

# Preliminary archaeometry investigation of artifacts from the Medieval Bosnian town of Dubrovnik (Ilijaš, BiH)

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Article info	Abstract: The aim of this paper was to analyse archaeological artifacts found in the
Received: 28/02/2024 Accepted: 24/09/2024	medieval town of Dubrovnik, near Sarajevo, using FAAS and SEM-EDS techniques. A total
	of 11 samples of different types were chosen: ceramic sherds, an iron nail, slag, and a piece
	of brocade thread. The results of the ceramic samples showed high levels of iron and
	manganese, most probably due to the geological bedding of the location. Trace amounts of
Koywords	chromium, copper, nickel, lead, and zinc further support this assumption, which means that
Keywords: Archaeometry	the clay used to make ceramic was supplied in the vicinity of Dubrovnik. A painted sample
Medieval Bosnia FAAS	of green ceramic had high levels of lead, suggesting that this metal was deliberately added
SEM-EDS Dubrovnik	to strengthen the properties of the vessel. SEM-EDS measurements of the slag showed the
Golden thread	presence of As, Hg and Sn, and one possible explanation is that they were used in gold or
	silver refining processes, which according to historical reports were performed in
*Corresponding author:	Dubrovnik. A piece of golden thread has proven useful in determining the time frame of its
Almir Olovčić E-mail: almirolovcic@hotmail.com	origin. EDS measurement showed that the type of the manufacturing process used in the
Phone: +32470928516	production of this golden thread did not exist before the 14th century.

# INTRODUCTION

During the Medieval times, the territory of present-day Bosnia and Herzegovina (BiH) was at the crossroads of armies, politics, religion, and trade. Trading documents from the medieval period are probably the most important source for the researchers and historians of medieval Bosnia. From there, they can find out a lot about trade routes, types of merchandise and the places named. Most of the time, these place names have yet to be ubicated, but some are well known and located, although the sources about them are scarce and border on legends and myths. One such location is Dubrovnik, a medieval town, 30 kilometers northeast, of Sarajevo, the capital of Bosnia and Herzegovina. Its origin is shrouded in mystery and unknown facts that have yet to be discovered. But, based on the folk legends, the town was founded back in those days when the Bosnian ruler Kulin Ban gave permission to two Dubrovnik merchants to exploit mines and ores

between the city of Olovo and Jagodna mountain, who then erected the city and smelted iron and silver ore, mined from the above-mentioned mountain (Filipović, 1924). The main objectives of this study were: (1) to determine the content of the selected metals: Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn in ceramic fragments, from the location of the medieval Bosnian town Dubrovnik by flame atomic absorption spectrometry technique (further FAAS); (2) to determine the composition of ceramic fragments, slag, and piece of golden thread using scanning electron microscopy and energy dispersive Xray spectroscopy technique (SEM-EDS); (3) based on the results obtained by two techniques used to gather at least some knowledge about the medieval lifestyle of the inhabitants who lived at the location of Dubrovnik. In addition, this paper presents the first results of the study of the ceramic potsherds, iron slag and accompanying

of the ceramic potsherds, iron slag and accompanying artifacts excavated from Dubrovnik, in 2017 archaeological campaign.

#### Location

The old town of Dubrovnik is situated on a hill above the river Misoča, which is created by the confluence of two streams Zenik and Rijeka, at an altitude of 882 meters (coordinates: 34TBP8641274566, Figure 1.). It is oriented east-west and looks as if it had a well (cistern) in the town center (Mazalić, 1939). Many medieval necropolises are in the vicinity, the most famous being Kopošići (Filipović, 1924). Unfortunately, there are not many historical accounts of the formation and history of this town. The first information about Dubrovnik dates back to 1404. Dubrovnik is also mentioned in 1468/69., that is, only a few years after the Ottomans conquered these regions (Aličić, 2008). The next mention of Dubrovnik come from 1503 and 1519, that is, two peace treaties concluded between the Hungarian kings and the Ottoman Empire. The last mention of Dubrovnik dates from 1709, when the mosque in Dubrovnik was abandoned, and since there was no crew, and apparently no residents in the suburbs, it was not repaired (Kreševljaković 1953). By that time, the area of Dubrovnik and its surroundings had lost its military, economic, and commercial importance, so it was abandoned, and the population moved to much lower areas closer to new communications. Dubrovnik was among a few trading places (trgovište in Bosnian) in medieval Bosnia that existed in the second half of the 14th and the first half of the 15th century, but after the Ottoman conquest, which happened in the 1463, the number of these trading places was halved (Andelić, 1963).

#### MATERIAL AND METHODS

All artifacts that were part of this study were collected during the 2017 archaeological campaign. A total of 11 samples were chosen for analysis, based on their significance and importance; more valuable artifacts, like brocade thread and painted ceramic (K10) were chosen for non-destructive analysis by SEM-EDS technique. Although a small number of artifacts were included in the analysis, nevertheless they will provide valuable first data for any subsequent analysis or research in this area. Table 1. summarizes the artifacts that were part of this study, with short descriptions of each of them. Figure 2. shows the material used in this study.



Figure 1. Location of Medieval town of Dubrovnik in Bosnia

Only incomplete, broken ceramic fragments were utilized for the analysis. Into the open PTFE vessel containing 0.2 g (± 0.2 mg) of finely powdered and homogenized sample, 25 mL of concentrated HNO<sub>3</sub> was added. After the evaporation of nitrogen oxides, the reaction vessel was sealed and left to react for 12 hours at 60°C. The dissolved samples were then adjusted to 50 mL with Milli-Q water. For SEM-EDS observations, a JEOL JSM-6610LV microscope was used. Before the analysis, all the samples were carefully washed with ethanol, in order to clean the surface used for analysis from soil and dirt, accumulated over time. Previously, a thin coating of Au was added to the non-conducting samples (ceramic samples) using a coating device (LEICA SCD005). As for the quantification, elements with  $Z \leq 5$  could be quantified, with a detection limit of approximately 0.1 mass%, and a resolution of 126 eV.

Table 1	. Artifacts	used	during	this	study

Sample	Type of	ts used during this study Short description of
Bampie	sample	samples
Dub 1	Black ceramic	Fragments of coarse clayed ceramic, probably fired
Dub 2	Black ceramic	under reduction conditions, as can be seen by color and
Dub 3	Black ceramic	from roughly shaped vessels. White, different
Dub 4	Black ceramic	sized inclusions of rock suggest use of low-quality, unpurified clay for molding and baking of pottery vessels.
Dub 5	Black ceramic	Fragment of vessels edge, fine ceramic, better quality clay. Reducing conditions.
Dub 6	Grey ceramic	Fragment of grey, unglazed ceramic. Reducing conditions.
Dub 8	Red ceramic	Fragment of red, partially glazed ceramic, black colored inside. Probably fired under combination of reduction and oxidation conditions, since the red glaze color is not uniform.
RF	Slag	Greyish black piece of metallic slag, resembling iron type slag.
K10	Glazed pottery	Green glazed type of Islamic pottery, fine grained clay.



Figure 2. Samples from the Dubrovnik used for the analysis

### **Quality control**

Recovery evaluations were conducted for all types of samples to ensure the accuracy of the research. The analyzed samples were spiked with a standard solution of each metal at three different levels of concentration to cover the measurement range. The recovery values ranged from 89% to 101% for all metals determined. The recovery values are presented in Table 2.

Table 2. Recovery values for spiked samples	5
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Metal	Recovery (%)
Cd	98
Cr	96
Cu	90
Fe	99
Mn	97
Ni	89
Pb	98
Zn	101

Three times the standard deviation of the blank solution signal was used to calculate the detection limits (LOD). The LOD values were: Cd (0.002 mg/L), Cr (0.006 mg/L), Cu (0.003 mg/L), Fe (0.006 mg/L), Mn (0.003 mg/L), Ni (0.01 mg/L), Pb (0.01 mg/L), Zn (0.001 mg/L).

# **RESULTS AND DISCUSSION**

The obtained results will be presented and discussed separately for FAAS and SEM-EDS measurements. The challenge of comparing the results will be complex due to the lack of previous similar analyses in B&H. Therefore, interpretation and discussion will involve reference to neighboring countries and Europe, focusing on the same period and similar ceramic and slag types.

#### **Results obtained by FAAS technique**

In the Table 3. results for the samples measured by FAAS technique are presented.

The results obtained by the FAAS technique, for the measured metals, most probably reflect the specific geological background of this geographical area. In the case of the ceramic samples DUB 1 to DUB 5, iron (Fe) was the most abundant element, particularly in the sample DUB 5 where the level of Fe exceeded 5000 µg/kg. Manganese was another metal that was found in significant quantities in the above-mentioned samples. The results for these two metals could potentially be explained by the fact that Dubrovnik is situated between two geological zones, Vareš and Čevljanovići, which are known for their rich deposits of iron and manganese minerals. Braunite, a manganese-silicate mineral, is particularly abundant in these zones, while hematite (Fe2O3) is a commonly associated mineral in these deposits (Vujanović, 1962). Vujanović also reports significant quantities of lead, chromium, copper, and nickel in the primary minerals of the area. Therefore, the presence of these elements in the ceramic samples can be attributed to the geological composition of the clay used in pottery production. Regarding zinc, its presence in the samples can also be explained by the geological setting of the location. Significant amounts of zinc have been found in the Borovica – Vareš-Čevljanovići geological zone at a few locations (Operta & Huseyni, 2016).

#### **Results obtained by SEM-EDS technique**

DUB 6, DUB 8 and K10 ceramic fragments; RF slag of iron type, an iron nail, and a piece of golden brocade thread were chosen for the analysis by SEM-EDS technique, and their results are presented in Table 4, 5 and 6, respectively.

Metals content/ Sample				μg	/kg			
	Mn	Fe	Cr	Cu	Ni	Cd	Pb	Zn
Dub 1	195.8	4856.0	49.9	14.9	41.5	0.79	14.6	44.8
Dub 2	1284.8	5046.9	10.8	10.8	22.8	3.5	227.3	693.3
Dub 3	158.3	4639.0	37.4	17.1	28.8	< LOD	32.1	65.9
Dub 4	203.4	4703.1	33.1	14.1	36.8	<lod< td=""><td>11.9</td><td>39.6</td></lod<>	11.9	39.6
Dub 5	196.6	5172.4	31.7	16.0	25.8	0.25	32.2	130.5

Table 3. Results obtained by FAAS technique for five ceramic samples from Dubrovnik.

\*<LOD below the limit of detection

Table 4. Results for the SEM-EDS analysis of samples DUB 6, DUB 5 and K 10 (in wt.%).

G		DUB 6		DUB 8	K	10
Sample	Sit	te 1	Site 2	/	/	1
Spectrum	1	2	1	1	Glaze	Body
0	55.28	32.59	55.84	55.89	35.05	58.33
Mg	0.65	0.75	0.47	0.79	1.27	0.69
Al	13.94	18.35	8.84	8.33	3.9	7.18
Si	22.3	35.57	28	22.23	13.22	18.97
K	2.47	3.69	1.89	1.1	0.36	2.22
Ca	1.47	2.42	1.06	4.52	3.05	8.39
Ti	<lod< td=""><td>0.56</td><td><lod< td=""><td>0.42</td><td><lod< td=""><td>0.48</td></lod<></td></lod<></td></lod<>	0.56	<lod< td=""><td>0.42</td><td><lod< td=""><td>0.48</td></lod<></td></lod<>	0.42	<lod< td=""><td>0.48</td></lod<>	0.48
Fe	2.73	4.71	2.9	5.98	1.3	3.42
Cu	1.16	1.37	1	0.74	4.48	<lod< td=""></lod<>
Cl	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>0.31</td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>0.31</td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td>0.31</td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>0.31</td></lod<></td></lod<>	<lod< td=""><td>0.31</td></lod<>	0.31
Pb	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>37.37</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td>37.37</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>37.37</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>37.37</td><td><lod< td=""></lod<></td></lod<>	37.37	<lod< td=""></lod<>

\*<LOD below the limit of detection

K10 sample was a typical representative of green Ottoman glazed pottery from the areas ruled by Ottoman Empire for several centuries. A fragmented, green glazed sherd, with a crack at the surface of the glaze was chosen as a suitable for the analysis (Figure 3).

The glaze itself, at the surface of the ceramic has a twofold role. The first and more important is to prevent absorption of liquid and corrosion, while the other is purely decorative (Oztoprak et al., 2016). It mostly consists of silicon dioxide, as the primary constituent that gives it a glassy appearance, and metal oxides, which give distinctive colors (Yoon et al. 2001, 253; Oztoprak et al., 2016). As for the Ottoman glazed pottery, it is known for its high lead content, with the green coloring coming from the presence of  $Cu^{2+}$  and  $Fe^{2+}$  ions in the glaze matrix (Oztoprak et al., 2016; Correia & Chaves, 2018, 1160; Kuzmanovic et al., 2021). The analysis of glazed ceramics is in most cases focused on two areas: the glaze itself and the actual body of ceramic, i.e., the area beneath glaze, since they represent two separate parts, with different ratios and content of metals. In our work, we also took the same approach.

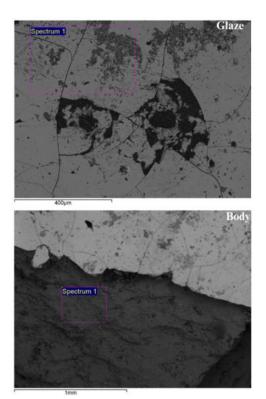


Figure 3. EDS image of the sample K 10

The glaze from Dubrovnik showed a high value for copper, resulting in a distinctive green color. Based on a large dataset of different medieval ceramics, analyzed by Tite et al. (1998), Dubrovnik ceramic can be grouped into lead - alkali type of the medieval ceramic, where the content of lead oxide is 25-35% and alkali content (soda plus potash) are 5-10%. On the other hand, the inner part showed no traces of lead or copper, so there was no transfer of Pb or Cu ions from the glaze to the inner parts of the ceramics. Additionally, the red coloring of the inner part could be due to the presence of Fe3+ ions, in the reducing atmosphere during the production process (Lyubomirova et al., 2017). Iron, although a minor constituent of ceramic, can give valuable insight into the nature of the raw materials used and firing conditions, such as the temperature during baking a clay (Wagner & Wagner, 2004). The results for this sample are in accordance with the results from Bulgaria (Yoleva et al. 2015, Lyubomirova et al., 2017), Morrocco (Correia & Chaves, 2018), Serbia (from the old city Ras, near Novi Pazar and Beograd, a fortress during the Austrian rule) (Vasilic et al., 2020; Kuzmanovic et al., 2021), Italia (Bruno et al., 1994) and Cilicia (Turkey) (Burlot & Waksman, 2022).

The DUB 6 sample was examined at two different sites, each at a different level of magnification (Figure 4.). The results obtained by the EDS mapping clearly indicate the presence of compositional heterogeneity among the grains. It is significant that the large inclusions observed at site 2 can be predominantly attributed to coarse quartz inclusions. This observation potentially suggests the use of unrefined sandy clay, meaning that it was utilized in the form in which it was originally collected, without undergoing sieving (Yoleva et al., 2015). The medium and small-sized inclusions, on the other hand, mainly consist of magnesium and potassium. Furthermore, the presence of iron and copper in this sample contributes to the red coloring observed at the fragment's edges, as clearly depicted in Figure 2 (DUB 6).

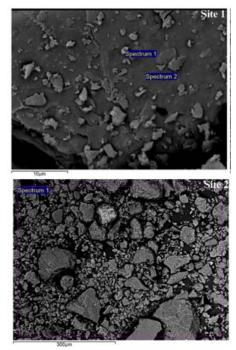


Figure 4. EDS image of the sample DUB 6

When it comes to the sample DUB 8, its most noteworthy characteristic is its coloring (Figure 1, DUB 8). The outer surface is adorned with a delicate red coating, occasionally featuring black to grey color inclusions. Conversely, the interior is coarse and black. This pattern suggests that the ceramic underwent firing under alternating reducing and oxidizing conditions, with the reducing conditions preventing the color transformation from black to red (Wagner and Wagner, 2004; Tite, 2008). Furthermore, among all the samples examined by the SEM-EDS technique, this sample exhibited the highest iron content, likely accounting for its distinctive red hue. Figure 5. reveals the EDS image of sample DUB 8, highlighting the significant heterogeneity observed in its inclusions, with quartz being the predominant component.

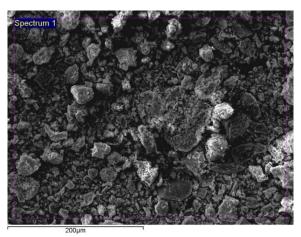


Figure 5. EDS image of the sample DUB 8

To wrap up the discussion of samples DUB 6, DUB 8 and K10, it is important to mention one more aspect of the ceramics, namely the CaO content. According to Tite (2008), a content below 5% suggests the use of non-calcareous clay and a content above 10% suggests the use of calcareous low-refractory clay. Based on SEM-EDS results, ceramic from Dubrovnik, showed that sample DUB 6 is representative of non-calcareous clay, while the K10 and DUB8 samples are calcareous clay (Tite, 2008; Vasilic et al., 2020).

A significant quantity of iron nails was discovered during the excavations (Bujak, 2018). Among these nails, one with a white spot at its head was selected for analysis. The examination revealed that this area is predominantly composed of CaO, indicating it is likely lime. Furthermore, the substantial carbon content (15.37%) suggests that the nail may have been in contact with an organic matter, which was probably used to join the wooden beams and construction plaster.

 Table 4. Results of iron nail analysis by means of SEM-EDS technique (in wt.%).

Elements	Percentage (%)
С	15.37
0	48.19
Al	0.48
Si	0.69
Cl	0.08
Ca	34.57
Fe	0.63

Two of the most interesting findings from Dubrovnik were a piece of metallic slag and brocade threads, and the latter was found inside an intact ceramic pot, in situ (Bujak, 2018).

The visual appearance of the metallic slag (sample RF) suggested that it most likely contains high amounts of Fe, in the magnetite form. This was confirmed by basic testing of its properties on different surfaces, where it showed magnetic traits, across different parts, meaning that its magnetism was unevenly spread across the sample. This assumption was confirmed by SEM-EDS measurements on different parts of the sample (total of four distinctive spots and five spectra). The results are summarized in Table 5, and Figure 6. shows EDS image of the sample RF.

Table 5. Results of RF sample analysis by means of SEM-EDS technique (in wt.%).

	1 5 5		1 ( )		
Site	Α	В		С	D
Spectrum	1	1	2	1	1
0	33.07	8.12	48.12	36.11	12.02
Al	0.68	<lod< td=""><td><lod< td=""><td>0.29</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>0.29</td><td><lod< td=""></lod<></td></lod<>	0.29	<lod< td=""></lod<>
Mg	<lod< td=""><td>0.18</td><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	0.18	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
Si	2.05	0.22	0.49	0.36	<lod.< td=""></lod.<>
S	0.44	<lod< td=""><td>0.28</td><td>5.83</td><td><lod< td=""></lod<></td></lod<>	0.28	5.83	<lod< td=""></lod<>
Cl	0.35	3.34	0.43	6.12	<lod< td=""></lod<>
K	0.49	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
Ca	2.37	2.06	1.38	8.05	<lod< td=""></lod<>
Fe	58.01	50.8	24.67	9.4	3.14
As	2.54	0.19	1.45	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
Cu	<lod< td=""><td>1.18</td><td>0.56</td><td>0.55</td><td><lod< td=""></lod<></td></lod<>	1.18	0.56	0.55	<lod< td=""></lod<>
Ag	<lod< td=""><td>33.91</td><td><lod< td=""><td>33.29</td><td>46.02</td></lod<></td></lod<>	33.91	<lod< td=""><td>33.29</td><td>46.02</td></lod<>	33.29	46.02
Sn	<lod< td=""><td><lod< td=""><td>22.61</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>22.61</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	22.61	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
Hg	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>38.82</td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td>38.82</td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>38.82</td></lod<></td></lod<>	<lod< td=""><td>38.82</td></lod<>	38.82

\*<LOD below the limit of detection

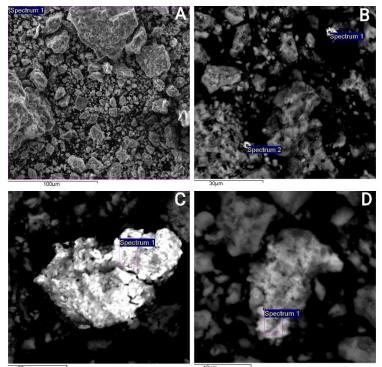


Figure 6. EDS image of the sample RF.

As can be seen from the EDS image, it is easy to distinguish heavy (brighter) and light (darker) elementcontaining particles, with grains of different dimensions and relatively heterogenous chemical composition. Some parts of the RF sample have high quantities of iron, which corresponds to its content in the magnetite ore (Fe3O4), and Figure 6a clearly demonstrates that is almost completely composed of Fe and O. Additionally, during the SEM analysis of the sites A and B, we encountered strong magnetic interference and we were unable to take better images with the instrument.

The most important aspect of this sample was the relatively high quantities of As, Ag, Sn and Hg in some of its parts. This can be easily seen from the sites C and D of Figure 6., where we have large grain inclusions of Ag, Hg and Sn. A possible explanation for the appearance of these metals in the sample could be twofold. First, during medieval times, Hg was used for the so-called mercury silvering, using the amalgamation technique (La Niece 1993; Giumlia-Mair, 2020). Second, arsenic, apart from its primary ores realgar and orpiment which in the BiH are found together with the mercury ores, can also be found in the ores that were used as a source of silver during medieval times. As already mentioned, Dubrovnik lies between two mineralogical zones, Vareš and Čevljanovići, where there are deposits of tetrahedrite (Cu, Fe, Ag, Hg)12(Sb, As, Bi)4S13, proustite (Ag3AsS3) and cinnabar (HgS) were recorded (Operta, 2009). So, there is a possibility that As found its way to the sample simply because it was a part of the primary ore, which was used in the metallurgical process, and therefore represented the geological bedding of the location.

The presence of As, Ag, Sn and Hg in the RF sample can significantly contribute to our grasp of historical industrial processes in the region. These elements may provide valuable insights into the historical mining, metallurgical, and manufacturing activities that took place in the area. Understanding the occurrence and distribution of these elements in a sample could shed light on the utilization of specific ore deposits, mining techniques, and the production of various materials during different historical periods. Analysis of additional samples can help in reconstructing the intricate relationship between the local geological resources and the industrial processes that shaped the region's historical development. Further investigation and analysis of additional artifacts from Dubrovnik, as well as a thorough examination of the geology of the surrounding area, are necessary to determine the origin and purpose of the samples, especially the RF one. Without these crucial pieces of information, it is impossible to conclusively assert whether the sample was involved in deliberate smelting activities in Dubrovnik or if it merely represents the natural geological composition of the region. As for the other elements present, their low concentration suggests that the primary ore used in the process also had these metals present only as impurities.

The most interesting artifact that was analyzed was a part of the brocade thread, found inside an intact ceramic pot. Figure 7. shows the analyzed piece of the brocade thread, under the x12 and x80 magnification and the distance between the coils. Analysis revealed that the thread was made of a combination of Au/Ag, with uniform distance between the coils of the thread of 257.803  $\mu$ m. The Au content was 63.94% and Ag 36.06%.

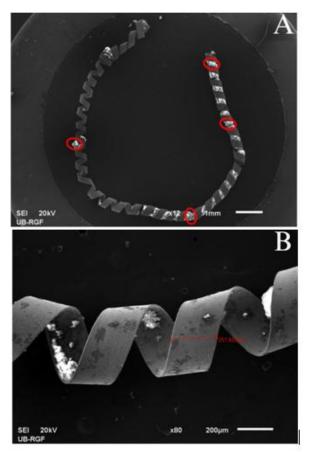


Figure 7. EDS image of the sample of golden brocade, under different magnifications

A substantial body of the literature addresses various aspects of manufacturing techniques, non-destructive analysis, and interpretation of threads from Medieval Europe (Járó, 1990; Caratzani & Rehren, 2006; Costa, de Rever & Betbeder, 2012; Balta, Demetrescu & Lupu, 2020; Karatzani, 2021; Güzel, 2023). Here, we aim to contextualize our sample within a broader European framework, focusing on its type and dating. In terms of type, the primary classification revolves around the twist of the strip around the organic core, namely S or Z twist. In our case, the organic material likely served as a belt, as the brocade thread was discovered alongside a belt buckle in the same ceramic vessel (Bujak, 2018). Although no visible traces of the belt remain due to the probable textile decay over time, SEM images revealed distinct remnants of organic matter (Figure 7A, marked by red circles).

Further chemical analysis is required to determine its type and composition. Based on the twist type, our sample falls into the S-type category, which is more prevalent. In addition, our sample can be identified as a strip featuring gilding of gold onto a silver wire base on all sides, a technique developed in the 14th century (Karatzani and Rehren, 2006). Technologically, two manufacturing methods exist, aiding in approximate dating. The earlier method involves "beaten and cut" strips from the 13th century, while the later method employs "cast, drawn and rolled strips" from the 14th century onwards (Karatzani and Rehren, 2006; Balta, Demetrescu & Lupu, 2020). The latter displays a uniform width throughout its length and the characteristic parallel lines due to wire drawing, both of which are evident in our sample, suggesting a 14thcentury timeframe. Chemical analysis by means of EDS measurements revealed that the brocade wire consists solely of gold and silver, without any copper or zinc impurities, which helps to distinguish between European and Oriental wire types, the later one using very pure precious metals, with only small quantities of impurities (Hoke and Petrascheck-Heim, 1977; Járó, 1990; Balta, Demetrescu & Lupu, 2020). Considering these data, our brocade wire most likely originates from the Orient and was produced no earlier than the 14th century.

# CONCLUSIONS

Although a relatively small number of samples was analyzed in this paper, the results obtained can nevertheless provide a valuable first insight into the life and practice of the Dubrovnik inhabitants, but at the same time pave a road to further analysis and investigations. Based on the results, we can mark some of the samples as particularly interesting. DUB 2 sample had almost tenfold values of Mn, Zn and Pb compared to other samples measured by FAAS technique. A possible explanation would be that the clay used for ceramic was brought from another location, but without additional analyses of the raw material, this cannot be reliable concluded. Analysis by SEM-EDS technique showed that, unlike DUB 8 and K10 (body), a relatively high aluminum, non-calcareous clay with high potassium content was used for the sample DUB 6. Sample K10 was representative of a typical Ottoman type, green glazed pottery, found throughout Balkan Peninsula. The most interesting sample was without a doubt the brocade thread, found inside an intact ceramic pot, buried inside soil. Based on the data provided by SEM and EDS for this sample, it can be concluded that its time frame can be attested to the 14th century.

In order to draw any definitive conclusions regarding this location, additional analysis needs to be made. This would include XRD measurements of the ceramic findings and raw clay material, to determine the mineral phases and changes between source material (clay) and the finished product (ceramic). In addition, the analysis of the organic matter present in the brocade, although in minute quantities, could lead to conclusions about the type of the material that surrounded it and possibly light up its presence inside the pot, buried deep in the ground.

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## Summary/Sažetak

Cilj ovog rada bio je analizirati arheološke artefakte pronađene u srednjovjekovnom gradu Dubrovniku, u blizini Sarajeva, korištenjem FAAS i SEM-EDS tehnika. Odabrano je ukupno 11 uzoraka različitih tipova: keramičke ulomke, željezni ekser, šljaka i komad brokatnog konca. Rezultati keramičkih uzoraka pokazali su visoke nivoe željeza i mangana, najvjerovatnije zbog geološke slojevitosti lokacije. Količine hroma, bakra, nikla, olova i cinka u tragovima potvrđuju ovu pretpostavku, što znači da je glina koja se koristila za izradu keramike dopremljena u okolici Dubrovnika. Oslikani uzorak zelene keramike imao je visok nivo olova, što sugerira da je ovaj metal namjerno dodan kako bi se ojačala svojstva posude. SEM-EDS mjerenja troske pokazala su prisutnost As, Hg i Sn, a jedno od mogućih objašnjenja je da su korišteni u procesima rafinacije zlata ili srebra, koji su se prema istorijskim izvještajima obavljali u Dubrovniku. Komad zlatne niti se pokazao korisnim u određivanju vremenskog okvira njegovog nastanka. EDS mjerenje je pokazalo da tip proizvodnog procesa koji se koristio u proizvodnji ovog zlatnog konca nije postojao prije 14. stoljeća.