)	(2.0)	(0.8)	(0.7)	(0.1)	(0.4)	(0.3)	(0.1)		
S2.33	Olive	68.6	19.6	7.3	2.9	0.5	0.8	n.d.	0.3	n.d.	n.d.
	green	(0.8)	(1.5)	(0.6)	(0.5)	(0.1)	(0.2)		(0.1)		
S2.34	Olive	57.5	27.1	8.0	2.4	1.1	1.0	1.3	0.6	0.8	0.3
	green	(2.5)	(1.3)	(0.7)	(0.2)	(0.3)	(0.1)	(0.2)	(0.1)	(0.2)	(0.1)
S2.36	Green–	55.8	26.2	10.4	2.9	0.7	1.3	1.2	0.8	0.3	0.4
	brown	(1.6)	(1.0)	(0.5)	(0.3)	(0.1)	(0.3)	(0.2)	(0.3)	(0.1)	(0.1)
S2.37	Olive	66.0	19.9	6.8	2.7	1.2	0.8	1.0	0.6	0.7	0.3
	green	(3.0)	(1.6)	(0.4)	(0.5)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)
S2.42	Yellow	75.5	19.7	4.4	n.d.	n.d.	0.3	n.d.	n.d.	n.d.	n.d.
		(0.9)	(0.2)	(0.3)			(0.1)				

Typical, fluorescence corrected, Raman spectra of the glazes of pottery samples from the Belgrade Fortress and the Studenica Monastery are shown in

Fig. 5. The 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 the Belgrade Fortress and the Studenica Monastery were very similar: two broad bands originating from Si–O stretching modes centred between 920 and 950 cm^{-1} and less intense Si–O bending modes centred at about 490 cm^{-1}.

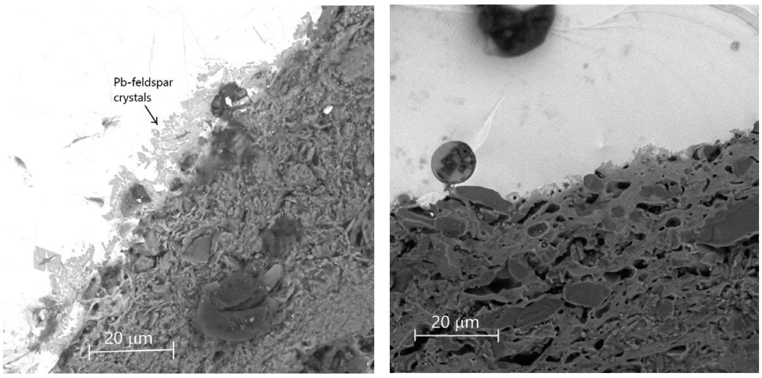

Fig. 4. SEM photographs of body-glaze interfaces of the samples BG-4 (left) and BG-5 (right).

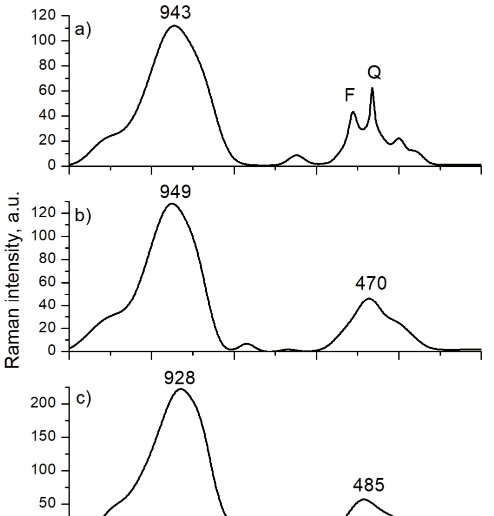

Fig. 5. Raman spectra of glazes from representative pottery fragments: a) BG-2; b) BG-10 and c) S2.36. Abbreviations: Q-quartz, F-feldspar.

When the tetrahedral units are weakly connected, the stretching modes are more intense than the 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, the findings acquired by these two techniques confirmed that the applied glazes were lead-based.

The Raman spectra of the glazes of all the investigated pottery samples often showed additional narrow peaks originating from crystalline phases such as undissolved quartz (463 cm^{-1}) and feldspars (513 cm^{-1}),[26] as illustrated at Fig. 5a. Traces of gas bubbles were detected on the surface of the glazes of some samples from the Belgrade Fortress (BG-2, BG-5, BG-8, BG-9, BG-11, BG-13 and BG-15) and on five samples from the Studenica Monastery, similar to other samples from this excavation site investigated in an earlier study.[14] This could be a consequence of a fast firing process or an inappropriate maximum firing temperature that result in decomposition of the glaze and the body indicating that the glaze was not matured properly.[27]

Colorants. The macroscopically observed colours of glazes were 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. Representative Raman spectra of brown glazes of pottery samples from the Belgrade Fortress and the Studenica Monastery are presented in Fig. 6. As shown in an earlier study,[14] iron oxides were responsible for brown shades of glaze of pottery from the Studenica Monastery because characteristic bands for hematite, Fe_2O_3 (228, 248, 295, 410, 504, 619 and the strong mode at 1325 cm^{-1}) and magnetite, Fe_3O_4 (≈670 cm^{-1}), were 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 the chemical composition of spinels by Raman spectroscopy,[28] but combining these results with SEM-EDS analysis indicates the use of Fe-based spinels for dark brown colorations. Magnetite was identified only in the case of the BG-3 sample. A broad Raman doublet at 1374 and 1590 cm^{-1} characteristic for amorphous carbon black 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]

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 from the Studenica Monastery.[14] As illustrated in Fig. 7, only a glassy Raman signature together with bands originating from crystalline precipitates were detected for both the green and yellow glazes.

EDS analyses identified Fe in yellow glazes, whereas Cu was detected in the majority of the green glazes (Table II). When the Raman spectrum of a glaze shows only a glassy signature, then the colour was achieved by dispersion of ions (Fe^{3+} or Cu^{2+}) in a glassy matrix.[29] Several samples, *e.g.*, BG-1, BG-6, BG-11 (Table II), with a green glaze did not contain any significant Cu content, but the amount of Fe_2O_3 was rather high and varied from 2 wt. % to7 wt. %. The green colour could be produced by Fe^{2+} formed in a reducing atmosphere even when there was no copper in the glaze.[30] The presence of amorphous carbon, detected in the Raman spectrum of the green glaze of sample BG-1 (Fig. 7), supports this claim.

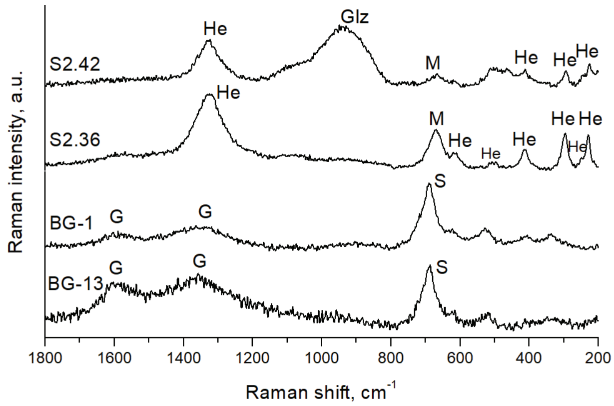

Fig. 6. Raman spectra of brown glazes of the representative pottery samples from the Belgrade Fortress and the Studenica Monastery; abbreviations: He – hematite, M – magnetite, G – graphite, S – spinel, Glz – glaze.

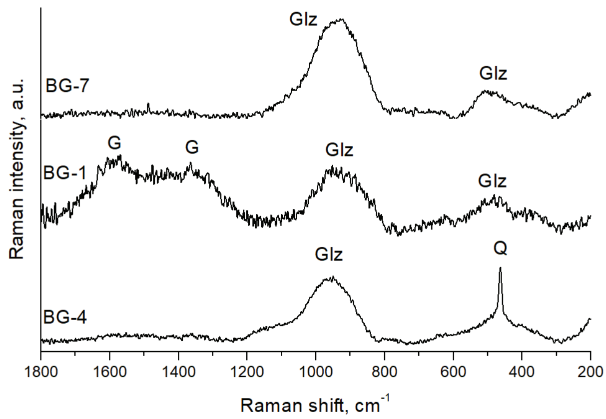

Fig. 7. Raman spectra of green glazes of representative pottery samples from the Belgrade Fortress; abbreviations: Glz – glaze, G – graphite, Q – quartz.

CONCLUSIONS

Glazed pottery samples from the archaeological site Belgrade Fortress, dated to the beginning of the 15th 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. The combined results of SEM-EDS and micro-Raman spectroscopic analyses revealed that the samples were covered with a 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 colouring of the green and yellow glazes.

Selected ceramic samples, all shards of decorated jugs, show the 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, where pottery have been produced from the mid-14th to mid-15th 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 despite originating from different workshops (which is manifested by the different composition of clay paste used for ceramic body of the vessels). In addition, the results of an earlier investigation of glazed pottery found at Novo Brdo[15] 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)[27,29,31] indicates that the glazing technology was within Byzantine tradition. A better understanding of the production of medieval pottery in the Balkans could contribute to a comprehensive analysis of glazed ceramic of the Byzantine world.

SUPPLEMENTARY MATERIAL

Additional data are available electronically at the pages of journal website: https:// //www.shd-pub.org.rs/index.php/JSCS/index, or from the corresponding author on request.

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И З В О Д

ПРИМЕНА АНАЛИТИЧКИХ ТЕХНИКА ЗА ОТКРИВАЊЕ ТЕХНОЛОГИЈЕ ГЛАЗИРАЊА СРЕДЊЕВЕКОВНЕ КЕРАМИКЕ НАЂЕНЕ НА БЕОГРАДСКОЈ ТВРЂАВИ

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Средњевековна глазирана керамика из 15. века, нађена на Београдској тврђави у Србији, је испитивана оптичком микроскопијом, дифракцијом X-зрачења на праху (XRPD), скенирајућом електронском микроскопијом са енергетски дисперзивном спектроскопијом X-зрачења (SEM-EDS), микро-раманском спектроскопијом и мултиваријантном статистичком анализом. Декоративни стилови испитиване керамике су типични за радионице из различитих области средњевековне српске државе: Рас, Крушевац и

Београд/Смедерево. Поређење је вршено са керамичким узорцима из истог периода нађених у манастиру Студеница, најстаријој до сада откривеној радионици, који су коришћени као референтни материјал за област Рас. Керамика са Београдске тврђаве има транспаренту оловну глазуру. Код већине испитиваних узорака глазуре су добијене наношењем смеше олово оксида и кварца на тело керамике, а код само два узорка глазуре су добијене наношењем чистог олово-оксида. Браон нијансе глазуре потичу од Fe-спинела, а од бакра и гвожђа потичу зелене и жуте нијансе глазура. Добијени резултати указују на технологију глазирања преузету из византијске традиције.

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