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Modern Semi-Majolica and Glazed Ceramics from Rzeszów – Research on the Findings from the Archaeological Sites on 3 Maja Street

Abstract

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Steadily growing collection of modern ceramics of the present Podkarpackie Voivodeship, has not yet been fully documented. Historical research demonstrates that Rzeszów, located on the communication route with Russia, occupied a very important position in trade relations with the East and West. The archaeometric study was performed on two fragments of semi-majolica plates and six fragments of glazed jugs, pots and tripod vessels. Vessels were made of fine-grained paste of smectite/illite, kaolinite/illite and kaolinite/illite/smectite clay. The richness of colours and shades is surprising. In the case of semi-majolica, the underglaze paintings were made with the use of frit pigments, while the overglaze ornament was made with the use of Pb-P-Ca-Si paste. 'Slip-painting' technique was also used. Glazes were coloured with iron, copper and cobalt compounds of various combinations and concentrations which provided different shades. In the case of semi-maiolica quartz-argillaceous primer with a potassium-bearing substance was applied, surfaces under glazes were covered with flux-bearing substances.

Key words: Podkarpackie, Rzeszów, semi-maiolica, glazed pottery, SEM/EDS

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1. Introduction

The steadily growing collection of modern ceramics, discovered during numerous archaeological research conducted in the area of the present Podkarpackie Voivodeship, has not yet been fully documented. The reason for such a state of affairs was the limited interest of archaeologists in this subject. This is evidenced by a modest database of literature, most of which is limited to reports and studies from excavations, which describe the ceramic findings from the 16th to the 19th centuries. This problem concerns not only the Podkarpackie voivodeship, but also other parts of our country (see Gajewska 1991, 159–169), although in recent years the situation seems to be improving. The number of publications is also increasing. However, we will limit ourselves to mentioning only some of them (see: Buko 1997; Gajewska and Kruppé 2017, 109–141; Gardawski and Kruppé 1955, 123–141; Glinkowska and Orawiec 2016, 205–229; Kruppé and Milewska 2015; Olszacki and Różański 2018; Lelek 2004; Lubelczyk 2017; Morysiński 2000, 129–158; Rodak 2017, 149–167; Starski 2015; Supryn 2008; Trzeciecki 2016; Wojenka 2016, 231–240). The potter's settlement from Przemyśl in Zasanie region remains relatively best described; however, its horizon dates back to a much earlier period (the second half of the 13th and 14th centuries; Auch 2007, 131–175; 2009, 141–162; Kunysz 1965, 336–345; 1967, 137–141; 1968, 176–183). The same can be said about the materials obtained during the research of the old town center in Rzeszów (Czopek and Lubelczyk 1993). Several individual texts have been published on the collections from Lesko (Zielińska-Durda 1988, 267–278), Będziemyśl (Lubelczyk 1994, 73–94), Łańcut (Lubelczyk 1999, 359–370), Strzyżow (Lubelczyk 2002, 227–251), Przemyśl (Poradyło 2007, 73–84) and Krasiczyn (Poradyło 2007, 73–84). Quite a few works have been devoted to a particular type of vessel produced at that time, the so-called semi-majolica from workshops in Miechocin (Szarek-Waszkowska 1968, 256–263; Szetela-Zauchowa 1994, 45–72), Rzeszów (Kotula 1953, 303–318) and Jarosław (Supryn 1975, 239–264). In this connection, we should also mention the unpublished study by M. Bober (2005), in which the author attempts to synthesize the knowledge on modern ceramics from the Podkarpackie Voivodeship.

Therefore, the comprehensive study of the collection of modern ceramics obtained during the 2017 archaeological excavations on 3 Maja Street in Rzeszów is keenly anticipated, as it can provide a wealth of valuable information. During the research works, a total of over 5,400 fragments were collected, which typologically and chronologically correspond to the classification system developed by Sylwestr Czopek and Antoni Lubelczyk (1993). In accordance with the above-mentioned categorization, the majority of the discovered artefacts belong to group B, which consists of ceramics formed by dint of a high-speed wheel and then fired in an oxidizing atmosphere. The foregoing group can be further divided into two smaller sub-categories based on to the type of raw material used, namely BI, which includes traditional, brick-like items made of ferruginous clay and BII, which includes products made of white kaolinitic clay, in many cases covered with olive, green, brown, orange and grey colored glazes.

There is currently no study in the literature concerning Rzeszów's past that would cover the issues of pottery production. Some scattered information on this subject can be found in written sources and articles on economic issues. Certainly, craftsmen involved in the production of ceramics were working in the settlements around the later location of the town. Then, after the year 1354, they became a part of the Rzeszów community, which was settled under the Magdeburg rights. However, the first source materials about potters in Rzeszów date back to the end of the 16th century. During that time, together with blacksmiths, gunsmiths, swordsmen, carpenters, saddlers and locksmiths, potters created a common guild of craftsmen which was governed by the guildmaster and a potter, Łukasz Szczygieł, held this office in the years 1593–1634. Józef Pęckowski (1913, 221) assumed otherwise, as he claims that the potters co-created the guild of coopers created under the privilege of Hieronymus Augustyn Lubomierski issued on December 30, 1699. Among the signatories of the act was the potter and guildmaster, Wojciech Szafrański. At that time, there were also 6 other potters in Rzeszów – the city records reveal the names of some of them, including Mikołaj (mentioned in 1611), Krzysztof (1612–1613), Kasper (1619) and Szymon Szczygieł (1634; Przyboś 1957, XIV; 1958, 72; Motylewicz 1994a, 267). Back then, Rzeszów was a significant center of pottery production, one which was probably not inferior to other big cities. It was recognized not only for the production of the traditional pottery, but also the semi-majolica dishes modelled after Italian maiolica, which began to arrive in Poland in the 16th century (Fryś-Pietraszkowa 1970, 76; Meyza 1991, 118).

H.G. Stephan (1987) has recently addressed the issue of the genesis and dissemination of the ornamented glazed vessels in modern Europe. The term *majolica* (from the word *Majolica* – Majorca, or faience) will be understood as a kind of dish-like ceramics with tin or tin-lead enamel, produced in Italy between the 15th and 18th century, whose production developed under the influence of similar objects from Arab countries in the Middle East and Spain. The most important centers of majolica production in Italy were: Florence, Orvieto, Siena, Castel Durante, Gubbio and Derucio. Initially, in the second half of the 15th century, the most common patterns were those based on eastern motifs, decorated with green or purple colors. Between 1475 and 1530, the goods were decorated with floral designs, as well as the images of peacock feathers or various figures. The color palette was also systematized, as it embraced white, purple, yellow, orange and green colors. In the 16th century, ornamentation lost its decorative sense, as it was supplanted by figural scenes. The manufactured items were white, with yellow and blue colors put on top. In the next century, decorating majolica with figural scenes and monochromatic cobalt became very popular (Kubalska-Sulkiewicz 2015, 245).

A more complex problem concerns the definition of semi-majolica vessels (also known as mezzamajolica, faience). The researchers from Warsaw (Meyza 1991, 118–121; Mierosławski 1979, 139–140) believe that this term is inappropriate since it refers to products with specific technological properties. For this reason, they propose to use the term pseudomajolica, which shall include dishes covered with transparent enamel and underglaze paints (as in the case of majolica), but with tin glaze used as the undercoat in lieu of the white engobe. Such a technique produces items with a heavily baked, thick layer of coating (Mierosławski 1979, pp. 139–140). The following definition was recently updated by K. Meyza (1991, p. 119), who claims that the term in question is a conventional name for a group of several, technically different types of ceramics, related by the presence of an ornament painted under a transparent lead enamel, that shall cover the period from the 16th c. to the beginning of the 18th c.. *Słownik terminologiczny sztuk pięknych* (i.e. *The terminological dictionary of fine arts*) (Kubalska-Sulkiewicz 2015, 108) describes semi-majolica as vessels made of regular clay, fired at oxidising temperature. They are brick-colored and covered with a white coating on which colored decorations can be applied. During the final stages, such items were coated with clear glaze. The term *mezzamajolica* is also commonly used in Czech literature (Vydrová 1973). The above-mentioned general definition was adopted by several researchers, including M. Supryn (1975, 239), who deals with artefacts from Jarosław, as well as Franciszek Kotula (1953, 303), Czopek and Lubelczyk (1993, 25), who focus on findings from Rzeszów. The same view is shared by Maciej Trzeciecki (2016, 173–174), the author of the study of ceramics from Płock. Teresa Szetela-Zauchowa, who examines semi-majolica from Miechocin, states that these products should be referred to as engobe ceramics - according to the researcher, this name is more correct and accurate. Szetela-Zauchowa defines semi-majolica as ceramic products painted with both white and colorful clays, which were later covered with transparent lead enamel. The already-mentioned engobe was used mainly as a backdrop for colorful patterns. At the same time, it imitated tin or tin-lead coating, commonly used in Italian maiolica. The semi-majolica from Miechocin typically involved two varieties of engobe, namely the white one and the brown one (Szetela-Zauchowa 1994, 46–48); the latter one is prevalent on the vessels discovered during the research of 3 Maja Street in Rzeszów.

The significance of Italian influences on the pottery workshops in Rzeszów, Miechocin, Jarosław and Łańcut is emphasized by E. Fryś-Pietraszkowa (1970, 76), Maria Supryn (1975, 241–263) as well as Czopek and Lubelczyk (1993, 25). The latter assume that, apart from the Italian impact, potters in Rzeszów were also inspired by oriental elements; however, they do not mention the source of such a claim. The above-mentioned artefacts are frequently described as the so-called Rzeszów majolica, which dates from the third quarter of the 16th century to the beginnings of the 18th century (Czopek and Lubelczyk 1993, 25–27; Kotula 1953, 303–318; 1956, 24). The ability to manufacture this variety of dishes is a sign of the extraordinary craftsmanship of the potters, who were seen as serious competitors for other pottery centres, such as Jarosław and Miechocin, which were famous for their mezzamajolica products. For this reason, conflicts between these cities and guilds could occur, as evidenced by the situation in Sokołów Małopolski, where the local pottery guild severely restricted the influx of *glass or painted pots* brought by merchants from across the Vistula (Reinfuss 1955, 16–17.).

Historical research demonstrates that Rzeszów, which was located on the communication route with Russia, occupied a very important position in trade relations with the East and West. The route became especially important in the late Middle Ages and the early modern period (see Kurtyka 1994, 105–117; Leśniak 1994, 205–206; Motylewicz 1994a, 229–230; 1994b, 354–356; Wyrozumska 1977, 51–57). The city also played an important role in the merchandise trade, presumably ceramics included. This is evidenced by a specially separated square, designed exclusively for potters, on which ceramics were sold even during the postwar period. To this day, the spot is referred to as "pottery square" (Kotula 1985, 105).

Major changes took place at the end of the first half of the 17th century, when potters, saddlers, masons and woodworking craftsmen left the locksmith's guild to form a joint saddlery guild (Motylewicz 1994a, 243). Certainly, this guild was somewhat connected to the prerogative issued by Jerzy Ignacy and Aleksander Lubomirscy on 8 October 1718, which states that *potters cannot do without masons* (Pęckowski 1913, 225–226). Starting from the middle of the 17th century up to the beginnings of the 18th century, only four craftsmen involved in pottery were recorded, whereas in the years 1701–1750 documents mention only one (Motylewicz 1994b, 349). The reasons for such a situation should be sought primarily in the economic and political crisis in Rzeszów (Motylewicz 1994b, 343–347), as well as in the gradual downfall of guild pottery. Both imported and locally produced dishes made of glass, porcelain, faience or metal became increasingly popular in kitchens and on tables (Reinfuss 1955, 16–19). The production of dishes was then directed towards the needs of small-town and rural communities. Rural potters also experienced a period of renaissance, as they produced ceramics that were cheaper but not inferior to those produced in the city workshops (Kotula 1956, 28–29). Within the timeframe mentioned above, various pottery centers, such as Medynia Głogowska and Zalesie developed - here, the potters specialized in folk ceramics modeled after semi-majolica, as well as miscellaneous flower pots and simple dishes. These items were then sold at trade fairs, including those held in Rzeszów (Ruszel 1994, 331–337).

The surfaces of archaeological and modern ceramics were subjected to various decorative procedures, many of which were also of a utilitarian nature. The enamel layer provided resistance to the potential penetration of fluids and damage caused by the stored and thermally processed substances. Furthermore, it also provided aesthetic value thanks to the use of multi-coloued glazes of varying degrees of transparency, applied to different elements of vessels. Owing to the invention of underglaze and overglaze ornamentation, the existing palette of colous and patterns was significantly expanded. The invention of glazing of ceramic surfaces dates back to the Bronze Age and developed first in the areas known as the cradles of glass–making, i.e. in Mesopotamia and Egypt. It is conceivable that the ability to manufacture glass objects stems from experimenting with it in the form of glazes (Płoński 1972). The close contact between modern Europe and the East was established, especially with Ottoman Turkey and, by extension, with Persia (Supryn 1975; Balcer 2018). The designs and technologies could have come from either the West or the East, along different routes. Extensive technological research needs to be conducted to identify the above relationships and such an investigation on the Podkarpackie ceramics has not been carried out so far. This paper serves as an introduction to a more elaborate project, one which is aimed at pinpointing the features associated with particular modern workshops in the Podkarpacie voivodeship, by comparing them and determining the sources of the applied technological concept.

2. Research material and methods

The study was performed on eight samples of artefacts ‑ two fragments of semi-majolica plates and six fragments of jugs, pots and tripod vessels. Macroscopic photographs of the samples and their descriptions are provided in Table 1. For ease of reference, the pottery that cannot be categorized as semi-majolic will be referred to as “glazed pottery” or “unpainted pottery” throughout the article.

The majority of the fragments were retrieved from the excavation marked with number 6, that is located at the western façade of the former Piarist Convention building (now the Regional Museum). These are samples 5C (90–100 cm level), 7C (70–90 cm level), 7D (150–170 cm level), 11B-1, 11B-2 (40–60 cm level), 11B-3 (20–40 cm level) and 12-1 (120–140 cm level). In the excavation, we managed to find sundry structures which were then assessed on the basis of portable materials, written sources and radiocarbon tests and dated from the early Middle Ages to modern times. However, for the most part, these were mainly the remnants of the Piarist monastery that has been functioning there since the middle of the 17th century (Kocańda *et al.* 2018, 157). All the above-mentioned levels were characterized by a significant degree of the mixing of soil layers, which consisted of dark brown and light brown soil, pieces of bricks, crushed mortar and stones. These strata can be interpreted as utilitarian layers, or putting it another way, construction and demolition levels related to the monastery buildings that exist in the area. The only sample (i.e. a fragment of a vessel marked as sample 5F) obtained from the excavation number 2, which was located near the tenement house No. 10, was sent for analysis. The said excavation revealed a multi-level surface made of timbers. Based on the results of dendrochronological dating, the surface has its origin in the 17th and the second half of the 18th century (Kocańda *et al.* 2018, 153–155). The vessel in question, on the other hand, comes from the third layer, in which at a depth of 130–150 cm a fourth level of wood was exposed. This layer was light grey in color and consisted of sticky clay mixed with black soil.

The methods adopted for the purpose of the following project include polarized light microscopy in transmitted light, performed by means of an Olympus BX51 and scanning electron microscopy with X-ray microanalyzer on the NanoNova FEI with EDAX microanalyzer. Micromorphology observations were made on thin sections sprayed with graphite in the BSE mode. The concentrations of elements show the results of semi-quantitative analysis; moreover, they are always expressed by dint of weight percent. Concentration of oxygen was not taken into account, so that the bulk of analyses may not equal 100 wt %.

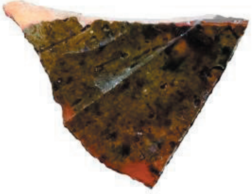
3. Research results – semi-majolica

Sample 5C

The ceramic mass is fine-grained and homogeneous, composed of aluminum, potassium, magnesium, calcium and iron aluminosilicates. It is a mixture of kaolinite (its presence is indicated by the low proportion of Si/Al, cf. Fig. 3), illite and smectite. Cryptocrystalline compounds of titanium are also present. The raw material contains about 2 wt. % Fe, which required firing in an atmosphere with limited access to oxygen, since after being exposed to oxidizing conditions, the clay would be pink. The concentration of calcium is the highest in the whole set of the analyzed ceramics (ca. 2.5 wt. % Ca), but marl was not used, as it typically contains much more Ca (Ryka and Maliszewska 1991, 208). Thus, calcium can be a natural component of the used clays. There were no concentrations of this element other than aluminosilicates with different cations.

The slip is a layer about 100 micrometers thick, composed of oval quartz grains of similar size, im-

Table 1. Macroscopic pictures of the fragments of the examined semi-majolica and glazed ceramics.

Code of sample	Macroscopic description	Image	
5C	Semi-maiolica, a fragment of plate. A navy-blue and dark-red ornaments. Convex floral design, bluish glaze. Light-grey section. Disadvantages: uneven glaze cover, craquelures, thick and blistering navy-blue paint, detachment of dark red paint, stains of blue glaze. Numerous small black stains.		
11B-3	Semi-maiolica, a fragment of plate. Brown background covered by glaze, creamy linear overglazed ornament. Brick-red section. Disadvantages: loss of glaze, craquelures, loss of glaze transparency, blistering of creamy ornament.		
5F	Fragment of a pot or jug spout. Two-sided brown glaze, internal surface covered with a black, opaque crust. Brick-red-grey section. Disadvantages: dark brown stains, hairy smudges.		
7C	Fragment of a pot. Two-sided glaze, navy- blue with greenish shade on external surface, dark green on the internal one. Brick-red-grey section. Disadvantages: stainy, uneven coloration, cracks.		
7D	Fragment of a middle part of a pot. Two-sided glaze, brown on external surface, executed in a 'fish-scale' ornament (dated in the Rzeszów region for the 17th and 18th centuries, Czopek, Lubelczyk 1993, 36). Light green glaze on internal surface. Light-brick-red section. Disadvantages: dark stains, craquelures.		
11B-1	Fragment of a middle part of a pot. Two-sided glaze, on external surface two-coloured, creamy, matt, opaque and brown, on internal: yellow, transparent. Grey section. Disadvantages: uneven glaze thickness, stains, craquelures.		
11B-2	Fragment of a pot spout. Two-sided green glaze, on external surface partially covered with a black, opaque crust. Brick-red-grey section. Disadvantages: blistering, craquelures, stains, detachments.		
12-1	Fragment of a tripod. Light-green glaze. White section. Disadvantages: craquelures, uneven thickness of glaze.		

mersed in argillaceous minerals. These include iron, calcium and magnesium aluminosilicates that are visibly enriched in potassium (7,61 *vs.* 1,79 wt. % K), when compared with the ceramic mass. It is possible, although not verifiable at this stage of research, that a mixture of illite and/or plant ashes or other potassium carrier substances may have been used.

Other elements of the stratigraphic cross-section are the coppery-red and blue paints, as well as glaze in non-ornamented areas. Under the red paint and above the slip there is a layer of clay similar to the one found in the ceramic mass. It was probably applied in order to obtain the convex effect of the strip ornament; unfortunately, this did not contribute to the permanent bonding of the paint to the base surface. The components of red paint are opaque, very fine (a few micrometers), granular, partially fused. The average thickness of the coppery-red layer is approximately 20 micrometers. The picture of blue paint is different: here, the layer is thicker (about 200 micrometers) and while large grains blend in, they retain their individual shape. The blue pigment is a cobalt-iron, lead-free glass composed, among others, of a large amount of potassium (12 wt. % K) and 3.6 and 2.8 wt. % of cobalt and iron, respectively.

Any contact between the paint layers and the base, as well as the glaze, is beneficial. At the edge of the pigment-free glaze that remains in contact with the base, one can notice secondary crystals, whose composition indicates the reaction between the components of the base and the enamel. The area of such occurrence is narrow (about 10 micrometers).

The clear glaze is not homogeneous, as it contains un-melted grains of the lead-silica frit and quartz. The glaze was therefore applied in the form of a suspension containing, among others, these components. Upon close inspection, one can spot transverse cracks and open bubbles in the glaze. These defects have a negative effect on the transparency of the enamel. The glaze has a thickness of about 50 μm. It is composed of Pb:Si in a ratio of about 4:1 to about 2,5:1; it was not, therefore, homogenized during the smelting process, which is a disadvantage. The iron and cobalt content is 1.3 and 1.1 wt. %, respectively, which translates into the bluish hue. A very thin area (about 3 micrometers) is found on the surface of the glaze, where the Pb:Si ratio is close to 1. The high content of silica ensures the hardness of this surface. The said area was formed (as with the other cases described below) by the evaporation of lead in the final stage of the smelting of the dish. The image created via scanning electron microscopy depicts the discussed section as a grey stripe on the brighter proper glaze.

The corrosive area is very thin, opaque, or bluish and semi-transparent. It is multilayered, stratified and contains numerous needle-shaped crystals, consisting mainly of lead, which is accompanied by silicon, calcium and phosphorus in the amount of approximately 10 wt. %, of each oxide. There is also calcium, which occurs separately, probably in the form of a carbonate, as well as lead and silica in the ratio of (in an outward direction) 7.7 – 6 – 3.2 (in the glaze: 4.4) - the components of the enamel. The total thickness of these areas is negligible (ca. 5 micrometers), which indicates that the advancement of the degradation processes is slow (Table 2–6).

Sample 11-B3

The following sample is a fragment of a dish with a fairly loosened layer of decoration. The color of the fracture is brick-red. The ceramic mass can be described as fine-grained and homogeneous. It is composed of calcium and potassium aluminosilicates (1.8 and 1.2 wt. % Ca and K), and while it has no visible pores, its texture is varied and chaotic. Also, the iron content is high, i.e. 5,72 wt. % Fe.

The brown shade on the surface of the dish is achieved by dint of a layer of granular pigments, characterized by having equal diameter. While most of them are opaque with a coppery tint, some are somewhat transparent and of pale blue hue or completely transparent and colorless. One may also encounter individual, large grains of quartz. The pigments have been applied in the form of a fairly thick layer (up to approx. 0.3 mm) on the surface of the dish; a fair share of them is embedded into the ceramic mass. The pigment layer is porous - in all probability it was too moist, thus the firing or drying of the dish caused the release of gases. The grains of fine pigments are either quartz or frit with extremely high silica content (only 1 wt. % Pb), as well as frit Al-Pb-Si with iron and frit Si-Al-Pb with iron and copper.

There is a layer of glaze on the pigments. On the decorative side it is even (approx. 0.2 mm thick) and adheres well to the base. A small number of cracks that are perpendicular to the surface of the dish is noticeable, together with few closed bubbles. On the non-ornamented side, the image is completely different: the enamel is thinner and uneven. The glaze consists of lead and silicon at a ratio of 5:1. Here, we can also find 2 wt. %. Cu, which is responsible for the subtle shade of green that is visible only under the petrographic microscope. The most external part of the glaze is an area of about 3 micrometers wide, in which the Pb:Si ratio is only 2.5. As in other cases, regardless of the manner in which it was created (i.e. intentional or not), it certainly protects the surface of the very soft proper glaze.

There is a creamy ornament on the surface of the glaze. It is made of paste, which is not homogeneous enamel, but a sinter made of phosphorus, calcium, lead, iron and copper. The sinter can be divided into two parts ‑ the upper layer is low in lead, but enriched in iron, probably due to the evaporation of lead. Both parts are well-bound. Within the sinter one can spot only a few small grains of lead-silica frit. Therefore, we are dealing with a paint that was made intentionally, or in other words, a sinter made of calcium phosphate and lead (Table 2–6).

4. Research results – glazed, unpainted ceramics

Sample 5F

The ceramic mass of this sample can be described as being of greyish-brick color. It is fine-grained, but the grains are uneven; the grain size reaches 0.3 mm. The chemical composition of the ceramic mass was not determined for this sample. The surface under the glaze is uneven and the glaze is "soaked into it".

The point of contact between the glaze and the ceramic mass is covered with dendritic short-columnar crystals, formed as a result of the reaction between the hot enamel and the components of the ceramic mass. These are lead aluminosilicates with complex compositions. The thickness of the area of contact is about 20 micrometers; furthermore, it is discontinuous. In all likelihood, the vessel was inaptly fired and cooled.

Dark brown glaze is very thin (about 20 micrometers). Its thickness is uneven; moreover, in some places it is loosened from the base. The glaze has a Pb:Si ratio of 5, but in the very thin area on its surface, this proportion is only 0.6. The only chromophore here is iron (1.85 wt. %. Fe).

The opaque, matt layer on the outer side of the potsherd is reminiscent of carbon deposit, but upon closer inspection, it turns out to be a glaze that is thicker than its outer counterpart. The glaze was also applied on a negligently smoothened base, thereby "soaking" into it. The image created by petrographic microscope reveals that the glaze is of greenish color. Curiously, it has a different proportion of Pb:Si than its equivalent on the external side.

In the glaze of the inner part of the vessel, needle-shaped crystals were formed. They pierced the entire volume of the layer. Their Pb:Si ratio equals 8, while the concentrations of other elements are negligible. The investigated variety of a crystal is, in terms of its composition, most similar to a natural counterpart, the yellowish-green ferrisurite $(Pb, Ca)_{2,4}Fe^{3+}{}_2(Si_4O_{10})(CO_3)_{1,7}(OH)_3{\cdot}nH_2O$ (www.mindat.org/min-1501). The above-mentioned mineral is formed under hydrothermal conditions either in lead deposits (e.g. Le Rivet deposit, Occitania, France) or other metallic deposits, in which lead is a natural admixture (e.g. Monte Avazza near Udine, Italy). The habit of ferrisurite is also needle-shaped. Undoubtedly, the presence of this phase should be treated as a flaw in the enamel, as the said mineral was formed due to the presence of too much moisture in the enamel mass combined with a relatively low kiln temperature.

The black incrustation on the outer wall of the fragment of the vessel is composed of pure lead or lead oxide, as well as phosphorus and calcium at a ratio of approximately 1:1, mixed with a small amount of iron and aluminum. The foregoing combination is sinter, which may have developed during the production of the vessel. Both the presence of the above-mentioned crystals and sinter are indicative of the defectiveness of the glaze (Table 2–6).

Sample 7C

Here, the greyish-cream ceramic mass is fine-grained and homogeneous. It is composed of potassium, iron, calcium and magnesium aluminosilicates. The concentration of potassium and iron is very high, as it amounts to 6,76 and 5,91 wt. %. K and Fe. In the base of glaze, the concentration of almost all elements is slightly lower, as a result of their diffusion into the enamel; however, the concentration of sodium is almost doubled. Due to the lack of sodium feldspars build-ups, its source must be different; thus, sodium compounds were probably added intentionally.

Within the ceramic mass there are occasional, large (approx. 0.5 mm) areas of glaze that are partially dissolved in the enamel. The thickness of the area in which dendritic crystals occur on both sides of the vessel is approx. 50 micrometers. On the other hand, the thickness of the area in which the ceramic mass changes is approx. 150 micrometers.

The navy-blue glaze is cracked, and the fractures are mostly parallel to the surface of the vessel, which indicates high viscosity of the glaze during melting process. Within the glaze, there are large, closed or almost closed bubbles, filled with numerous copper-colored flaky clusters. The contamination of the bubbles indicates poor cleanliness of the kiln atmosphere. The ceramic mass or enamel mixture was rich in gases, which then sought an outlet during the firing process, yet the glaze was too sticky and it closed them in. The presence of these bubbles and the fact that they were filled with iron compounds produced undesirable visual effects on the glaze, i.e. the emergence of dark spots. The navy-blue glaze is about 3 times thicker than the dark green one. The Pb:Si ratio is approx. 5. Additionally, the investigated glaze contains high copper concentration (4 wt. %) and certain amount of iron (2.2 wt. %.). Finally, the outer surface of the enamel includes an area that spans several micrometers, in which lead evaporated – here, the Pb:Si ratio is 0.9.

The homogeneous enamel is covered with incrustation approx. 30 micrometers thick, in which phosphorus and calcium can be found. What is more, individual grains of potassium feldspar are melted into it. Importantly, this is a sinter, not a dirt residue. The foregoing imperfection, which adversely influences the aesthetics aspects of the glaze was probably created during smelting process. The exact source of contamination, as well as the reason behind its presence, are unknown.

The dark green enamel is much thinner than the navy-blue one. It is composed of lead and silicon in a ratio of 3, as well as aluminum and iron (3,94 and 3,12 wt. % Al and Fe). The dendritic clusters formed at the point of contact between the dark green enamel and the base cover a large portion of the cross-section of the layer. It should be noted that the only chromophore here is iron. The near-surface area of the dark green enamel is heavily cracked, but it has no incrustation as with the navy-blue enamel. The inner, dark green glaze is harder than the dark blue one – in other words, these are two different types of enamel (Table 2–6).

Sample 7D

In the following sample, the ceramic mass is varied in granularity and the size of angular grains is up to 0.3 mm. The argillaceous components here are iron, potassium and calcium aluminosilicate(s) in the form of smectite/illite. There is also titanium in the form of cryptocrystalline clusters.

The base under the glaze is decorated with "fish scale". When we compared it to the ceramic mass, it appears to be enriched with potassium and titanium. The base under the green glaze, on the other hand is rich barium, phosphorus, sodium, iron and titanium. Barium occurs in the ashes of some plants (Kabata-Pendias and Pendias 1999, 134–139). The lack of calcium indicates that the phosphorus in the base comes from plant ashes rather than from animal source. The point of contact between enamel and the base reveals areas which are 10 micrometers thick and which are covered with dendritic crystals, formed through the reaction of enamel and ceramic mass. In certain places, this connection is disrupted, as evidenced by the visible "soaking" of the glaze into the base. This, in turn, indicates that the glaze was applied on an unfired surface.

The brown and green glazes are similar in thickness. Both glazes are basically homogeneous, although in the brown one there are few compact clusters of fine- and evenly-grained substance. The chromophores in both glazes are iron and copper and while there is more iron in the brown glaze, the green glaze is dominated by copper. The ratio of lead and silicon in the brown glaze oscillates between 4.7 and 7.3, while in the green glaze between 4.5 and 6. Both glazes contain aluminum, equivalent to 2 and 3 wt. %. Al. Both glazes have a specific composition due to the presence of cadmium and – in the case of the brown glaze – also zinc.

All things considered, the analyzed piece of ceramics presumably comes from an extensively exploited vessel, as evidenced by the mechanical cracks in the glaze, which occur mainly on its outermost surfaces.

Sample 11B-1

The grayish-white ceramic mass is fine-grained and unevenly-grained. On both surfaces, i.e. the external and internal, additional clay is used, possibly as a "patch". The said cover is clearly more coarsely-grained than the ceramic mass. It contains pores of irregular shapes; this indicates the excessive moisture of the layer. The patch is made up of aluminosilicate with a ratio similar to that of kaolinite (Fig. 3), but containing almost 3 wt. % K and 2,6 wt. % Fe.

The transparent glazes, both brown and yellow, are similar in thickness, homogeneity and width of the contact area. In the yellow glaze the Pb:Si ratio is 4 and the chromophores are copper and iron (1,42 and 1,61 wt. % Cu and Fe). There are very few open bubbles here; however, they contain coppery flakes of iron compounds. The presence of such pollution is undeniable, but we are unable to determine at what stage it occurred, i.e. vessel production or post-depositional production.

Cream-colored, opaque, rough enamel is characterized by having a different morphology. It is a narrow and uneven layer, in which the roughness effect was achieved due to the granularity and unevenness of the base and the presence of short-column crystals (lead, potassium, iron and copper aluminosilicates) within the whole enamel.

The Pb:Si ratio in the discussed glaze is very high, when compared to other glazes, as it equals 2.2. The chromophores here are iron and copper (1,91 and 1,45 wt. % Fe and Cu). The surfaces of the glazes are cracked due to the exploitation of the vessel (Table 2–6).

Sample 11B-2

The moderately isotropized greyish-brick-red ceramic mass is fine- and even-grained, with few larger grains of quartz and feldspars. A relatively low proportion of silicon to aluminum indicates the presence of kaolinite (Fig. 3), and the concentrations of iron and potassium, which are up to a few percent (3.34 wt. % K, 2.75 wt. % Fe) suggest the presence of illite or illite-smectite.

The glaze on the external surface is thin and homogeneous; furthermore, it covers a moderately even base. The glaze on the internal surface is slightly thicker and significantly fractured ‑ the cracks are perpendicular to the surface of the vessel.

The glaze on the internal part is composed of lead and silicon in the proportion of 3.5; it is, therefore, quite hard. Additionally, the glaze contains copper (1.8 wt. % Cu) and iron (1.7 wt. % Fe) acting as chromophores. The narrow contact area is made of dendritic crystals, i.e. lead, iron, copper potassium and calcium aluminosilicates.

Black incrustation is found on both the external and internal surfaces, but it appears to be more developed on the former, up to point of decreasing visibility of the glaze. The incrustation is multi-layered. Within the glaze there have been a number of processes aimed towards the formation of colomorphic areas, enhanced with phosphorus and calcium. On the glaze, however, there is fine-grained sinter with a large amount of phosphorus and calcium, as well as lead and iron with copper. In view of the above, it can be speculated that the incrustation was formed during the production stage of the vessel. This, in turn, may indicate that the vessel was a reject (Table 2–6).

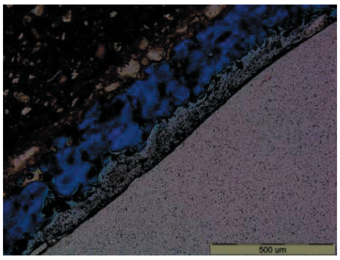
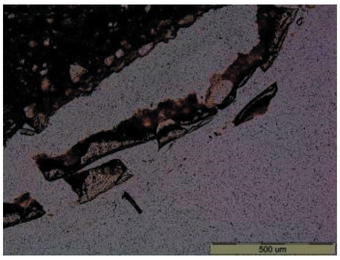
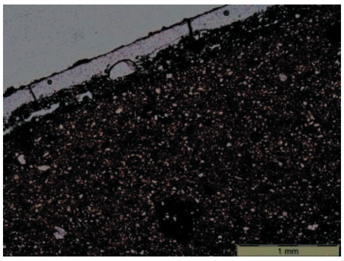
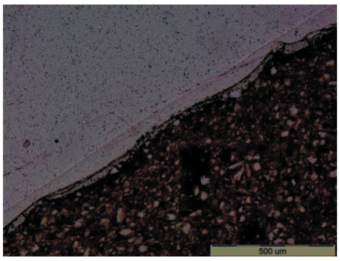
Sample 12-1

The white ceramic mass is fine-grained and homogeneous. Its chemical composition corresponds to that of kaolinitic clay (Fig. 3) with low calcium content (1,06 wt. % Ca), which in all probability is a natural component of the used clay; however, such a claim will have to be confirmed via raw material analysis.

The glaze was applied to a moderately even base, which appears to be enriched with potassium and titanium, when compared to the ceramic mass. Moreover, is seems to be homogeneous. The fractures perpendicular to the surface of the vessel can be categorized as craquelure cracking. The glaze is composed of lead and silicon in a proportion of about 5. It also contains copper (approx. 1.5 wt. % Cu) and iron (approx. 1 wt. % Fe).

The contact area within the ceramic mass includes numerous elongated pores, which are parallel to the surface of the item. At the border of the glaze and base, dendritic crystals were formed, covering the area that is approx. 10 micrometers thick (Table 2–6).

Table 2. Micromorphology of the studied ceramic fragments in the image of polarized light microscopy in transmitted light. All microphotographs were taken with parallel polarizers. The photograph in the left column is marked as "L", the photograph in the right column is marked as "R".

Sample code	Description	L	R
1	2	3	4
5C	(L) cross section through navy-blue ornament. From left: dark brown paste, narrow engobe zone with quartz grains, cobalt pigment layer, blue glaze layer. (R) section through the red strip. The glaze together with the underglaze pigments (opaque strip) and the „patch" of paste-like underneath breaks away from the lighter engobe.		
11B-3	(L) cross-section through the red plane. Under the transparent glaze, a thick layer of glaze pigments different in appearance, a large quartz grain, and pores within the pigment layer are visible. They were applied to a carefully leveled surface. (R) A very thin layer of glaze on the unpainted part of the dish.		

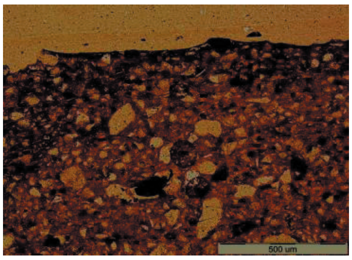
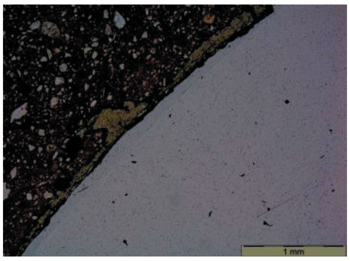
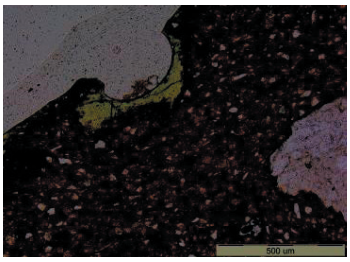
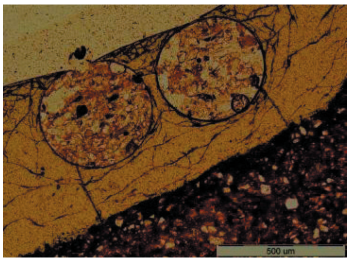
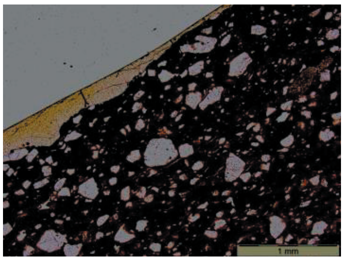
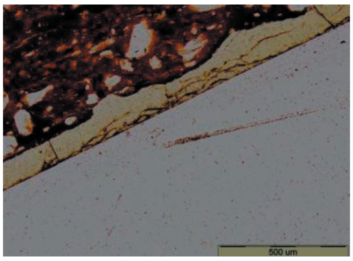
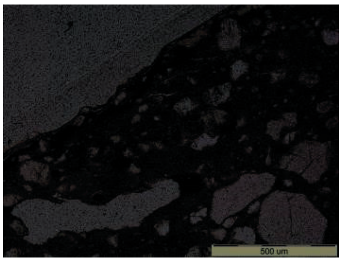
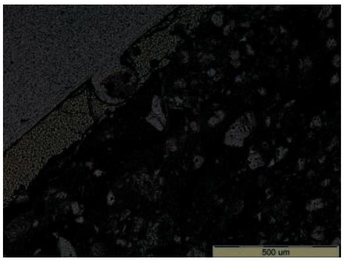
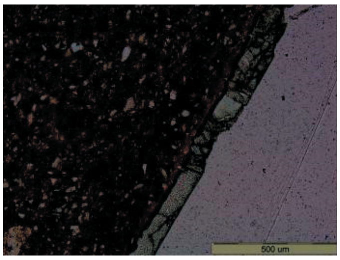
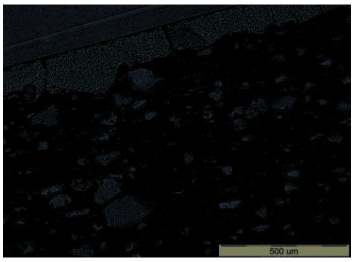
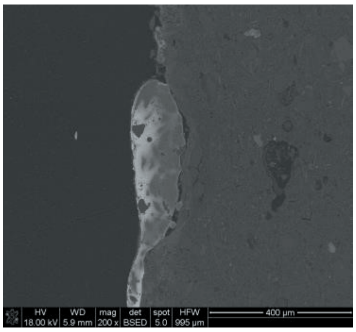
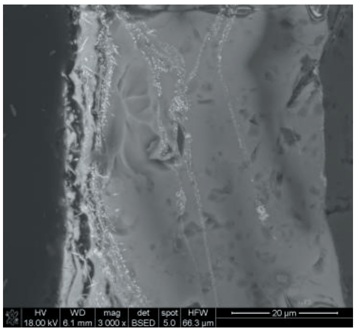
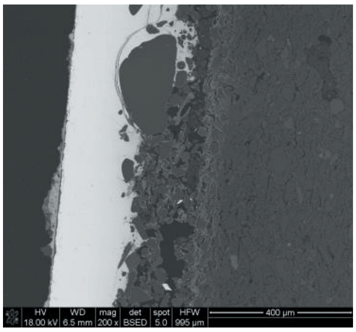
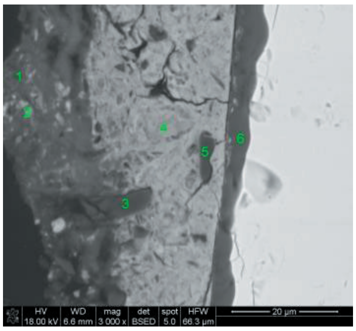
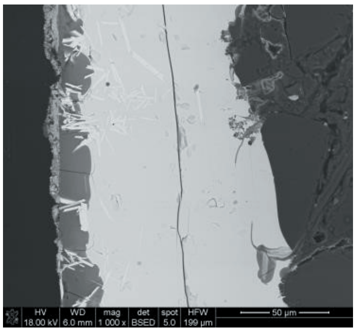
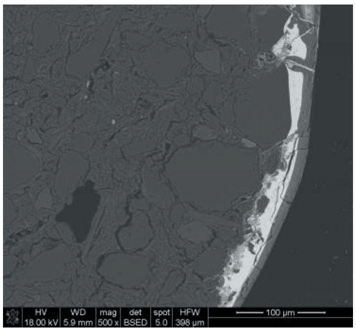
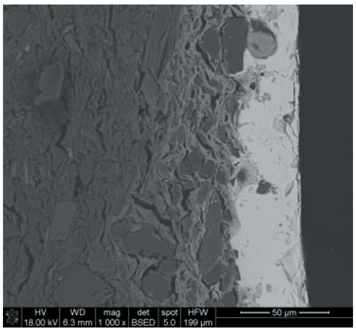
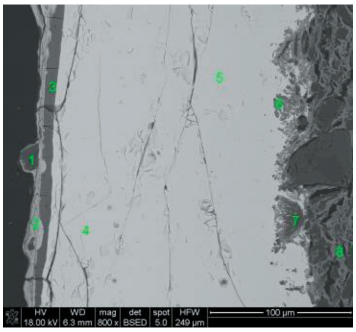
1	2	3	4
5F	(L) cross-section through the outer surface of the dark brown glaze. It is very thin, detaching from the ground, locally with opaque stains. (R) cross-section through the black surface: it is a green glaze soaking into the ground, covered with a narrow opaque crust.		
7C	(L) cross-section through dark green surface. Glaze soaks into the unevenness of the ground. (R) cross section through navy blue surface. Closed blisters within the glaze, filled with iron flakes, numerous cracks visible.		
7D	(L) cross-section through the outer surface, brown, executed as a "fish scale" pattern. The glaze is homogeneous. (R) cross-section through the inner surface, light green. Visible density of cracks in the outermost part of the surface.		
11B-1	(L) cross-section through the outer, creamy, rough surface. The glaze is narrow, partly peeled, applied to an uneven substrate. (R) cross-section through the inner surface. Yellow glaze with an open bubble. Under both layers a zone of paste different from the ground is visible ("patches").		
11B-2	(L) cross section through the outer surface with black crust. Below the crust a true glaze occurs. (R) cross-section through the inner surface: the glaze is thicker but heavily cracked.		
12-1	Section through the light green glaze. Just below it, a strong sintering zone is visible.		

Table 3. Microphotographs of semi-maiolica and glazed ceramics from scanning electron microscope. The description of the microphotograph in the left column is marked as "L" and the description of the microphotograph in the right column is marked as "R". In the marked points, EDS chemical analyses were performed, which are distinguished in Table 4.

Sample code	Description	L	R
1	2	3	4
5C	(L) cross section through the blue spot (decoration defect). From the left: glaze spot, engobe zone, paste. Dark areas inside the spot: cobalt frit grains. (R) section through the external part of the colorless glaze. Multilayer corrosion zone visible, glaze underneath. From the left: peeled off layers with varying proportions of Pb, P, Ca, Si.		
11B-3	(L) section through a transparent glaze with a red substrate. From the left: thin, bulging crust - creamy ornament (enlarged in photo R), glaze (light strip), underglaze zone with numerous pores, contact zone, paste. (R) cross-section through a cream ornament. From the left: the upper part of the sinter (1, 2), the lower with frit pigment grains (3–5), glaze enriched in silica (6, gray strip), light proper glaze.		
5F	(L) cross section through the black outer surface. Proper glaze – a bright area, a layer enriched with silica on its surface – a gray area. Both glazes are penetrated by lead aluminosilicate. Grit sintered crust on the surface. In the contact zone – poorly developed dendritic crystals. (R) section through the brown inner glaze. Visible unhomogeneity of glaze: silica enriched layer (gray) and proper glaze (light). The contact zone is disturbed, irregularly formed dendritic crystals are present in it.		
7C	(L) cross-section through dark green glaze. From the left: paste, contact zone, glaze (light strip). (R) section through dark blue glaze. From the right – a substrate with a dendritic crystal zone (p. 8, 7, 6), light glaze (p. 4, 5), dark zone enriched in silica (p. 3), crust - sintered quartz grain (p. 1, 2).		

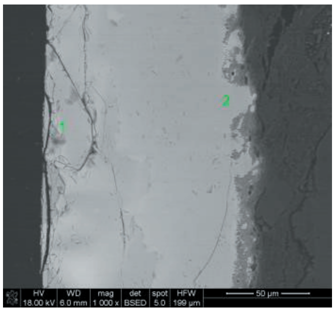
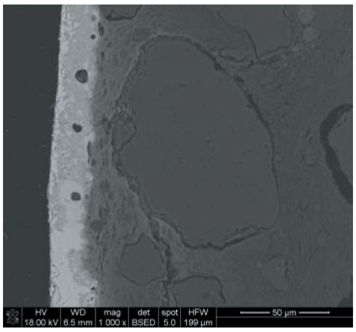
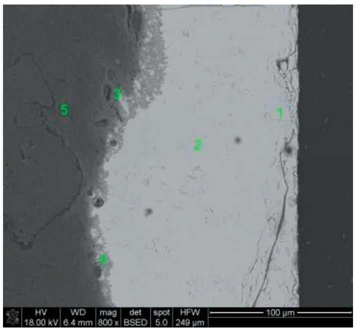
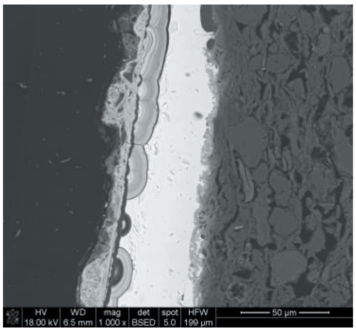
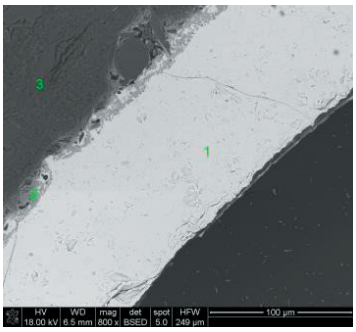
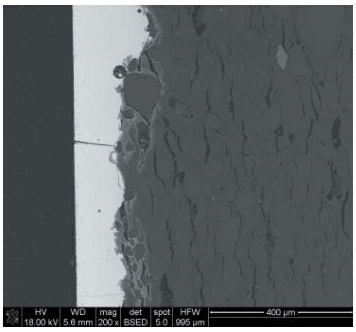
1	2	3
7D	Cross-section through the glaze on the 'fish scale' ornament. From the left: glaze with numerous surface cracks (1), contact zone with dendritic crystals (2).	
11B-1	(L) cross section through matt, creamy glaze. From the left: glaze with numerous bar crystals and unmelted quartz grains, contact zone, substrate with large quartz grain. (R) section through the yellow, transparent glaze. From the left: ceramic mass (5), contact zone with dendritic crystals (3, 4), glaze - cracked at the surface (1,2).	 
11B-2	(L) section through the glaze with black crust. From the left: sintered crust, colomorphic zone, glaze (light band), continuous contact zone (dendritic crystals), paste. (R) section through the green glaze. From the left: substrate / paste, contact zone, glaze (light strip), gray narrow zone enriched in silica.	 
12-1	Cross section of light green glaze. From the left: glaze (light strip), contact zone (dendritic crystals and paste impregnated with glaze, paste.	

Table 4. The results of semi-quantitative EDS chemical analyses [wt. %] of glazes. "<LD" denotes the absence of an element or concentration below the detection limit.

Code of the sample	**The analysed area**	**P**	**Mg**	**Ba**	**Ca**	**Na**	**K**	**Si**	**Al**	**Pb**	**Cd**	**Zn**	**Fe**	**Co**	**Cu**	**Ti**	**Pb/Si**
5C	Bluish glaze - covering the decorated surface	<LD	1,07	<LD	0,94	<LD	4,89	21,14	0,84	51,24	<LD	<LD	**1,48**	**1,57**	**<LD**	<LD	2,4
	The glaze on the undecorated surface	<LD	<LD	<LD	0,82	<LD	<LD	15,31	1,26	65,89	<LD	<LD	**1,35**	**1,14**	**<LD**	0,70	4,3
11B-3	Transparent glaze covering red background	<LD	<LD	<LD	<LD	<LD	<LD	13,79	0,79	71,38	<LD	<LD	**<LD**	**<LD**	**2,04**	<LD	5,2
5F	Brown glaze	<LD	<LD	<LD	0,80	<LD	0,80	13,60	2,00	70,02	<LD	<LD	**1,85**	**<LD**	**<LD**	<LD	5,2
	Brown glaze with black residue	<LD	<LD	<LD	0,81	<LD	<LD	10,69	2,32	74,64	<LD	<LD	**1,17**	**<LD**	**<LD**	<TI	6,8
7C	Dark-green glaze (bottle-green)	<LD	0,77	<LD	<LD	<LD	<LD	18,41	3,94	56,20	<LD	<LD	**3,12**	**<LD**	**<LD**	<LD	3,1
	Navy-blue glaze	<LD	<LD	<LD	1,18	<LD	0,4	13,45	2,30	63,20	<LD	<LD	**2,05**	**<LD**	**3,95**	<LD	4,7
7D	Brown glaze	<LD	<LD	<LD	<LD	<LD	<LD	10,54	2,32	74,44	1,37	<LD	**1,11**	**<LD**	**1,77**	<LD	7,1
	Brown glaze	<LD	<LD	<LD	<LD	<LD	<LD	11,68	3,11	72,61	0,87	<LD	**0,82**	**<LD**	**1,48**	<LD	6,2
	Brown glaze	<LD	<LD	<LD	<LD	<LD	<LD	10,18	2,41	74,33	0,89	1,49	**1,20**	**<LD**	**1,53**	<LD	7,3
	Light green glaze	<LD	<LD	<LD	<LD	<LD	<LD	11,71	2,95	71,63	1,35	<LD	**2,80**	**<LD**	**1,53**	0,79	6,1
	Light-green glaze	<LD	<LD	<LD	<LD	<LD	<LD	15,55	3,16	69,45	<LD	<LD	**1,41**	**<LD**	**<LD**	<LD	4,5
11B-1	Yellow glaze	<LD	<LD	<LD	0,67	<LD	<LD	15,25	4,06	60,92	<LD	<LD	**1,42**	**<LD**	**1,61**	0,64	4,0
	Creamy glaze	<LD	<LD	<LD	0,72	<LD	<LD	22,04	4,60	48,06	<LD	<LD	**1,91**	**<LD**	**1,45**	1,07	2,2
11B-2	Malachite-green glaze	0,71	<LD	<LD	1,55	<LD	0,70	15,1	2,91	59,93	<LD	<LD	**1,83**	**<LD**	**2,18**	<LD	4,0
12-1	Light-green glaze	<LD	0,73	<LD	<LD	<LD	<LD	15,09	3,95	61,27	<LD	<LD	**1,15**	**<LD**	**4,05**	<LD	4,1

Table 5. The results of semi-quantitative EDS chemical analyses [wt. %] of pigments and coloured pastes. "<LD" denotes the absence of an element or concentration below the detection limit. Chromophores are underlined.

Code of the sample	The analysed area	P	Mg	Ba	Ca	Na	K	Si	Al	Pb	Cd	Zn	Fe	Co	Cu	Ti
5C	Navy-blue frit	<LD	1,70	<LD	0,94	<LD	12,03	43,56	0,87	0,64	<LD	<LD	**2,80**	**3,63**	**<LD**	<LD
11B-3	Grained pigment	<LD	1,48	<LD	1,34	0,97	4,43	24,40	13,09	16,66	<LD	<LD	**6,93**	**<LD**	**1,04**	0,60
	Grained pigment entrenched in the base	<LD	<LD	<LD	1,79	0,60	1,92	10,19	31,82	21,13	<LD	<LD	**7,51**	**<LD**	**<LD**	0,83
	Grained pigment	<LD	<LD	<LD	<LD	<LD	1,06	56,78	0,60	1,06	<LD	<LD	**0,60**	**<LD**	**0,67**	<LD
	Grained pigment	<LD	1,37	<LD	1,79	0,59	1,92	31,82	10,19	21,13	<LD	<LD	**7,51**	**<LD**	**1,10**	0,83
	Creamy ornament	12,15	<LD	<LD	19,78	<LD	<LD	1,67	0,64	42,64	<LD	<LD	**1,31**	**<LD**	**2,20**	<LD

Table 6. The results of semi-quantitative EDS chemical analyses [wt. %] of the ceramic masses and the contact areas between semi-majolica and glazed ceramics. "<LD" denotes the absence of an element or concentration below the detection limit, "n.o." states for "not observed".

Code of sample	Localisation in the sample	P	Mg	Ca	Ba	Na	K	Si	Al	Pb	Fe	Co	Cu	Cd	Zn	Ti	Si/Al
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
5C	Ceramic mass	<LD	0,70	2,76	<LD	<LD	1,79	33,18	19,57	1,07	2,25	1,13	<LD	<LD	<LD	2,57	1,7
	Engobe (slip)	<LD	0,84	2,37	<LD	0,68	7,61	33,76	15,93	2,19	2,31	<LD	<LD	<LD	<LD	<LD	2,1
11B-3	Ceramic mass	1,36	1,64	1,87	<LD	<LD	2,05	35,67	13,54	1,15	5,72	<LD	<LD	<LD	<LD	0,93	2,6
5F	n.o.																
7C	Ceramic mass	<LD	1,29	1,90	<LD	0,82	6,76	39,98	13,19	1,05	5,91	<LD	<LD	<LD	<LD	<LD	3,0
	Engobe (?) (slip)	<LD	1,42	1,34	<LD	1,42	4,49	26,40	12,89	20,26	4,30	<LD	<LD	<LD	<LD	<LD	2,0
	Engobe (?) (slip)	<LD	1,62	1,43	<LD	1,15	3,79	27,95	10,46	15,98	4,73	<LD	1,15	<LD	<LD	<LD	2,7

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
7D	Ceramic mass	<LD	0,89	2,04	<LD	<LD	2,88	46,65	17,94	<LD	3,05	<LD	<LD	<LD	<LD	1,72	2,6
	Engobe (?) (slip) “fish scale”	<LD	0,71	1,18	<LD	<LD	4,58	34,12	17,77	<LD	2,20	<LD	0,89	0,89	0,56	2,53	1,9
	Engobe (?) (slip) light-green	<LD	0,69	<LD	2,66	0,85	4,55	27,74	16,26	16,06	2,56	<LD	0,66	0,88	<LD	5,54	1,7
	Engobe (?) (slip) light-green	0,73	0,92	<LD	4,04	<LD	3,55	36,37	21,52	<LD	3,69	<LD	0,75	1,11	<LD	4,64	1,7
	Grain in engobe (?)	0,61	<LD	<LD	1,09	<LD	<LD	60,85	1,47	<LD	1,28	<LD	0,96	1,20	<LD	8,88	–
11B-1	Ceramic mass (“the patch”)	<LD	1,12	0,90	<LD	<LD	2,89	32,04	20,49	3,45	2,56	<LD	<LD	<LD	<LD	1,17	1,6
	Engobe (?) creamy surface	<LD	0,9	0,72	<LD	<LD	3,38	27,17	18,21	12,01	2,18	<LD	0,81	<LD	<LD	3,01	1,5
11B-2	Engobe (?) under the black external glaze	<LD	1,00	1,5	<LD	0,96	3,34	36,63	16,25	2,36	2,75	<LD	<LD	<LD	<LD	<LD	2,3
	Engobe (?) under the green glaze	1,37	<LD	2,49	<LD	<LD	1,05	33,65	17,32	<LD	3,33	<LD	<LD	<LD	<LD	<LD	1,9
12-1	Ceramic mass	<LD	0,60	1,06	<LD	<LD	<LD	31,37	21,77	<LD	<LD	<LD	<LD	<LD	<LD	<LD	1,4
	Engobe (?)	<LD	0,59	0,72	<LD	<LD	1,25	23,30	16,90	15,79	1,97	<LD	0,99	<LD	<LD	5,24	1,4
	Engobe (?) the lower part	1,08	0,7	1,19	<LD	<LD	0,94	29,15	20,91	3,96	1,59	<LD	0,66	<LD	<LD	1,13	1,3

5. Discussion

5.1. The characteristics of glazes in semi-majolica and glazed unpainted ceramics

All of the tested glazes are lead-silicate ones. The advantages of using such enamels have been known for a long time. They are easy to prepare and apply and the visual effects they provide (i.e. gloss and shine) are unparalleled; however, the final effects depend on many factors. These include: the type of raw material (in the strict sense, so different substances used to introduce a given element have to be distinguished), the degree of granularity, chemical purity (in all kinds of glasses even minimal admixtures can change the properties of the product), the proportion of the ingredients, the diligence in applying paints and glazes (e.g. preventing the intrusion of air), the quality of the untreated vessel (e.g. lack of porosity), the method of firing and cooling and the cleanliness of the kiln. In practice, the adjustment of these numerous parameters has always been carried out by trial and error method (Shaw 1971).

Lead-silicate glazes first appeared in the Western world at the turn of the eras. They contained from 45 to 60 wt. % PbO, to approximately 2 wt. % alkali and between 2 and 7 wt. % aluminum oxide. Glazes of this composition were common in Byzantium and in the Islamic world (Iraq, Iran, Egypt, Mauritania), as well as in medieval Europe. At the same time, the invention of tin glazes developed in the Islamic world and although they are not discussed here, they played a significant role in modern European ceramics (Tite *et al.* 2008).

The concentration of lead in semi-majolica glazes varies between 51,24 and 71,38 wt. % and in non-semi-majolica glazed ceramics between 48,06 and 74,33 wt. %. The lowest Pb value was recorded in the opaque glaze (sample 11B-1). The Pb:Si ratio varies between 2.4 and 5.2 in semi-majolica glazes and between 3.1 and 7.3 in other glazes. The only exception is, again, the opaque cream glaze of sample 11B-1, where Pb:Si is 2.2. Consequently, it is evident that glazes with a high amount of Pb, i.e. soft and not very viscous, were clearly preferred. In some cases there is a difference between external and internal glazes of the same vessel – they differ not only in color, but also in the Pb:Si ratio. These were simply different glazes (Fig. 1). The one exception in the set is the glaze in 7D sample, which contains cadmium and zinc.

The composition of the studied glazes is very similar to the composition of the glazes from medieval workshops in Przemyśl (Auch 2016), while at the same time it clearly differs from the composition of Iznik glazes that were popular in modern Europe (Paynter *et al.* 2004). Furthermore, the above-presented composition varies, although to a lesser degree, from the composition of Mauritanian glazes from medieval Spain (Molera *et al.* 2001).

On the surface of some glazes, there is a very thin, several micrometers long, uninterrupted layer deficient in PbO. Higher concentration of silica enhances glaze firmness and its resistance to external factors: abrasion and the influence of acidic or alkaline substances. Since this layer is very thin, probably due to lead evaporation

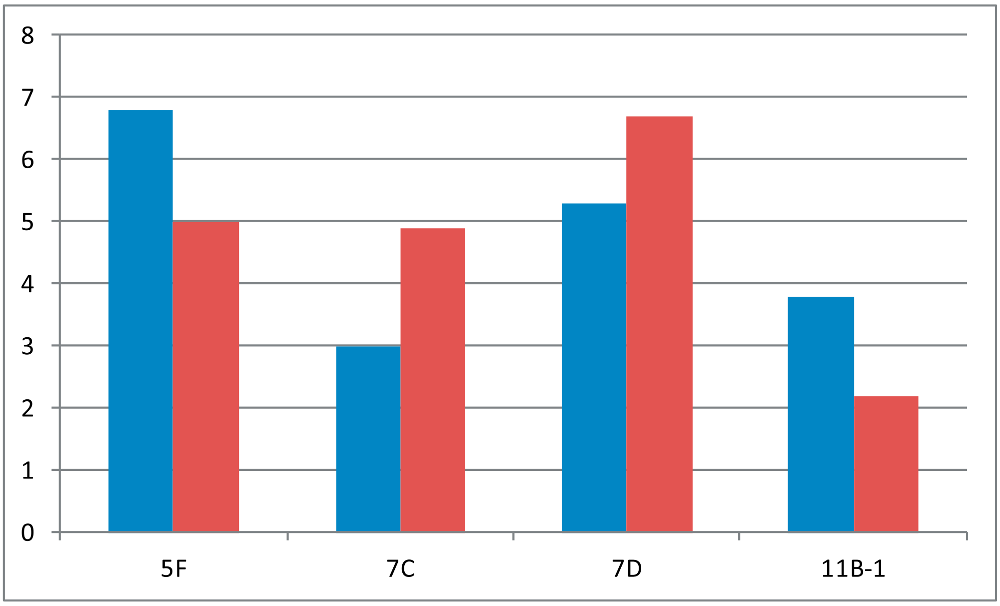


Fig. 1. The graph showing Pb:Si differences in glazes applied on internal (left post) and external (right) surfaces of the examined vessels.

in the last stage of the firing process (Tite *et al.* 1998), it is difficult to say whether the above-mentioned procedure was intentional. Such layers are present in three samples (Table 3, 7).

Among the components of glazes, one can distinguish intentionally added aluminosilicates, in the form of suspension composed of kaolinite, smectite or other argillaceous minerals. The aim of such a procedure was to improve the rheological properties of the glaze, its adhesive capacity and ensure clogging of the on the surface of the vessel. The amount of added clay depended on the firing conditions and was regulated experimentally by the glazer (Rada 1993; Shaw 1971). Proving the use of such a suspension is not an easy task. The elements of the added argil and those present in the ceramic mass can be, and usually are, identical. Experimental studies (Molera *et al.* 2001) show that the use of argil in glazing sets results in a narrower area of contact than otherwise, but in order to perform a valid interpretation, it is necessary to have a point of reference, and this may be difficult in the case of archaeological material.

We can, however, look at the amount of aluminum in the glazes and ceramic masses. The amount of aluminum in the studied glazes varies between 0.79 and 1.26 wt. % in semi-majolica and between 2.00 and 4.60 wt. % in glazed ceramics moreover, it is the highest in the atypical opaque glaze (sample 11B-1). The comparison of aluminum concentration in enamels and ceramic masses reveals clear differences between the two ceramic groups (Fig. 2A). In semi-majolica, there is a lot of aluminum in ceramic masses in relation to enamel, whereas in unpainted ceramics there is much less aluminum. The conclusion drawn from this situation can be twofold. First of all, semi-majolica was produced on biscuit (hence the slight diffusion of aluminum into the enamel), while the enamel of the remaining ceramics was applied to the unstable, unfired base. Second of all, a certain amount of argil was added to the enamel masses of the unpainted ceramics.

The comparison of Si/Al proportions of glazes and ceramic masses also reveals a clear difference between semi-majolica and unpainted glazed vessels (Fig. 2B). The Si/Al ratio in ceramic masses is an estimated (i.e. with the exclusion of cations) characteristic of the argillaceous minerals found in it. The Si/Al ratio in glazes may reflect the presence of these elements resulting only from their diffusion into the enamel, but also the presence of additional aluminosilicates in the suspension or the glazing frit, as well as the application of the enamel to the unfired base (greater diffusion of Al, Si). The high Si/Al value in all glazes is due to the presence of silicon with sand or frit. However, significantly higher concentration of silicon in glazes of semi-majolica than in their ceramic masses, when both are compared with other ceramics, does not result from the use of exceptionally large amounts of silica (Table 4), but from the lack of (or weak) diffusion of silicon into the enamel. Regarding the similar concentrations of Al in the glazes of semi-majolica and other ceramics, as well as such a distinct diversification of the factors discussed above, the differentiation is due to the fact of firing (or lack thereof) the vessels, rather than the potential admixture of argil into the glazing suspension. Importantly, the argil was incorporated into the glazing suspension only in one case, namely the matt, creamy glaze of sample 11B-2.

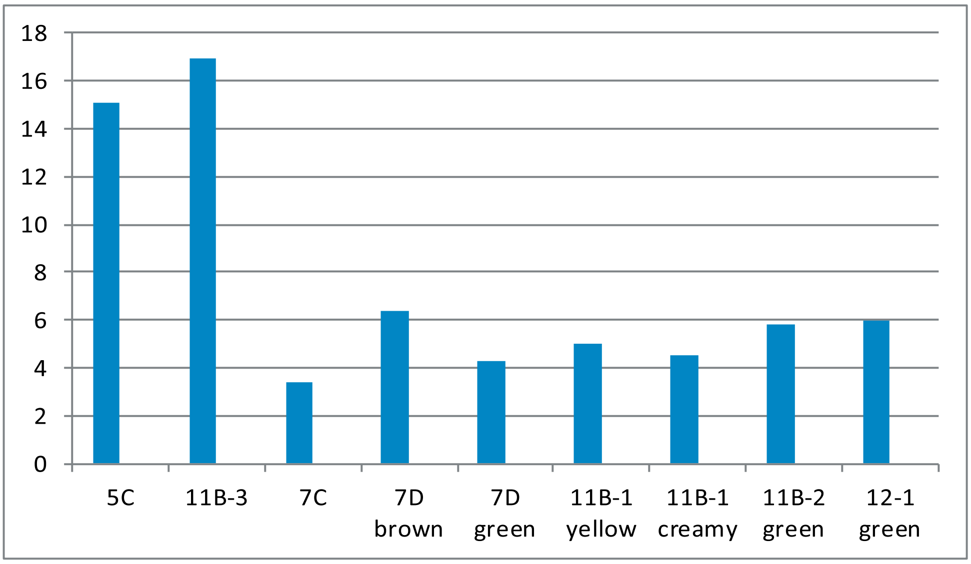


Fig. 2. The graph depicting Al paste *vs.* Al glaze ratio in tested samples.
5C and 11B-3 represent semi-maiolica.

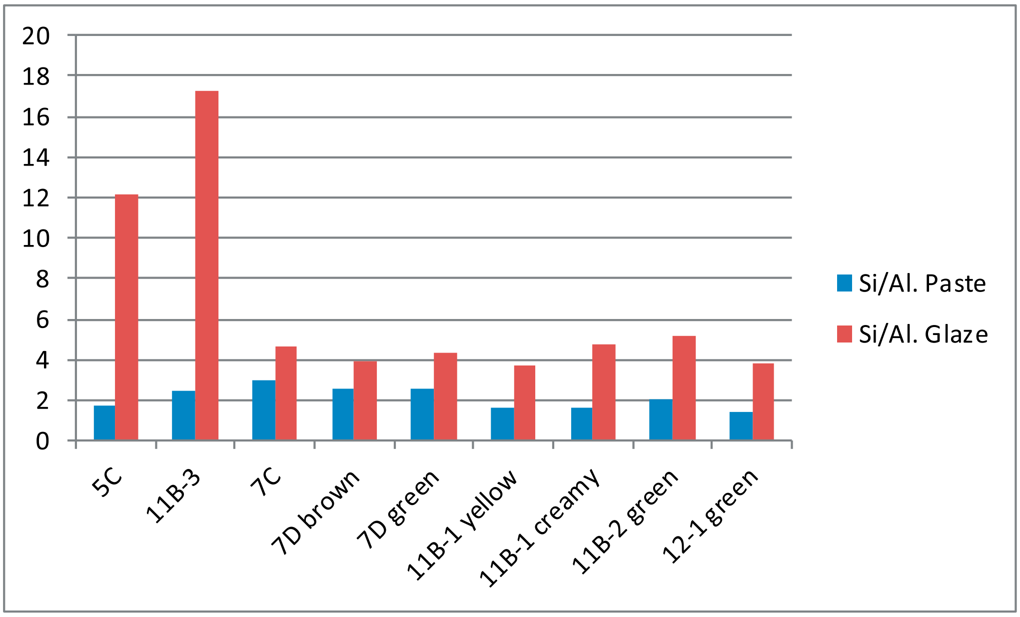


Fig. 3. The graph depicting Si/Al glaze *vs*. Si/Al paste ratio in tested samples.
5C and 11B-3 represent semi-maiolica.

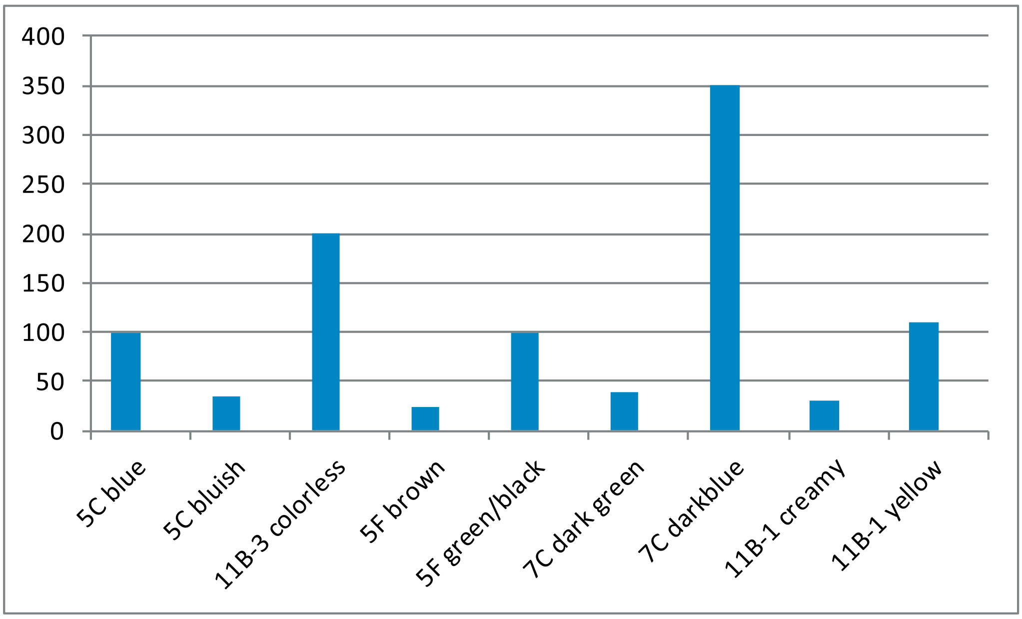


Fig. 4. Diversification of glaze thickness expressed in micrometers (vertical axis).

The thicknesses of the glazes vary, also within the outer and inner sides of the same vessel (Fig. 4). According to the authors, this may be an individual trait of a workshop or a glazer.

Lead for glazing could also be used in the form of lead-silicate frit or as a powder of lead oxides: red lead, lithargite, massicot or basic lead carbonate, white lead. These substances were not only by-products of silver purification in the cupellation process, but also deliberately produced semi-raw materials included in the trade turnover (Rozmus 2014). In all probability, the raw material was extracted from intensively exploited Silesian-Cracow deposits, but other locations should also be taken into account, namely the areas of present-day Ukraine, specifically, the region of Truskawiec (Dobis 1938) and the Świętokrzyskie Mountains, where galena was exploited from the 14th century (Rubinowski 1971). This issue can be solved through lead isotope testing and archival research. The analysis of the latter could help to determine the type of raw material purchased:

whether it was red lead, massicot, lithargite, white lead, or galena, or the unpurified or poorly purified product of galena and sphalerite weathering. Only in one case (sample 7D) it can be stated that the latter situation actually took place. This is indicated by the presence of cadmium and zinc. The most probable source of these elements is cadmium-bearing calamine, which should not be present in lead compounds (oxides and carbonates) purified in metallurgical processes. In the weathering area near Olkusz, where lead and silver, and since the 18th century also zinc minerals were exploited from the surface, cadmium has been present in the amount of approx. 1000 ppm, as an admixture in ore minerals (Mayer *et al.* 2001).

Glass sands are usually found near Tarnobrzeg and Roztocze (Kozłowski 1986, 367). It is a valuable and rare resource. Nevertheless, it was also possible to use more accessible, inferior (i.e. containing a small percentage of iron compounds) sands from the numerous dunes in the Sandomierz Basin (Kociszewska-Musiał 1988, 64). The exact source of sands can be precisely identified only by means of trace element analysis.

In one case (semi-majolica, sample 5C), lead-silica frit is detected in the glaze. Therefore, the frit was treated as a semi raw material for glazes. Its production site is obscure, but it could have been manufactured on site. Further research, especially concerning the potential discovery of crucibles with frit remnants, could possibly resolve this issue.

It should be stressed that the concentrations of lead and silica in the glaze are by no means a simple reflection of the concentration of these elements in the raw material. Molera *et al.* (2001) have demonstrated that, generally speaking, the amount of silica in glazing increases and the amount of lead decreases in relation to the raw material, but depending on the initial proportion, the final ratios might be variable. Thus, it is impossible to strictly determine the amount of raw material used solely on the basis of the information concerning the chemical composition of the glaze.

5.2. The characteristics of the glaze-base interaction in semi-majolica and unpainted ceramics

The preparation of the base in the process of decorating the vessel was of various nature. It consisted in levelling the surface by smoothing, repairing defects with "patches" of clay (which can be observed in one of the tested samples) or applying slips of different compositions. Furthermore, the relevant literature mentions the application of suspensions made of plant ashes, greasy argil or flour and water (Walton and Tite 2010; Herakliusz see Auch 2016). All these measures were aimed at increasing the adhesiveness of the base to the applied layer and obtaining optimal aesthetic results.

A typical slip (engobe) was used in the semi-majolica with a light grey cross-section (sample 5C). It is a thin layer composed of fine-grained quartz grains that are homogeneous in terms of size that have been mixed with clay minerals. High potassium content, in relation to the ceramic mass base, suggests that raw plant ash, potash or cream of tartar (potassium hydrogen tartrate, obtained during wine production) could have been used. The use of a specially selected argillaceous mineral, rich in potassium (white illite clay), is also likely, albeit such claims transcend the results obtained by this study, since we did not observe the presence of potassium feldspar grains. Potassium, which was used as a flux, increased the adhesion of the slip to the ceramic mass. Often described as 'slip-painting', they are viewed as predecessors of polychromatic under-glaze decoration. After the year 1200 A.D., the use of under-glaze paints without quartz began in Iran (Mason and Tite 2007).The "slip-painting" priming was also applied in the semi-majolica with a dark-red background (sample 11B-3). Here, the base of the glaze, which is responsible for its distinct color, is made of a layer of various, evenly-grained frit pigments (this will be discussed later on), mixed with a handful of quartz grains.

Sophisticated surface treatments for glazing are also observable in the case of glazed ceramics. Here, the base is made of ceramic mass enriched with certain elements (K, Na, Ba, P, Fe, Ti) or an argil "patch", whose structure is different from the structure of the base (i.e. the proper ceramic mass). In all of the above cases, plant ash suspension could have been used, but other substances, such as cream of tartar should also be considered. Furthermore, a very thin layer of potassium or sodium-bearing argil (i.e. white illite, smectite or a mixture of both of them with kaolinite) may also have been used. The inclusion of particular clay is indicated by the presence of titanium. All of the above-mentioned elements, with the exception of titanium, act as a flux and facilitate the binding of the enamel with the base. Iron compounds found under the green glaze of the sample 7D also rectified the color effect of the glaze.

The contact areas between the ceramic mass and the glaze are crucial, when it comes to the physicochemical properties of the vessels. They are responsible for the appearance of the glaze and its adhesion to the surface, and therefore, for its stability. The contact area includes the near-surface section of the ceramic mass, whose chemical composition and morphology differs from the proper ceramic mass, as well as the dendritic-crystals section, which is located within the glaze (Shaw 1971). Currently, attempts are being made to interpret the conditions of vessel production on the basis of the width of contact areas, but due to the multiplicity of factors influencing the process, conclusions must be drawn very carefully (Tite *et al.* 1998) and this should be heavily emphasized.

The breadth and continuity of the secondary-crystals area, as well as their chemical composition stem from the following factors: the reaction between the aluminosilicates in the base (ceramic mass with a specific, not accidental mineral composition) and the glaze which has a specific, not accidental chemical composition, the temperature of firing, the firing and cooling time (Shaw 1971), the application of the glaze to the unfired base or to the biscuit and the use of argil in the glazing suspension (or lack thereof) (Molera *et al.* 2001). In accordance with a well known phenomenon in both natural and technological processes, the higher the firing temperature and the longer the firing and cooling time, the thicker the reaction area becomes and the bigger the crystals get. It has been experimentally proven that under the same firing conditions, the thinnest area will be the one created on the kaolinite base. When extremely high-lead glazes (Pb:Si = 9) are used, the crystal area fills in the entire volume of the glaze. Crystals formed on the base of non-calcareous raw material are lead aluminosilicates, but their composition is highly diversified within the glaze itself (Molera *et al.* 2001).

Glazed ceramics from the investigated set are similar in terms of the width of the contact areas, regardless of the type of base used, glaze thickness and Pb:Si ratio. The width of the contact area within the ceramic mass oscillates between 30–50 micrometers, however, in two cases (the external glaze of sample 11B-2 and the glaze of sample 12-1) it can be up to 100 micrometers. The area covered with dendritic crystals is up to 10 micrometers, except for the opaque glaze of sample 11B-1, where crystals fill in the entire volume of the glaze. Despite having identical thickness throughout, the contact area is characterized by varying continuity, which points to disruptions in the technological process. It cannot be asserted that the firing conditions were identical, but it can be assumed that the process was carried out in such a way as to achieve a specific result for ceramics and glazes of different composition. The results have always been obtained through practical tests, which still take place in small workshops (Shaw 1971). The number of firing sessions is still to be determined. In the case of unpainted glazed ceramics, the unevenness of the base (Table 2) indicates the application of the glaze to an unfired vessel and single firing. This is further confirmed by the difference in proportions of aluminum in ceramic masses and glazes of semi-majolica as well as ordinary glazed ceramics and the variation in Si/Al proportions (Fig. 2).

The firing temperature would have to be about 850 –900°C, as evidenced by the properties of the ceramic mass (i.e. isotropization, but not vitrification). This seems plausible. In the case of semi-majolica, where the surface treatment was fairly sophisticated, the firing was at least double. The light grey semi-majolica vessel (5C) was fired in conditions with restricted access to oxygen or reduced oxygen, then decorations were applied and the vessel was fired once again. The red vessel (11B-3) was treated in a similar way. The melting of some pigments from the 'slip-painting' area into the ceramic mass base was probably due to the high concentration of flux, i.e. iron. For this vessel, one more firing was performed, in order to consolidate the creamy strip of the glaze ornament.

5.3. Characteristics of the colored elements: ornaments and glazes

The color palette of the examined fragments is rich. The coloring effects were obtained by means of pigments and glazes, the shade of the ceramic mass and the color of the slip. In semi-majolica, both under-glaze ("frit pigments") and over-glaze ("cream sinter ornament") decorations were used.

As regards the light grey semi-majolica vessel (5C), here, the slip described elsewhere was used. The grains of quartz amplified the transparency effect by extending the path of light rays, while the argillaceous components, which turned yellowish after firing, optically warmed the background. On top of all this, there was the effect of bluish glaze achieved with the use of cobalt and iron. It should be mentioned that glazed ceramics with a bluish background were a popular product of Ottoman workshops in Iznik in the 16th century (Denny 2004, 129). The deep red of the semi-majolica 11B-3 is created not only because of the color of the ceramic mass, but also due to the layer of frit pigments (which are described below). In the case of glazed ceramics, the base enriched with iron (7D) also modified the green shade of the glaze.

The color effect of the glazes depends on several factors: the chemical composition of chromophores, the concentration of chromophores and the chemical composition of the environment in which they are immersed, the color of the base and the degree of transparency of the glaze. We have access to the information concerning these parameters; in most cases, however, we do not know exactly which raw materials were used, and this is also an important factor affecting the final color effect (Shaw 1971).

Table 5 summarizes the chemical composition of the colored parts, highlighting the elements responsible for the coloring. Cobalt, iron and copper, in various configurations, act as chromophores – iron is the stand-alone chromophore in four cases, while copper assumes such a form in one case. In the remaining cases, iron and copper always co-exist and so do iron and cobalt. Hence, the question arises, whether such a composition of coloring substances is a consequence of not purifying the raw material from iron (which in turn, indicates their cheapness or the use of impure sand in local workshops) or whether it was a conscious purchase, motivated by aesthetic reasons. It is evident that the application of different proportions of chromophores (e.g. iron and copper) yields decidedly different color effects (e.g. malachite green *vs.* apple green), thus it can be assumed that pure pigments mixed in the desired proportions were used in some cases.

In the set of the examined samples, we observe as many as three distinctly different shades of green: dark bottle-green (7C), apple green (7D and 12-1) and malachite-green (11B-2). The bottle-green glaze is the only one that contains exclusively iron, while the remaining glazes contain iron accompanied by copper. More specifically, the malachite-green glaze has a Cu:Fe ratio of 2,18:1,83 wt. %, while the apple-green glaze has ratio of 4,05 to 1,15 wt. %. Also, the malachite glaze contains calcium and sodium – they might be used as modifiers of the green shade, together with iron and copper (Table 4).

The cream, opaque glaze on the surface of the vessel 11B-1 was created owing to the presence of numerous crystals of lead, potassium, iron and calcium aluminosilicates. These crystals were formed through the reaction of the base components (ceramic mass) and the glaze, including the argil that was added to the glaze. Based on the rather elegant appearance of this surface, it can be assumed that this effect was achieved intentionally, by long firing and cooling of the vessel. Perhaps it was an attempt to imitate tin-lead glazes used in Italian majolica, and other derivative products.

The next question concerns the form in which the coloring agents were added. The morphology and composition of the granular substances indicate that the coloring agents in both examples of semi-majolica were certainly added in the form of frit pigments. The grains of cobalt frit (sample 5C), the outline of which is still visible despite its strong tendency to melt away, are very large in comparison with the grains of frit used in sample 11B-3. Cobalt frit (smalt) is a silicate potassium glass, with a high concentration of iron, used in addition to cobalt. The correlation between the grain size of pigments (including cobalt pigments) and the intensity of a given color is well-known, as it was described by Johannes Kunckel (Estaugh *et al.* 2005), an 18th century glazier and alchemist. To illustrate, large grains of cobalt glass are known to produce a navy-blue color, which is observable in one of the analyzed examples.

In view of the fact that Podkarpacie region has no cobalt deposits, such pigments were undoubtedly imported. While the discussed pigments were known since antiquity, the 16th century brought a breakthrough in their production. More to the point, in 1520 various cobalt oxides (zaffre) were created, whereat the year 1540 brought the invention of cobalt glass, i.e. smalt. Cobalt pigments were certainly produced in Saxony and the Bohemia from the raw materials in the Ore Mountains. Cobalt was mined in Saxony from 1470, and the first mill for the grinding pigments was built there in 1635. The production and trade of cobalt pigment turned out to be so profitable that the Saxon elector taxed it, at the same time issuing a strict ban on any private activity concerning the above-mentioned substance. By 1654, 34 mines were already in operation (Hammer 2004). The prices of smelt remained at an average level (Harley 1982).

Another large cobalt deposit, Qamsar, was located in central Iran (Zucchiati *et al.* 2006). It supplied the eastern market, including the entire Muslim world. Due to the wide use of cobalt pigments in Eastern ceramics (including Ottoman ceramics), cobalt frit producers in this part of the world must have been plentiful. Certainly, the cobalt pigments from this deposit were also sold on European markets (Matin and Pollard 2015). Cobalt from Levant, in the form of cobalt oxides (zaffre), was marketed in Europe *via* Venice (Saliba 2004). Smaller deposits of cobalt are relatively numerous, both in Europe and in the Middle East. Among the former, one can mention the Lower Silesian Przecznica (Łodziński *et al.* 2009), and Saxony, which imported cobalt ores from Italy and Hungary in the 19th c. (Hammer 2004). After initial processing, all the mining output was transferred to pigment manufacturers and traders. A number of issues, including establishing the exact locations and numbers of European pigment trade centers, as well as pinpointing the differences between their products (such as cobalt pigments) has yet to be resolved, as it is insufficiently researched.

The dark red background of the second majolica vessel (sample 11B-3) was created by the application of a mixture of frit pigments. All of them were made on the basis of lead-silicate enamel mixed with aluminum and potassium. They are therefore fundamentally different from cobalt frits, as they are dominated by dark red pigments that are high in iron. Apart from the red pigments, there are also blue pigments with copper and colorless pigments with a very small amount of chromophores. The observed diversity is either the result of using a mixture of pigments in order to achieve the expected effect or it was caused by brush contamination. The grains were evenly distributed on the base, and then the glaze was applied. The form in which the grains were applied remains unknown. Despite very high lead content, the glaze was not viscous enough to penetrate the pigment area and blend well with the base, which led to the emergence of defects that can be observed macroscopically. In all probability, the firing temperature was too low. Ceramics with underglaze decorations, that contain pigments used without a medium that would have been preserved until now, appeared for the first time in Islamic Syria (Mason *et al.* 2001).

The pigments identified in the "slip-painting" layer in the dark red half-majolica are different from the smalt described above. They are very fine, evenly-grained, angular or slightly rounded. Their Pb:Si ratio is different than in the glazes, in favor of the amount of silicon. The high amount of aluminum, which hardens the frits enamel, is also noticeable. Unfortunately, no data on this type of pigment can be found in the literature. Consequently, the place of their production remains a mystery.

As attested by the monk Teofil (1998), frit pigments have been widely used by glaziers since at least the Middle Ages. Notwithstanding, raw mineral pigments were also exploited, such as chromite found in Islamic ceramics (Tite 2011). Copper pigments could have been produced on site from patina or slag that was left over from metal smelting; they could also be imported (not necessarily from a distant region – e.g. from the Świętokrzyskie region, Rubinowski 1971) as mineral coloring agents. Furthermore, they could be a result of fritting in workshops. The same applies to iron and iron-manganese pigments. In each case, the pigments had to have a certain, unified grain size. Attaining this result required a lot of experience.

The composition of the creamy ornament on the semi-majolica with a dark red background (sample 11B-3) is interesting. It consists of calcium phosphate, lead and silicon, as well as iron and cobalt. The structure of this paint is not homogeneous - it is not enamel, but a sinter. The surface of the ornament is blurred, sometimes clearly blistered, in short – defective.

Using phosphorus as an opacifier of glasses and enamel and for the production of white glasses and enamel is an old technological custom, known from tesserae in ancient mosaics (Silvestri *et al.* 2016), the Byzantine glass-making traditions (Maltoni and Silvestri 2019), as well as Venetian and Islamic workshops (Wypyski 2006). Experimental studies have shown that obtaining impeccable results requires pre-calcination of bone meal at 700°C (Maltoni and Silvestri 2019). In the semi-majolica from Rzeszów, the achieved effect is unsatisfactory; hence it should be seen as an unsuccessful attempt to make ornaments in this way. Defining the conditions for the production of this ornamentation requires further research by means of Raman spectroscopy, which will enable the phase identification of the components and thus the reconstruction of the conditions under which the product was manufactured.

We should also mention the red stripe ornament on the bluish semi-majolica (5C). Here, the convexity effect was achieved by putting a narrow layer of argil on the base. It was only then that the frit pigments were applied. Unfortunately, this treatment did not contribute to the durability of the ornament.

5.4. Ceramic masses

The first features of ceramic masses that can be seen in macroscopic view are their fineness and color. In the case of semi-majolica, the vessel with grey cross-section (5C) was made of clay characterized by kaolin-illite-smectite composition. A small amount of Ca is probably a natural component of the clays. In the second fragment of semi-majolica (11B-3), illite and smectite (or illite-smectite) clay(s) was/were used, with double amount of iron and lower calcium content, when compared to sample 5C.

In the set of glazed unpainted ceramics there are at least four fragments in which the ceramic mass is, or was intended to be, white-fired. In all cases, the ceramic mass is made of kaolinite-illite clay, as evidenced by the high concentration of aluminum and the low value of Si/Al ratio, the presence of which results from the chemical composition of kaolinite (cf. Fig. 2B). The whitest clay (sample 12-1) has iron concentration below the detection limit, while the grey ones (7D, 11B-1) have iron concentration of approx. 2–3 wt. %. This which translates into the grey effect during reduction firing or firing with limited oxygen access.

The ceramic base of glazes cannot be porous or vitrified. To eliminate the first problem, colloidal smectite was sometimes applied to the surface, as it clogged the pores. In order to remove moisture from the base, vessels were sometimes heated (Shaw 1971, 49). Different bases required different consistency (viscosity) of the glazes, and the consistency was determined by means of experiments. The composition of ceramic masses was marked near the decorated surfaces; hence it usually contains a small amount of lead, or alternatively, also chromophores (Table 4–6).

The surfaces for decorations were prepared with varying degrees of precision, from carefully smoothed (half-majolica, vessel 12-1), to vessels with uneven surfaces, even patched (11B-1). Other surface modifications have been discussed above. No frits were observed in the ceramic masses, except for the 7D sample, where the presence of irregular, randomly distributed enamel grains, was detected. On the one hand, the abovementioned example is reminiscent of the 'fritware' technique, used in experiments with proto-porcelain in the East and West (Mason and Tite 2007), but on the other hand, the presence of the grains might have been an accident.

The potential raw materials used for the production of ceramic masses are abundant in the Podkarpacie region. These include mainly the tertiary (usunąć Baden) Cracovian loams, but also fluvisol and other quaternary raw materials. White-burnt clays, composed of kaolinite (approx. 60%), illite (approx. 25%) and quartz (approx. 15%), are found in the Świętokrzyskie region's jurassic deposits. The clays of similar composition were also known to exist in the vicinity of Cracow (Budkiewicz and Tokarski 1971). A detailed identification of the place of origin of the raw material (and perhaps also the mixing of its several types) will be possible after detailed analyses of the raw material are performed.

5.5. Defects of the glazes and corrosive phenomena

On and within the surfaces of many glazes there are unintentional defects resulting from production, use and post-depositional history. Open bubbles with micro-crystals composed of lead and iron, and probably also oxygen, occur in the glaze of the semi-majolica (5C) ‑ these are the black spots visible in the macroscopic photograph. They were formed when the vessel was in the kiln or as a result of other burning-related actions, e.g. a fire.

Open and closed bubbles in the glaze are also present in samples 7C and 11B-1, in both cases within the thickly applied navy-blue and yellow glazes, respectively. The presence of these bubbles results from excessive moisture of the glazing paste, regardless of the form in which it was applied (i.e. powder or fine frit) and/or the high moisture of the base. The small flaky clusters of iron compounds that are closed within the bubbles suggest that the atmosphere of the kiln was not particularly clean. The presence of such bubbles is not the result of a fire, since in that case the glaze would drain off. The cracks in the glaze are caused by the differences in the thermal expansion of the ceramic mass and enamel. Such fractures are virtually inevitable; however, their quantity depends mainly on the adopted methods of firing and cooling (Shaw 1971, 26). The concentration of cracks near the surface of the vessels results from exploitation, but it can also stem from mechanical damage inflicted after depositing the object in the sediment.

Another variety of flaws, that is visible only under the scanning electron microscope, is the accumulation of substances partially resembling the composition of the glazing enamel. The substances are structurally connected with glazes or the ornament. As regards their morphological make-up, they assume the form of parallel, narrow, partially loosening areas. On the surfaces of two glazes, one can find black, thin areas consisting of lead, phosphorus, calcium and iron (5F) and lead, phosphorus and calcium (11B-2), respectively.

In other cases (5C, 7C, 11B-2), we have recorded corrosion areas within the external surface of the glaze, in the form of colomorphic or cryptocrystalline regions, that are either loosening from the base (5C) or are closely bound to it. When compared to the chemical composition of the glazes, they exhibit variable concentrations of lead and silicon, as well as the presence of calcium and phosphorus. The latter two are not independent residues, but together with the other mentioned elements, they create a sinter. Furthermore, they are also incorporated into needle-shaped crystals, which are composed with the addition of lead and silicon. Therefore, the presence of these elements is not an unambiguous result of their existence within the sediment. Notwithstanding, the genesis of such overlays is not clear. The composition of the creamy, opaque ornament on the surface of the glaze of the semi-majolica with the red background (11B-3) may be a hint. It is, as mentioned above, a sinter paint composed of lead, silicon, phosphorus and calcium. Such substances were widely used and could have possibly contaminated the atmosphere of the kiln. This issue can be clarified once the kiln is found and its remains are examined.

6. Conclusions

The analysis of the several fragments of vessels revealed a wealth of valuable information about the raw materials used and the production technology employed. However, due to the same circumstances, it is impossible to comment on the characteristics of the workshop(s). Such opinions can be expressed only after examining representative groups of semi-majolica and glazed ceramics from several documented sites. Similarly, only then will the comparative research on the resource base be meaningful.

Table 7. The stratigraphic diagram of the technological and corrosion layers of the examined samples („n.o." states for „not observed").

Semi-majolica		**Glazed unpainted ceramics**										
Sample 5C	**Sample 11B-3**	**Sample 5F External surface (brown)**	**Sample 5F Internal surface (black)**	**Sample7C External surface (navy-blue)**	**Sample 7C Internal surface (dark green)**	**Sample 7D External surface (fish scale, brown)**	**Sample 7D External surface (green)**	**Sample 11B-1 External surface (creamy)**	**Sample 11B-1 External surface (yellow)**	**Sam-ple11B-2 External surface (black)**	**Sample 11B-2 External surface (green)**	**Sample 12-1**
Thin layer of secondary changes	Thin layer of secondary changes	(–)	Black incrustation	Black incrustation	(–)	(-)	(–)	(–)	(–)	Thin layer of secondary changes	Thin layer of secondary changes	(–)
Glaze: area with increased silica content	Glaze: area with increased silica content	Glaze: area with increased silica content	Glaze: area with increased silica content	Glaze: area with increased silica content	(–)	(–)	(–)	(–)	(–)	(–)	Glaze: area with increased silica content	(–)
(–)	Overglaze ornament	(–)	(–)	(–)	(–)	(–)	(–)	(–)	(–)	(–)	(–)	(–)
Glaze Pb:Si = 2,4 – 4,3	Glaze Pb:Si = 2	Glaze Pb:Si = 5,5 – 6,8	Glaze Pb:Si = 4,6	Glaze Pb:Si = 5,0	Glaze Pb:Si = 3,0	Glaze Pb:Si = 4,7 – 7,3	Glaze Pb:Si = 4,5 – 6	Glaze Pb:Si = 2,2	Glaze Pb:Si = 4,0	Glaze (n.o.)	Glaze Pb:Si = 4,0	Glaze Pb:Si = 4,1
Pigments	Pigments	(–)	(–)	(–)	(–)	(–)	(–)	(–)	(–)	(–)	(–)	(–)
Slip: quartz, clay, enriched with K		(–)	(–)	Enriched with Na	Enriched with Na	Enriched with K, Ti	Enriched with P, Ba, Na, Fe, Ti	"Patch" of clay	"Patch" of clay	"Patch" of clay	"Patch" of clay	Enriched with K, Ti
Contact area	Not visible due to the pigment area	Contact area		Contact area		Contact area		Contact area		Contact area		Contact area
			The base – frit grains									
Light grey ceramic mass	Brick-red ceramic mass	Dark-brick-red ceramic mass		Greyish-cream ceramic mass		Ceramic mass with individual enamel particles		Greyish-cream ceramic mass		Greyish-cream ceramic mass		White ceramic mass

The investigated vessels were made of fine-grained ceramic mass, a part of which was evenly grained, while the other part was unevenly-grained. Its chemical composition indicates the use of smectite/illite clay, kaolinite/illite clay and kaolinite/illite/smectite clay. The basic vessels were made with care, although not without errors. The latter include the uneven surface, which required repairs ("patches") and the presence of small, fissured pores, that were occasionally irregular. The firing took place at a temperature of approx. 850–900°C, i.e. before vitrification, which hinders the adhesion of the glaze. The unpainted vessels required a single firing, whereas semi-majolica vessels were burnt twice and the vessel 11B-3 was burnt three times. Depending on the needs, the firing was carried out in oxidizing or reducing atmosphere. The latter ensured obtaining white or light grey fractures, provided that the ceramic mass incorporated iron.

The richness of the colors and shades is surprising. In the case of semi-majolica, the underglaze paintings were made with the use of frit pigments, while the overglaze ornament was made with the use of lead-phosphate-calcium-silicate paste. Apart from painting the ornaments, the "slip-painting" technique was also used. The glazes were colored with iron, copper and cobalt compounds in various compositions and concentrations, which provided different shades. In the light grey semi-majolica, quartz-argillaceous primer with a potassium-bearing substance was applied, while in the glazed unpainted vessels, the surface under the glaze was covered with plant ashes or other flux-bearing substances, which did not leave any micromorphological traces.

It should be noted that the chemical compositions of glazes and ceramic masses and the methods of conducting the firing process, are closely related. Therefore, relying solely on the results of chemical analyses of the glazes in order to differentiate the set, draw conclusions about the characteristics of the workshops and indicate the sources of raw material may lead to erroneous conclusions. Identifying the types of raw materials, in the strict sense (e.g. galena *vs.* red lead), on the basis of the studied chemical composition is risky ‑ the fact of obtaining different effects from different raw materials carrying the same element is well-known. Good knowledge of recipes is based on the good knowledge of specific ingredients, not the chemical composition, as emphasized by glazing technologist (Shaw 1971, 52).

The technological traits of semi-majolica described above suggest that the sources of aesthetic and technical inspiration behind it might not necessarily be found in the West. In this respect, its similarity to Eastern items is clear, especially regarding the features of the ornamentation. Eastern ceramics were known in the Western European world (Denny 2015), including Hungary, where they appeared even before the Ottoman occupation (Gerelyes 2008). Needless to say, the influence of the Islamic ceramics on the Italian Renaissance majolica and the popularity of both throughout Europe are well-documented (Greenberg (ed.) 2004).

The research problems that arise during the examination of the Podkarpackie semi-majolica sets and glazed unpainted ceramics concern the basic technological features and their similarity to the ceramics from other significant western and eastern centers. Additional issues, such as the provenance of raw materials and the direction of trade routes are also pivotal and again, both should be taken into account. In this aspect, it seems crucial to combine the results achieved by dint of archaeometric research and archival studies.

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