1 **Archaeometric characterization of 17th century tin-glazed Anabaptist (Hutterite)**

2 **faience artefacts from North-East-Hungary**

3

4 Bernadett Bajnóczi[a1], Géza Nagy[a], Mária Tóth[a], István Ringer[b], Anna Ridovics[c]

5

6 [a]Institute for Geological and Geochemical Research, Research Centre for Astronomy and

7 Earth Sciences, Hungarian Academy of Sciences, H-1112 Budaörsi út 45., Budapest, Hungary

8 [b]Rákóczi Museum of the Hungarian National Museum, H-3950 Szent Erzsébet u. 19.,

9 Sárospatak, Hungary

10 [c]Hungarian National Museum, H-1088 Múzeum krt. 14-16., Budapest, Hungary

11

12

13 Abstract

14 The paper presents the first results of a long-term project aiming to reconstruct the production

15 technology of the Anabaptist (Hutterite) tin-glazed ceramics produced in Eastern-Central

16 Europe. Microanalytical investigations were performed on 17th-century faience artefacts (six

17 samples) excavated at Sárospatak, North-East-Hungary. The results are compared with

18 analytical data on the direct or indirect precursor, Italian maiolica.

19 The studied Hutterite faience artefacts reveal similarities with the Italian maiolica.

20 Calcareous clay with 14 to 22 wt% CaO was used for the buff-coloured ceramic body. Up to

21 about 400 μm thick, tin-opacified white and blue lead-alkali glaze was applied on the biscuit-

22 fired body. The glaze suspension contained sand admixture and a significant amount of

23 common salt and was not fritted before application. The colorants used for the ceramic

24 colours are lead antimonate for yellow, cobalt with arsenic, nickel and iron for blue, copper

25 for green and manganese with minor iron for black. The ceramic colours were applied on the

26 unfired glaze and maturing occurred during the second firing. The main technological

27 difference when compared with the Italian Renaissance maiolica is the deliberate use of a

28 high amount of tin oxide (17 to 20 wt% $SnO_2$) together with 18 to 28 wt% PbO content for

29 white glaze of the studied Hutterite faience.

30

31 Keyword: Eastern-Central Europe, Anabaptist, Hutterite, faience, maiolica, tin glaze

32

[1] Corresponding author. Tel/fax: +36 1 319-3137, E-mail address: bajnoczi.bernadett@csfk.mta.hu, bajnoczi@geochem.hu

1

1. Introduction

Production of tin-glazed earthenware (faience) in Eastern-Central Europe was mainly propagated by the Anabaptists in the 16th to 17th centuries. The name "Anabaptist" refers to the third branch of the Reformation (Szebeni, 1998). Anabaptist movement started in the 1520s in Switzerland and quickly diffused to the nearby region of South Germany and the Tyrol. The movement was not united, taking a number of directions with differing viewpoints and degrees of radicalism. The main feature of their religious doctrines, confessional adult baptism and free church organisation resulted in their being from the beginning hunted, executed and forced to leave their homelands. In Eastern-Central Europe the German-speaking Anabaptist communities settled down very early in Moravia, then in the historical territory of Hungary (present-day Slovakia and Hungary) and from 1622 in Transylvania. The first colonies were established in Moravia. In these colonies they began to live in communities of shared property according to the ideas of their leader Jacob Hutter (+1536).

The Hutterites (in Hungary locally called New Christians or latter Habans) excelled in the crafts, among them in pottery production. They started to produce faience alongside their traditional lead-glazed pottery ware in the late 16th century in Moravia (Horvath and Krisztinkovich, 2005; Katona, 1974, 1983, 2001; Kybalová and Novotná, 1982; Pajer, 2007, 2011; Ridovics, 2008). The faience products are mostly white-glazed vessels decorated with flowers and festoons in the late Renaissance style using a reduced, attractive colour palette (yellow, blue, green and purple-black). The Anabaptist ceramic art was formed from particular elements of form, decoration and style of various origins – primarily Italian and Northern Renaissance elements ornamented with Eastern, Persian-Turkish plant motives – reconceptualised in the unique order of Haban pottery. The inspiration of the contemporary Italian maiolica, the "bianchi" di Faenza, highly popular all over Europe, was fundamental (Horvath and Krisztinkovich, 2005; Katona, 1974; Kybalová and Novotná, 1982; Marsilli, 2010; Pajer, 2007, 2011; Ravanelli Guidotti, 1996; Ridovics, 2008; Wilson, 2007). Faience was a high-quality luxury ware produced for high noble families; during the 17th century, especially from the second part, the Anabaptist products slowly spread among wealthy town people, minor nobility and members of the guilds as well. At the end of the 17th century Hutterite colonies started to disintegrate, and by the middle of the 18th century people were either being forced to convert to Catholicism and assimilated into the local population or they emigrated. The art of Anabaptist ceramic production was preserved in folk pottery as well as in the artistic faience ware produced by manufactures.

It is not certain from where the know-how of tin glazed pottery, the inspiration for the application of the faience technique in the Anabaptist ceramic workshops, has originated. Some researchers suggest the possibility that Anabaptist faience has a direct relationship with Italian maiolica. The tin-glaze technique had been brought by refugees (emigrants) from North Italy (e.g. Faenza) who joined their co-religionists in Moravia (Kybalova, 1995; Kybalová and Novotná, 1982; Marsilli, 1985, 2010). Other scholars (e.g. Pajer, 2007, 2011) think it more likely that the Italian influence was mediated and indirect, the direct source of inspiration being from a geographically and culturally closer region, probably South Germany, where this technology already existed in the 16th century.

While the production technology and the materials used for the Italian Renaissance maiolica are fairly well known thanks to Cipriano Piccolpasso's treatise on the potter's art written circa 1557 (Lightbown and Caiger-Smith, 2007) and to extensive archaeometric research (see the recent comprehensive paper published by Tite, 2009), similar sources are not available for Hutterite faience. No contemporary written documents are known about the production technology. A potter's diary reporting recipes of some Haban white and coloured glazes is known (Wartha, 1892); however, recipes were recorded later, only at the beginning of the 19th century. Systematic archaeometric investigation on Hutterite faience using modern analytical techniques has not yet been performed either in Hungary or other countries. Only a very few tin-glazed, lead-glazed and unglazed Hutterite archaeological ceramic artefacts from Southern Moravia have been analysed to date (Gregerová et al., 2007; Kuljovská, 2007; Trojek et al., 2010).

Our archaometric research aims to identify the raw materials used for the body, the glaze and the decoration (colours) as well as the reconstruction of the production technology (i.e. the firing conditions, the preparation method of the glaze). Today numerous public and private collections hold Hutterite-Haban ceramic objects (from the period of appr. 1593 to 1750), several hundreds of items exist. But due to the good quality of preservation, sampling of these museum and collection objects is usually limited. We therefore mainly focus on archaeological artefacts, which have previously gained little attention in Hungarian research.

This study presents the result of the microanalytical investigations performed on Hutterite faience fragments excavated at Sárospatak (NE Hungary, Fig. 1). Six samples were analysed in the first step of the archaeometric research. They obviously do not give a comprehensive overview of the whole Anabaptist faience production existing over circa one-and-a-half centuries in several production centres of Eastern-Central Europe. However, even these six analysed samples provide an interesting idea about the technology, especially if we

compare the results with the previously published analytical data of the possible model, Italian maiolica.

2. Materials and methods

2.1 Samples

In 2006 the team of the Rákóczi Museum of the Hungarian National Museum started the excavation of the remnants of a gun-foundry in the outer castle of Sárospatak (NE Hungary, Fig. 1) (Ringer, 2011). According to written sources (Détshy, 1970) the gun-foundry functioned in the 17th century, between 1631 and 1648 and was most probably destroyed by a fire in 1672. Fragments of Anabaptist faience objects were found in the late 17th century infillings of the remnants, at several occurrences, mainly in the southern part of the gun-foundry.

In the frame of this study six samples from different faience objects were analysed (inventory numbers: sample 1: SRM 2010.07.15.1, sample 2: SRM 2010.07.15.2, sample 3: SRM 2010.06.25.1, sample 4: SRM 2010.06.22.1, sample 5: SRM 2010.06.24.2, sample 6: SRM 2010.06.23.1). The studied artefacts are mainly white-glazed ceramics: a fragment of a jug (Fig. 2a; sample 1) and fragments of several other objects, most probably bowls (Fig. 2b, c, d, e; samples 2, 3, 4, 5). Also found was a fragment of a tazza with opaque blue glaze on the stand and on the external side of the dish and white glaze on the internal side of the dish (Fig. 2f; sample 6). Several fragments of the objects, especially of the bowls, were found (Fig. 2b, c, d), and one fragment of each object was chosen for detailed study. Both sides of the objects are glazed and half of the analysed shards are non-decorated (samples 3, 4, and 5). On one side of the other artefacts there are blue, yellow, green and black decorations (samples 1, 2 and 6); they represent all the decoration colours used for Hutterite faience (Fig. 2). Decorative motives, e.g. the blue lace motif on sample 1 (Fig. 2a), black numbers on sample 2 (Fig. 2b) or the blue ornaments on sample 6 (Fig. 2d) are typical of Hutterite faience.

These artefacts were chosen for study due to their possible local provenance. Written sources documented that in 1645 Prince György I. Rákóczi invited Hutterites from Csejte (today Čachtice in Slovakia) to Sárospatak (Román, 1955, 1959). The Hutterite colony in Sárospatak existed until c. 1680 when due to conversion to Catholicism it was dissolved, the craftsmen emigrated or were assimilated into the local community. The colony had a ceramic workshop operated by one master and four assistants (Román, 1959). Figure 75 drawn on sample 2 (Fig. 2b) indicate most likely the date of production, i.e. 1675, which would fit in with the active period of the local Hutterite ceramic workshop. However, archaeological

excavation of the local Hutterite settlement with the ceramic workshop has only started recently (in 2010) and until now ceramic finds have not been analysed. Therefore the provenance of the studied faience fragments based on the comparison with the local Hutterite products cannot currently be determined.

2.2 Analytical methods

From the selected samples, after washing with water polished cross-sections were made from slices cut perpendicular to the glaze-ceramic body interface. After coating the cross-sections with carbon, the microstructure of the ceramic body, glaze and colours was examined using the backscattered electron (BSE) mode of a Zeiss EVO MA 15 scanning electron microscope (SEM) and a JEOL Superprobe-733 electron microprobe.

The 'bulk' chemical composition of the body, the glaze and the colours were determined using an Oxford Instruments Inca Energy 200 energy dispersive spectrometer (EDS) attached to the electron microprobe, run at 20 keV and 6 nA. During quantitative EDS analyses natural and artificial materials were used as standards. For the ceramic body, standards provided by the Taylor Co. (USA) were used: quartz for Si, corundum for Al, wollastonite for Ca, magnesium oxide for Mg, albite for Na, orthoclase for K, hematite for Fe and rutile for Ti. For the glaze and the colours well-known artificial glasses (NMNH 117218-4, -1, -2, -3, i.e. Corning archaeological reference glasses A, B, C and D, Vicenzi et al., 2002) were used as standards for the main elements, while $SnO_2$ for Sn, pure metals for Co and Ni, gallium arsenate for As, chalcopyrite for Cu and antimony telluride for Sb were applied. For all the 'bulk' measurements the count time was 100 seconds. PAP correction was automatically made by the Oxford Instruments software. The method is not able to distinguish between oxidation states of polyvalent elements; therefore all iron is expressed as FeO and all manganese as MnO. The detection limits of the spot (matrix) analyses is about 0.2 to 0.3 wt% for most elements, but not better than 0.4 wt% for CuO and $As_2O_3$, 0.5 wt% for $Sb_2O_3$ and 0.6 wt% for $SnO_2$. The limits of the areal analyses are lower by a factor of 0.63.

The area of 'bulk' EDS analyses for the ceramic body was $1000 \times 1000$ μm. On the other hand, the analysed areas of the glaze and the colours were set as large as possible depending on glaze/colour thickness and on the density of pores and cracks that have been eliminated as far as possible. The areas varied from $66 \times 66$ μm to $250 \times 250$ μm for the glaze and from $30 \times 30$ μm to $185 \times 185$ μm for the colours. Typical inclusions, such as quartz, feldspar, tin oxide and pigment particles, were included in the analysed area, but the body-glaze interface and the outermost part of the glaze were avoided. At least three area

measurements were performed on each body and glaze and the results were averaged. In addition, several spot analyses were performed for the determination of glassy matrix composition. During analysis the stability of beam/specimen current was repeatedly checked. The analytical totals of the body are between 67 and 78 wt%. There are several reasons for low totals of the quantitative analyses of ceramics (Ionescu et al., 2011); in this study the low totals are related to the high porosity of the body. The analytical totals of the glaze and the colours vary in the range of 88 and 100 wt% for various reasons, e.g. pores (and sometimes cracks), the possible presence of components that cannot be analysed and the analytical uncertainties. All analytical data were normalised to 100%. The glaze was analysed on both sides of the objects and no significant differences were detected, therefore we report here only the chemical compositions measured on the glaze under the decorations or on the thicker glaze. The chemical composition of the colour pigments was also measured using spot EDS analyses.

Phase composition of the ceramic body, the glaze and the yellow colour was determined on powdered samples (circa several hundred milligrams) by X-ray diffraction analysis (XRD) using a PHILIPS PW 1730 diffractometer in Bragg-Brentano geometry (instrumental and measuring parameters: CuKα radiation, 2-70° range of 2 theta scanning, 45kV acceleration voltage, 35 mA tube current, 1 sec/0.05° 2Θ data collection speed, graphite monochromator).

The colour pigments were identified by using Raman microspectroscopic analysis on the polished cross-sections using a HORIBA JobinYvon LabRAM HR800 dispersive, edge-filter based confocal Raman spectrometer (focal length: 800 mm) equipped with an Olympus BXFM microscope. The spectra were collected using the 632.8 nm emission of a He-Ne red laser, a 100× (N.A. 0.9) objective, a grating with 600 grooves/mm and a pinhole of 100 μm, which also acted as the entrance slit to the spectrometer. The Raman spectra of the inclusions were compared with the reference spectra of mineral phases of the RRUFF Project database (http://rruff.info).

## 3. Results

### 3.1 Ceramic body

The XRD analysis revealed that the ceramic body of the artefacts is generally composed of quartz, gehlenite, diopside, plagioclase, sometimes K-feldspar, hematite and traces of 10 Å phyllosilicate (illite) (Fig. 3a). Calcite was detected in only two samples (samples 1 and 6).

The BSE images indicate that the body has high porosity (Fig. 3b, c). Mainly quartz, K-feldspar, mica (biotite, muscovite), accessory minerals (e.g. apatite, zircon, Ti-oxide, monacite, ilmenite, garnet) and composite particles (e.g. quartz+K-feldspar, K-feldspar+biotite, quartz+mica) occur in the matrix, their sizes ranging from several up to 300 μm. Regarding the type, the quantity and the size of particles the samples show no noticeable difference. Only some tiny, discrete Pb±Sb-bearing particles occur in the body of sample 1; these were (most likely randomly) added to the clay before firing. Carbonate (calcite) particles of several tens of μm size rarely occur, but most frequently voids due to the dissociation of carbonate are present (Fig. 3b, c). Spot EDS analyses indicate the enrichment of calcium in the fine network of the matrix and around the particles. According to 'bulk' chemical analyses by EDS the ceramic body has 14.2 to 22.5 wt% CaO accompanied by 3.9 to 5.4 wt% FeO content (Table 1).

The glaze-ceramic body interface is usually sharp; no intermediate zone is visible. Only a small amount of newly-formed, acicular Ca-rich phases (wollastonite?) of 2-3 μm size were detected at and near the glaze-body boundary suggesting that the interaction between the body and the glaze was usually limited.

## 3.2 Tin glaze

The tin-opacified glaze covering the artefacts includes two types: the white one (all samples) and the blue one (sample 6 only).

The white glaze has a thickness of 170 to 430 μm on the front/decorated side in the studied cross-sections, except on sample 6, where the white glaze is 100 to 150 μm thick. The white glaze is thinner on the reverse/non-decorated side (140 to 250 μm). All of the white glazes contain high amounts of inclusions and rounded pores heterogeneously distributed in the vitreous matrix (Fig. 4a). The size of the pores usually ranges from several to 60 μm, sometimes up to 120 μm. The inclusions are mainly cassiterite particles and varying amounts of angular to rounded quartz and potassium feldspar grains up to 60 μm size. BSE images show two types of cassiterite in the white glaze (Fig. 4b): relatively large (up to 10 μm size) angular particles as well as small needles (up to 1-2 μm size) and aggregates of needles (up to 40 μm size) occur. In several cases the close intergrowth of the two types of cassiterite is clearly visible (Fig. 4b).

The 'bulk' compositions of the white glaze measured by EDS (Table 2) indicate that according to classification of Tite et al. (1998) it is a lead-alkali glaze with 22 to 28 wt% PbO content (except sample 4 with 18 wt% PbO content) and 5.8 to 7.4 wt% total alkali

(Na$_2$O+K$_2$O) content. The SnO$_2$ content ranging from 16.9 to 20.3 wt% confirms the high amount of cassiterite visible on the BSE images. Spot analyses of the glaze matrix show SnO$_2$ values of up to 6 wt%. The Na$_2$O content is greater than or equal with the K$_2$O content in the 'bulk' white glaze and the K$_2$O/Na$_2$O ratio is relatively low (0.5 to 1.0), except for sample 6, where the Na$_2$O content is lower than the K$_2$O content, and the K$_2$O/Na$_2$O ratio is 1.8. Chlorine has detectable amounts up to 1 wt% in the tin glaze.

The microstructure of the tin-opacified blue glaze is similar to the white glaze with fewer quartz and feldspar particles (Fig. 4c). The thickness of the blue tin glaze varies between 180 and ~300 μm and it is also of lead-alkali type with 28 wt% PbO, 8 wt% total alkali content and K$_2$O/Na$_2$O ratio of 1.6 (Table 2). Both types of cassiterite are present, but the SnO$_2$ content is lower (11 wt%, Table 2) than that of the white glaze on the same object (sample 6). The presence of significant CoO content (~0.7 wt%) associated with As$_2$O$_3$ (0.86 wt%) and some NiO (0.16 wt%) (Table 2), as well as the calcium-lead arsenate crystals preferentially deposited inside the pores (Fig. 4d) and also dispersed within the glassy matrix, indicate the use of cobalt colorant for the blue glaze.

3.3 Decorations

The yellow, blue, green and black ceramic colours were applied as paintings on the tin-opacified white glaze. The paintings can be as thick as the glaze (Fig. 5), their thickness sometimes exceeding 300 μm. The ceramic colours consist of coloured glass containing in 'bulk' more SiO$_2$ (38 to 56 wt%) than PbO (22 to 37 wt%) and the total alkali contents range from 6.5 to 9 wt% with K$_2$O/Na$_2$O ratio from 0.5 to 1.4 (Table 3). The SiO$_2$ and PbO contents as well as the alkali content of the vitreous matrix of the different colours vary considerably among the studied samples. Chlorine is present in the colours in concentrations of up to 1 wt%.

The yellow colour is opaque due to the presence of a high number of angular, few μm size, antimony-bearing pigment particles (Fig. 6a, b). The pigment is lead antimonate indicated by EDS spectra and confirmed by XRD. The Raman spectra of the lead antimonate particles (Fig. 7a) show an intensive band at about 510 cm$^{-1}$ along with peaks at 330-340 and 460 cm$^{-1}$ indicating that the original pyrochlore structure is distorted due to substitution of antimony by a larger cation like Zn, Sn or excess Pb (Rosi et al., 2009, 2011). However, in the studied yellow colour the structure of lead antimonate is probably modified by other cations: EDS spectra indicate iron, calcium and sodium as minor components in the lead antimonate pigment (e.g. in sample 1 up to 3.5 wt% FeO, 2.8 wt% CaO, 1.8 wt% Na$_2$O). The vitreous

matrix of the yellow colour has a small amount of antimony (especially in sample 1 with 1.2 wt% $Sb_2O_3$, Table 3). Slightly elevated iron content compared to that of the white glaze was also detected ($\geq 2$ wt% FeO, Table 3). The colour shows two different microstructures. In sample 1 pigment particles are distributed heterogeneously, frequently aggregating into clusters, with a few quartz and feldspars particles and relatively large pores occurring (Fig. 6a), while in sample 2 pigment particles are distributed homogeneously accompanied by higher quantities of quartz and feldspar particles and smaller pores (Fig 6b). Tin oxide may be present only in very small amounts in the yellow glaze of sample 2 (0.86 wt% $SnO_2$, Table 3).

Similarly to the tin-opacified blue glaze, the blue colour contains cobalt colorant (up to 1.4 wt% CoO) dissolved in the vitreous matrix accompanied with comparable concentrations of nickel and arsenic (up to 0.9 wt% NiO and 1.7 wt% $As_2O_3$, Table 3); discrete pigment particles were not identified. Slightly elevated iron content (1.1 to 1.4 wt% FeO) is characteristic compared to the white glaze. The blue colour may contain a small number of cassiterite particles if it is directly applied over the white glaze (Fig. 6c); also the underlying white glaze contains some cobalt and arsenic above detection limit (Table 2). Tiny arsenate crystals together with small-sized quartz particles and silica flakes (probably newly formed cristobalite) occur scattered in the vitreous matrix of the blue painting of sample 2 (Fig. 6d).

The green contains copper dissolved in the matrix as colorant (1 to 2 wt% CuO, Table 3). A few lead antimonate particles occur in the green colour of sample 1; however, its 'bulk' $Sb_2O_3$ content is very low (0.2 wt% $Sb_2O_3$). In both samples 1 and 6 the green colour is opaque due to the presence of abundant, homogeneously distributed cassiterite particles (Fig 8a). The $SnO_2$ content is 13.8 and 11 wt%, respectively (Table 3) which is lower than that of the white tin glaze applied on the same object, but in a range similar to that of the blue tin glaze applied on sample 6. In addition, the green colour of sample 6 contains some traces of quartz and feldspars. The white glaze under the green colour contains copper colorant (0.6 to 1.5 wt% CuO).

The black is usually applied as the last decoration, as e.g. contour lines (Fig. 2, 5). Black is associated with manganese, which is present in two forms: as an ionic colorant in the vitreous matrix (Table 3), and as discrete pigment particles. Rhombic manganese silicate crystals up to 5-6 μm size occur in the black colour of samples 1 and 6 (Fig. 8b, c). Raman microspectroscopic analysis shows the manganese silicate crystals to be braunite (Fig. 7b). Porous crystal aggregates up to 30 μm size occur in the black colour of sample 2 (Fig. 8d). Spot EDS analyses indicate that some aggregates are composed of manganese silicate, while others are made of manganese oxide. Raman microspectrometry revealed presences of

braunite and hausmannite (Fig. 7b). EDS spectra indicate iron, calcium and copper as minor components in the pigment particles (in sample 1: up to 5.7 wt% FeO, 1.1 wt% CaO, in sample 2: up to 5.7 wt% FeO in both types of particles, in sample 6: up to 7.5 wt% FeO, 1.8 wt% CaO, 2.6 wt% CuO). Elevated iron content compared to the white glaze is typical for the black colour (>0.7 wt%, Table 3). If applied directly over the green colour or the white glaze, the black contains abundant cassiterite particles (Fig 8a, b, Table 3). The white glaze below the black colour contains some manganese colorant (0.3 to 0.7 wt% MnO). If applied over the yellow colour, the black does not contain cassiterite, but a few lead antimonate inclusions (Fig. 8c). When applied over blue colour, the black contains some cobalt with nickel and arsenic (Table 3).

4. Discussion

4.1 Ceramic body

The chemical and phase analyses indicate that the buff-coloured body of the studied Anabaptist faience was produced using calcareous clay. The CaO content is in the same range for the faience bodies (14.2 to 22.5 wt%) as for most of the Italian maiolica bodies (14 to 25 wt% CaO, Tite, 2009). Calcareous ceramic body is typical for tin-glazed pottery due to its several advantages: e.g. calcareous clay fires to pale buff colour (due to the incorporation of iron into high-temperature calcium silicates and aluminosilicates developed during firing), has thermal coefficient matching more closely to those of lead-alkali glazes, and exhibits less shrinkage during firing compared to non-calcareous clay (Molera et al., 1998, Tite et al., 1998, Tite, 2009).

The presence of calcium silicate phases (gehlenite, diopside) formed during firing indicates that the firing temperature of the faience reached 800 °C (Cultrone et al., 2001); occasional presence of illite supports firing around 800 to 900 °C. Calcite detected by XRD and microstructure analyses in two faience samples is a primary phase and was not completely dissociated during firing due to its grain size (i.e. large calcite particles might have survived firing), therefore somewhat lower firing temperature, 750 to 800 °C can be estimated for these samples.

The absence of any significant reaction zone at the body-glaze interface suggests that the body was fired to biscuit before the glaze slurry was applied (Tite et al., 1998). Biscuit firing is also supported by the semi-finished products (fired, but non-glazed faience artefacts) found in archaeological excavations of Hutterite ceramic workshops in Southern Moravia (e.g. in Tavíkovice and Vacenovice, Pajer, 2007).

4.2 Tin glaze

The microchemical analyses revealed that the tin-opacified white and blue glazes covering the studied Hutterite faience artefacts are of lead-alkali type. Production of such a glaze involves preparation of slurry containing lead compound, alkali and silica with the addition of tin oxide (Tite et al., 1998). There are several ways to prepare the glaze suspension; however, the first step is the melting of lead and tin metals together to produce a mixture of lead and tin oxides (lead-tin calx or calcine) as mentioned in Piccolpasso's treatise (Lightbown and Caiger-Smith, 2007) and in Abu'l-Qasim's treatise on Persian pottery manufacture written in 1301 (Allan, 1973). Alkali can be added to the glaze suspension in the form of wine lees, tartar, common salt or soda. Due to its solubility in water, alkali is usually pre-fritted with silica (the latter is mainly in the form of sand) before making the glaze suspension. The vitreous frit made from alkali and silica is then mixed with the lead-tin calx and this mixture can be

(i) fritted as described in Abu'l-Qasim's treatise (Allan, 1973) or

(ii) not fritted, although sometimes further sand is added as in the case of the Italian maiolica (Tite et al., 2008, Tite, 2009).

The other preparation method involves mixing the lead-tin calx directly with sand as well as alkaline and other fluxes, and melting them together to vitreous frit as in the case of the 18th and 19th century French faience (Maggetti, 2012). After preparation employing one of the methods, the frit or the mixture is then ground to obtain a powdered raw glaze and diluted in water to prepare the suspension, to which sometimes clay or other compounds are also added.

The angular to rounded morphology of the quartz and feldspar grains observed in the tin glaze of the Hutterite faience indicates that these particles were only partially dissolved during glaze firing and can be interpreted as relics of the sand added to the glaze mixture. Two generations of cassiterite crystals with different morphology and size were detected in the tin glaze which can be related to the well-known phenomenon of dissolution and recrystallization of the tin oxide opacifier during firing (and subsequent cooling) (Molera et al., 1999; Tite et al., 2008). Angular tin oxide particles are remnants of the raw material, while fine needles are *in situ* newly-formed tin oxide crystallites. Heterogeneous distribution of the tin oxide particles and the partially resorbed sand grains in the Hutterite tin glaze indicate that the glaze mixture (lead-tin calx + frit + sand) was not fritted when the slurry was prepared before application. Therefore Hutterite potters applied similar production technique for preparation of the glaze as for the tin glaze of the Italian maiolica. Mason and Tite (1997) and Molera et al. (2001) supposed that the sand added to the glaze mixture, as well as the rounded

pores after bubbles in the glaze, contribute to the opacity of the glaze and less tin oxide is needed. However, recently Tite (2009) suggested that when sand is introduced in the glaze mixture the unfired, opaque glaze is more robust and less powdery and its surface is better suited to taking the painted decorations. Our faience samples having a glaze with relatively high tin oxide content and varying amounts of sand particles support the latter explanation.

The $K_2O/Na_2O$ ratio for the Hutterite tin glaze is generally lower (0.5 to 1.0) than for the maiolica glaze (1.1 to 6, Amato et al., 2010; Tite, 2009). The low ratio together with the detectable chlorine (~1 wt%) indicates that a significant part of the alkali was obtained from the common salt added to the frit. The tin glaze with more $K_2O$ than $Na_2O$ (with a ratio of 1.8) covers only sample 6, indicating the dominant use of K-bearing flux (wine lees, tartar).

The quality of faience, among other factors, depends on the quality of the tin glaze, i.e. its whiteness and opacity (Vendrell et al., 2000). The whiteness of the glaze can be achieved by (i) increasing its $SnO_2$ content, (ii) increasing its thickness and (iii) reducing the reddish hue of the ceramic paste; the latter can be enhanced by using calcareous (Ca-rich) ceramic pastes. Analyses of the Islamic and hispano-moresque (*múdejar*) tin-glazed pottery from Spain and Italian Renaissance maiolica indicate that for production of an opaque white glaze which can adequately conceal the ceramic body, the tin oxide content should be typically in the range of 4-5 to 9-10 wt% with glaze thicknesses ranging from <100 μm to 600 μm (Fig. 9, Molera et al., 2001; Vendrell-Saz et al., 2006; Tite, 2009). One example of the application of thick tin glaze on ceramics is the Late Renaissance "bianchi" di Faenza, on which an intense white glaze was produced by combining the usual tin oxide content (5.5 to 10.4 wt% $SnO_2$) with considerable thickness (500 to 980 μm, sometimes up to 1250 μm on the front/outer side of the ceramics, Tite, 2009, Amato et al., 2010). Our data indicate that the analysed Anabaptist faience artefacts with buff-coloured calcareous ceramic body are covered by an opaque white glaze with usual thickness, but with a significant amount of tin oxide inclusions. Elevated $SnO_2$ content (16.9 to 20.3 wt% $SnO_2$) was detected compared with the Renaissance maiolica: the $SnO_2/PbO$ ratio is 0.6 to 1.8 for the Hutterite white tin glaze (Table 2), while this ratio is lower (0.2 to 0.6) for most maiolica glazes (Tite, 2009). In contrast to the white glaze, the Hutterite blue tin glaze contains a smaller amount of tin oxide (11 wt%) for opacification, more probably due to its coloured character.

Very high tin oxide content (13 to 28 wt% $SnO_2$) with usual high lead oxide content (21 to 48 wt% PbO) in glazes with 30 to 550 μm thickness was found in some of Italian Archaic maiolica from the 13th and 14th centuries by Tite (2009) (Fig. 9). He explains that the use of very high tin oxide content in the early period of Italian maiolica production

reflects a lack of understanding of the amount of tin oxide necessary to achieve adequate opacity and whiteness. High tin oxide content, 14 to 20 wt% $SnO_2$ extending up to 24 wt%, higher than the tin oxide content of Renaissance maiolica glazes, is also characteristic for the white glaze of della Robbia terracotta sculptures and panels produced in the 15th and 16th centuries (Fig. 9, Barbour and Olson, 2011; Gianoncelli et al., 2008; Kingery and Aronson, 1990; Tite, 2009; Zucchiatti et al., 2003, Zucchiatti and Bouquillon, 2011). The glaze composition was deliberately modified by the della Robbia workshop to produce sculptural ceramics of high artistic quality. The high presence of tin oxide in the della Robbia glazes was applied in order to increase their whiteness and opacity as well as to increase their viscosity which can help to compensate the decrease in viscosity due to the higher lead oxide content of the glaze (up to 40 wt% PbO, Tite, 2009). It is obvious that the Hutterite potters also deliberately increased the tin oxide content of the glaze and that the white glaze of faience with its high tin oxide content and relatively low $K_2O/Na_2O$ ratio resembles the della Robbia glaze, the latter having a $K_2O/Na_2O$ ratio of 0.6 to 2.5 (Tite, 2009). However, it seems that the Hutterite potters did not increase the lead oxide content of the glaze, and so its moderate PbO content (18 to 28 wt%) resembles that of the (Late) Renaissance maiolica glaze (Fig. 9).

4.3 Ceramic colours

The decorations covering the surface of the white glaze on the Anabaptist faience are individual coloured glass layers. A transparent lead glaze, called *coperta*, typically covering the tin glaze of many maiolica objects from the 15th century (Lightbown and Caiger-Smith, 2007, Tite, 2009), does not appear on the studied faience samples. The ceramic colours are usually thicker, reaching several tens of μms, than the decoration layer of the *coperta*-free maiolica, which is up to about 50 μm thick (Tite, 2009).

Ceramic colours are chemically slightly different from the white glaze. The blue, green and black colours of each decorated sample have a higher total alkali content than the white glaze most probably indicating the use of a different frit (glass) for these colours (e.g. in sample 1 mostly 8 to 9 wt% $K_2O+Na_2O$ in the colours vs. 6.7 wt% $K_2O+Na_2O$ in the glaze, Tables 2 and 3). However, the yellow colour has a total alkali content similar to that of the white glaze on the same ceramic, indicating that a different (colourless) frit was used for the yellow than for the other colours. The less than 1 $K_2O/Na_2O$ ratio and the presence of chlorine are evidences of the use of common salt in the preparation of the ceramic colours of samples 1 and 2, while the more than 1 $K_2O/Na_2O$ ratio indicates the use of a higher amount of K-bearing flux for the colours of sample 6.

Two of the ceramic colours, yellow and green, are intentionally opacified, while the blue and the black are originally transparent colours. However, the latter is in several cases opaque due to the fact that among the ceramic colours the black especially is greatly incorporated into the underlying decorations or the white glaze during firing gaining tin oxide particles as well as other colorants. In addition, the presence of a small amount of copper, manganese or cobalt colorant in the white glaze under the colours suggests that diffusion processes occurred between the colours and glaze during firing. These phenomena indicate that the ceramic colours were applied on the surface of the unfired, powdery glaze, and then the opaque glaze and colours were matured simultaneously in a single step, during the second high-temperature firing, similarly to the production of maiolica. The reduced colour palette (yellow, blue, green and black) of the studied Hutterite faience also supports the theory that high-temperature, so-called in-glaze decorations were used.

The colouring and opacifying pigment for the yellow colour of the Hutterite faience under study is the artificial lead antimonate. This compound is analogous with the natural mineral bindheimite ($Pb_2Sb_2O_6(O,OH)$) and stable up to 1100°C (Dik et al., 2005) surviving the second high temperature firing. Similar pigment was used for the yellow and orange decorations of maiolica (Bultrini et al., 2006; Tite, 2009); however, lead-tin antimonate and lead-zinc antimonate were also identified in some 16th century maiolica glazes by Sandalinas et al. (2006) and Rosi et al. (2011). Lead antimonate was most probably produced by calcinating lead oxide and antimony oxide at temperatures starting from 750°C, since instead of sulphides or metals the mixture of oxides is necessary to produce lead antimonate in high concentration and as purely as possible (Dik et al., 2005). The detectable Na content of the pigment indicates the addition of a Na-bearing flux, i.e. NaCl, to the mixture (Dik et al., 2005). Iron incorporated into the lead antimonate pigment indicates the deliberate addition of iron as in the case of maiolica (Bultrini et al., 2006, Tite, 2009). Iron added to the mixture of lead and antimony in the form of iron scale (rust) was also mentioned in Piccolpasso's treatise (Lightbown and Caiger-Smith, 2007). Opaque colours can be produced in two ways (Maggetti et al., 2009): the pigment is mixed (i) with the raw materials of the glass, then fired, and after cooling the opaque glass is powdered, or (ii) with the already prepared, powdered, transparent (or coloured) glass. The use of the later preparation method is indicated by the presence of the angular and sometimes clustered lead antimonate particles as well as the quartz and feldspar particles, the latter being relicts of the additional sand added to the glaze suspension. The low antimony, but higher iron content of the vitreous matrix of the yellow colour probably indicates that the reaction of lead antimonate particles with the glass was limited.

The green decoration of the faience is opaque due to the addition of tin oxide to the glass; however, smaller amounts of tin oxide were used for opacification than for the white glaze. The green glassy decoration was coloured with copper colorant. Piccolpasso described in his treatise two types of green pigment: (i) "burnt copper" (*ramina*), which is copper oxide prepared by burning (oxidising) copper metal and its colour in lead-alkali glazes is green with bluish tint, and (ii) "mixed green", which is a prefired mixture of copper oxide, lead oxide and antimony oxide and its colour is green without any bluish tint (Lightbown and Caiger-Smith, 2007, Tite, 2009). Copper dissolved in the glassy matrix in combination of abundant lead antimonate particles was observed for della Robbia green glaze (Tite, 2009). Lead antimonate particles only very sporadically occur in the green glaze of the faience under study, therefore "burnt copper" was used for colouring, similarly to the Archaic and medieval green maiolica glazes (e.g. Ricci et al., 2005).

The cobalt colorant associated with nickel, arsenic and small amounts of iron in the blue colour as well as in the blue tin glaze of the Anabaptist faience indicates the use of a pigment made of impure cobalt oxide prepared by roasting arsenic-bearing cobalt-nickel ore minerals like arsenides, arsenosulphides or arsenates. In the blue glaze of terracotta sculptures arsenic appears around 1520, whereas arsenic is absent (i.e. below detection limit, <0.1 wt% $As_2O_3$ for PIXE) in blue glaze produced before 1520 (Padeletti et al., 2006; Pappalardo et al., 2004; Zucchiatti et al., 2006). The arsenic content of the pigment is separated from the cobalt and typically present in the form of newly-formed calcium-lead arsenate crystals in the vitreous matrix (e.g. Viti et al., 2003; Zucchiatti et al., 2006) as in the blue decorations of the 16th century *berettino* ceramics from Faenza (Tite, 2009). The same arsenate particles were also detected in the blue colour and the blue tin glaze of the studied faience artefacts. Based on the analysis of blue glasses and ceramic glazes Gratuze et al. (1996) suggested that the most probable source of cobalt pigment used by glassmakers and potters from the 13th to the 18th century is the Erzgebirge region of Saxony and Bohemia. In the Erzgebirge region the 'five-element' (Ni-Co-As-Ag-Bi(-U)) veins were exploited (Kissin, 1992). Two cobalt pigments were produced in this region: (i) *zaffre (safre, zaffer, zaffera),* invented around 1520, which is a roasted Co-Ni-Fe-As ore, that is, an impure cobalt oxide with a presence of arsenic due to incomplete roasting (Padeletti et al., 2004, Barilaro et al., 2008) and/or partial recuperation during processing (Zucchiatti et al., 2006) and (ii) *smalt (smalte),* invented around 1540-60, which is a potassium glass obtained by melting the roasted cobalt ore together with quartz (sand) and potash or added to molten glass (Mühlethaler and Thissen, 1969). Pigments characterised by Co-As-Ni-Bi(-Fe) element association from the Erzgebirge

region were used from the 15th to the 18th century (Gratuze et al., 1996). We suppose that Anabaptists might also have imported cobalt pigment from this region. The absence of discrete cobalt pigment particles in the blue colour of the studied faience artefacts indicates the use of smalt rather than zaffre.

In the black decoration of the Hutterite faience we detected manganese accompanied by minor iron. Manganese was used for colouring purple and brown decorations of maiolica (e.g. for Archaic maiolica, Alaimo et al., 2004; Ricci et al., 2005); however, in addition to manganese and iron, the presence of cobalt, nickel, copper and antimony indicating complex mixing of colours to produce black was detected in some della Robbia and maiolica glazes as well (Padelletti et al., 2006; Zucchiatti and Bouquillon, 2011). Manganese oxides, mostly pyrolusite ($Mn^{4+}O_2$) as well as manganese-iron nodules and concretions composed of several oxides and oxihydroxides of manganese and iron might have been used as pigments (Alaimo et al., 2004).

In the black colour discrete manganese-bearing particles occur: braunite (manganese oxysilicate, $Mn^{2+}Mn^{3+}_6SiO_{12}$) and hausmannite (manganese oxide, $Mn^{2+}Mn^{3+}_2O_4$). Similar compounds were also detected in the purple-brown-black decorations of Spanish tin-glazed ceramics, Italian maiolica (Molera et al., 2013; Pradell et al., 2013,), and Portuguese tiles (Coentro et al., 2012), and interpreted as newly-formed crystals or pigment remnants. The idiomorphic morphology of crystals in the black colour of two Anabaptist faience artefacts (samples 1 and 6) clearly indicate that the braunite was crystallized *in situ* during firing (and subsequent cooling). In one of the studied faience artefacts (sample 2) the pigment particles preserved the original morphology of the manganese pigment, but after firing their mineralogical composition became that of braunite and hausmannite. In the black ceramic colour, as temperature increased the $Mn^{4+}O_2$ (pyrolusite) pigment started to decompose (deoxidise) in air at about 550-600 °C to $(Mn^{3+},Fe^{3+})_2O_3$ (bixbyite), and at about 870-900 °C, or a higher temperature depending also on the iron oxide content, to $Mn^{2+}Mn^{3+}_2O_4$ (hausmannite) (Dent Glasser and Smith, 1968; Muan, 1959; Muan and Somiya, 1962; Roy, 1968). In tis case a reaction with the silica-rich molten glaze is responsible for the formation of braunite as suggested by Molera et al. (2013) and Pradell et al. (2013). Considering the phase equilibria in the system manganese oxide-$SiO_2$ in air, braunite can be stable at temperatures up to 1168 °C depending on the silica content of the system (Muan, 1959).

5. Conclusions

In comparing the 17th century Anabaptist (Hutterite) faience artefacts from NE Hungary under study with their direct or indirect precursor, Italian Renaissance maiolica, similarities as well as differences are observed between the production technologies of the two tin-glazed ceramics.

Similarities:

(i) use of calcareous clay for the ceramic body, which was biscuit-fired,

(ii) use of tin-opacified lead-alkali glaze, where the glaze suspension contained an admixture of sand and significant amount of common salt, and was not fritted before application,

(iii) use of similar colorants for ceramic colours: lead antimonate for yellow, cobalt with arsenic, nickel and iron for blue, copper for green, manganese with iron for black; decorations were applied on unfired opaque glaze and matured during the second firing.

Differences:

(i) higher amount of tin oxide added to the white glaze,

(ii) no application of outer transparent glaze (*coperta*), use of ceramic colours comparable in thickness with the opaque glaze.

The most important difference is the tin oxide content, which is definitely higher (17 to 20 wt% $SnO_2$) in the white glaze of the studied Hutterite faience artefacts compared to that of the white glaze of the Renaissance maiolica, and reaches the elevated tin oxide content typical for the white glaze of della Robbia terracotta. A high amount of tin oxide was deliberately used by the Hutterite potters to produce high-quality white glaze instead of increasing its thickness.

References

1   Alaimo, R., Bultrini, G. Fragalà, I., Giarrusso, R., Montana, G., 2004. Microchemical and
2       microstructural characterisation of medieval and post-medieval ceramic glaze
3       coatings. Applied Physics A79, 263-272.

4   Allan, J. W., 1973. Abu'l-Qasim's treatise on ceramics. Iran 11, 111-120.

5   Amato, F., Gualtieri, S., Fabbri, B., 2010. La rivoluzione tecnica dei "bianchi" di Faenza, in:
6       De Pompeis, V. (Ed.), La maiolica italiana di stile compendiario. I bianchi. Vol. 1.,
7       Umberto Allemandi & C., Torino, 33-38.

8   Barbour, D., Olson, R. J. M., 2011. New methods for studying serialization on the workshop
9       of Andrea della Robbia: technical study and analysis, in: Bouquillon, A., Bormand,
10      M., Zucchiatti, A. (Eds.), Della Robbia: dieci anni di studi – dix ans d'études. Sagep
11      Editori, 56-61.

12  Barilaro, D., Crupi, V., Interdonato, S., Majolino, D., Venuti, V., Barone, G., La Russa, M. F.,
13      Bardelli, F., 2008. Characterization of blue decorated Renaissance pottery fragments
14      from Caltagirone (Sicily, Italy). Applied Physics A92, 91-96.

15  Bultrini, G., Fragalà, I., Ingo, G. M., Lanza, G., 2006. Characterisation and reproduction of
16      yellow pigments used in central Italy for decorating ceramics during the Renaissance.
17      Applied Physics A83, 557-565.

18  Coentro, S., Mimoso, J. O., Lima, A. M., Silva, A. S., Pais, A. N., Muralha, V. S. F., 2012.
19      Multi-analytical identification of pigments and pigment mixtures used in 17th century
20      Portuguese azulejos. Journal of the European Ceramic Society 32, 37-48.

21  Cultrone, G., Rodriguez-Navarro, C., Sebastian, E., Cazalla, O., De La Torre, M. J., 2001.
22      Carbonate and silicate phase reactions during ceramic firing. European Journal of
23      Mineralogy 13, 621-634.

24  Dent Glasser, L. S., Smith, I. B., 1968. Oriented transformations in the system $MnO-O-H_2O$.
25      Mineralogical Magazine 36, 976-987.

26  Détshy, M., 1970. A sárospataki ágyúöntőház története (History of the gun-foundry in
27      Sárospatak). Technikatörténeti Szemle 5, 69-116.

28  Dik, J., Hermens, E., Peschar, R., Schenk, H., 2005. Early production recipes for lead
29      antimonate yellow in Italian art. Archaeometry 47, 593-607.

30  Gianoncelli, A., Castaing, J., Bouquillon, A., Polvorinos, A., Walter, A., 2008. Análisis
31      cuantitativo de la composición de los vidriados de della Robbia de Sevilla con un
32      espectrómetro portátil de fluorescencía de rayos X. in: Llorens, S. R., García-Heras,
33      M., Gener Moret, M., Montero Ruiz, I. (Eds.), Actas del VII congreso ibérico de
34      arqueometría. Madrid, 8-10 de octubre 2007, 309-318.

Gratuze, B., Soulier, I., Blet, M., Vallauri, L., 1996. De l'origine du cobalt: du verre à la céramique. Revue d'Archéométrie 20, 77-94.

Gregerová, M., Hložek, M., Kuljovská, Z., 2007. Micropetrografické a petrochemicé rozbory novověké glazované keramiky z locality Srachotín (Micropetrographic and petrochemical analyses of postmedieval pottery from Strachotín). Geol. výzk. Mor. Slez. v r. 2006, 95-100.

Horvath, J. E., Krisztinkovich, H. M., 2005. A history of Haban ceramics. A private view. A Canadian Collection of Hungarica, Volume IV, Vancouver, 398 p.

Ionescu, C., Hoeck, V., Ghergari, L., 2011. Electron microprobe analysis of ancient ceramics: A case study from Romania. Applied Clay Science 53, 466-475.

Katona, I., 1974. A habán kerámia Magyarországon (Haban ceramics in Hungary), Képzőművészeti Alap Kiadóvállalata, Budapest, 223 p.

Katona, I., 1983. Habán művészeti emlékek Magyarországon (Haban artistic records in Hungary), Múzsák Művelődési Kiadó, Budapest, 240 p.

Katona, I., 2001. Habánok Magyarországon (Habans in Hungary), Gesta Könyvkiadó, Budapest, 198 p.

Kingery, W. D., Aronson, M., 1990. The glazes of Luca della Robbia. Faenza 76, 221-225.

Kissin, S. A., 1992. Five-element (Ni-Co-As-Ag-Bi) veins. Geoscience Canada 19, 113-124.

Kuljovská, Z., 2007. Studium glazovaných artefaktů habánské fajáns (The study of the Habanien faience glazed artefacts), Diploma thesis, Masaryk University, Brno, 57 p.

Kybalova, J., 1995. Keramická sbírka Hugo Vavrečky: vystava fajánsí a porcelánu 17.-19. století (The ceramics collection of Hugo Vavrečka: exposition of faience and porcelain from 17th to 19th century). Umeleckoprumyslove muzeum, Prague, 22 p.

Kybalová, J., Novotná, J., 1982. Habánská fajáns 1590-1730, katalog vystavy (Haban faience, exhibition catalogue), Praha-Brno, 253 p.

Lightbown, R., Caiger-Smith, A., 2007. Cipriano Piccolpasso's The Three Books of the Potter's Art (I tre libri dell'arte del vasaio): A facsimile of the manuscript in the Victoria and Albert Museum, London, 2nd edition, Editions La Revue de la céramique et du verre, Vendil-le-Viel, France.

Maggetti, M., 2012. Technology and provenancing of French faience, in: Herrero, J. M., Vendrell, M. (eds.), International Seminar on Archaeometry and cultural heritage: the contribution of mineralogy, Bilbao, 27 de Junio 2012. Seminarios del la Sociedad Española de Mineralogía, Volumen 09, 41-64.

Maggetti, M., Neururer, Ch., Rosen, J., 2009. Antimonate opaque colours from the faience manufacture of Le Bois d'Épense (19th century, northeastern France). Archaeometry 51, 791-807.

Marsilli, P., 1985. Da Faenza in Moravia: ceramiche e ceramisti fra storia dell'arte e storia della riforma popolare. Atti del XVIII Convegno Internazionale della Ceramica „Influenze e rapporti della ceramica Italiana con i Paesi dell'Europa Centrale", Albisola, 7-26.

Marsilli, P., 2010. I „bianchi" in Germania e in Mitteleuropa, in: De Pompeis, V. (Ed.), La maiolica italiana di stile compendiario. I bianchi. Vol. 1., Umberto Allemandi & C., Torino, 23-28.

Mason, R. B., Tite, M. S., 1997. The beginnings of tin-opacification of pottery glazes. Archaeometry 39, 41-58.

Molera, J., Pradell, T., Vendrell-Saz, M., 1998. The colours of Ca-rich ceramic pastes: origin and characterization. Applied Clay Science 13, 187-202.

Molera, J., Pradell, T., Salvadó, N., Vendrell-Saz, M., 1999. Evidence of tin oxide recrystallization in opacified lead glazes. Journal of the American Ceramic Society 82, 2871-2875.

Molera, J., Vendrell-Saz., Pérez-Arantegui, J., 2001. Chemical and textural characterization of tin glazes in Islamic ceramics from Eastern Spain. Journal of Archaeological Science 28, 331-340.

Molera, J., Coll, J., Labrador, A., Pradell, T., 2013. Manganese brown decorations in 10th to 18th century Spanish tin glazed ceramics. Applied Clay Science 82, 86-90.

Muan, A., 1959. Phase equilibria in the system manganese oxide-$SiO_2$ in air. American Journal of Science 257, 297-315.

Muan, A., Somiya, S., 1962. The system iron oxide-manganese oxide in air. American Journal of Science 260, 230-240.

Mühlethaler, B., Thissen, J., 1969. Smalt. Studies in Conservation 14, 47-61.

Padeletti, G., Fermo, P., Gilardoni, S., Galli, A., 2004. Technological study of ancient ceramics produced in Casteldurante (central Italy) during the Renaissance. Applied Physics A79, 335-339.

Padeletti, G., Ingo, G. M., Bouquillon, A., Pages-Camagna, S., Aucouturier, M., Roehrs, S., Fermo, P., 2006. First-time observation of Mastro Giorgio masterpieces by means of non-destructive techniques. Applied Physics A83, 475-483.

Pajer, J., 2007. Archaeological excavations of Anabaptist ceramics in Moravia, in: Žegklitz, J. (ed.), Studies in post-medieval archaeology 2 - Material Culture from the end of the 15th century and its reflection in archaeological, written and iconographic sources. Prague, Archaia Praha o.p.s., 227-250.

Pajer, J., 2011. Anabaptist faience from Moravia 1593-1620. Catalogue of documents from institutional and private collections, Etnos Publishing, Strážnice, 86 p.

Pappalardo, G., Costa, E., Marchetta C., Pappalardo, L., Romano, F. P., Zucchiatti, A., Prati, P., Mandò, P. A., Migliori, A., Palombo, L., Vaccari, M. G., 2004. Non-destructive characterization of Della Robbia sculptures at the Bargello Museum in Florence by the combined use of PIXE and XRF portable systems. Journal of Cultural Heritage 5, 183-188.

Pradell, T., Molina, G., Molera, J., Pla, J., Labrador, A. (2013): The use of micro-XRD for the study of glaze color decorations. Applied physics A 111, 121-127.

Ravanelli Guidotti, C., 1996. Faenza-faïence "Bianchi" di Faenza. Catalogo della mostra (dal 27 settembre al 6 ottobre 1996), Museo Internazionale delle Ceramiche, Faenza. Belriguardo, Ferrara, 589 p.

Ricci, C., Borgia, I., Brunetti, B. G., Sgamellotti, A., Fabbri, B., Burla, M. C., Polidori, G., 2005. A study of Late Medieval transparent-glazed pottery and archaic maiolica from Orvieto (Central Italy). Archaeometry 47, 557-570.

Ridovics, A., 2008. A habán kerámia a 17. században (Haban ceramics in the 17th century), in: Mikó, Á. (Ed.), Mátyás király öröksége. Késő reneszánsz művészet Magyarországon (16-17. század), Publication of the Hungarian National Gallery, vol. II, Budapest, 86-97.

Ringer, I., 2011. I. Rákóczi György ágyúöntő műhelye: a kora újkori ágyúöntés technológiája (The gun-foundry of György Rákóczi I.: the technology of cannon casting in the Early Modern Age). A Sárospataki Rákóczi Múzeum füzetei 58, 35 p.

Román, J., 1955. Sárospataki kerámia (Pottery of Sárospatak), Magyar Népművészet, A Képzőművészeti Alap Kiadóvállalata, Budapest.

Román, J., 1959. A habánok Sárospatakon (Habans in Sárospatak). A Sárospataki Rákóczi Múzeum füzetei, 17, 40 p.

Rosi, F., Manuali, V., Miliani, C., Brunetti, B. G., Sgamellotti, A., Grygar, T., Hradil, D., 2009. Raman scattering features of lead pyroantimonate compounds. Part I: XRD and Raman characterization of $Pb_2Sb_2O_7$ doped with tin and zinc. Journal of Raman Spectroscopy 40, 107-111.

Rosi, F., Manuali, V., Grygar, T., Bezdicka, P., Brunetti, B. G., Sgamellotti, A., Burgio, L., Seccaroni, C., Miliani, C., 2011. Raman scattering features of lead pyroantimonate compounds: implications for the non-invasive identification of yellow pigments on ancient ceramics. Part II. *In situ* characterisation of Renaissance plates by portable micro-Raman and XRF studies. Journal of Raman Spectroscopy 42, 407-414.

Roy, S., 1968. Mineralogy of the different genetic types of manganese deposits. Economic Geology 63, 760-786.

Sandalinas, C., Ruiz-Moreno, S., López-Gil, A., Miralles, J., 2006. Experimental confirmation by Raman spectroscopy of a Pb-Sn-Sb triple oxide yellow pigment in sixteenth-century Italian pottery. Journal of Raman Spectroscopy 37, 1146-1153.

Szebeni, O., 1998. Anabaptisták. A reformáció harmadik ága (Anabaptists. The third branch of Reformation). Magyar Baptista Egyház, Budapest.

Tite, M. S., 2009. The production technology of Italian maiolica: a reassessment. Journal of Archaeological Science 36, 2065-2080.

Tite, M. S., Freestone, I., Mason, R., Molera, J., Vendrell-Saz, M., Wood, N., 1998. Lead glazes in antiquity – methods of production and reasons for use. Archaeometry 40, 241-260.

Tite, M., Pradell, T., Shortland, A., 2008. Discovery, production and use of tin-based opacifiers in glasses, enamels and glazes from the Late Iron Age onwards: a reassessment. Archaeometry 50, 67-84.

Trojek, T., Hložek, M., Čechák, T., Musílek, L., 2010. X-ray fluorescence analyzers for investigating postmediaeval pottery from Southern Moravia. Applied Radiation and Isotopes 68, 879-883.

Vendrell, M., Molera, J., Tite, M. S., 2000. Optical properties of tin-opacified glazes. Archaeometry 42, 325-340.

Vendrell-Saz, M., Molera, J., Roqué, J., Pérez-Arantegui, J., 2006. Islamic and Hispano-Moresque (múdejar) lead glazes in Spain: a technical approach, in: Maggetti, M., Messiga, B. (Eds.), Geomaterials in cultural heritage. Geological Society of London Special Publications 257, 163-173.

Vicenzi, E. P., Eggins, S., Logan, A., Wysoczanski, R., 2002. Microbeam characterization of Corning archeological reference glasses: new additions to the Smithsonian Microbeam Standard Collection. Journal of Research of the National Institute of Standards and Technology 107, 719-727.

Viti, C., Borgia, C., Brunetti, B., Sgamellotti, A., Mellini, M., 2003. Microtexture and microchemistry of glaze and pigments in Italian Reneaissance pottery from Gubbio and Deruta. Journal of Cultural Heritage 4, 199-210.

Wartha, V., 1892. Az agyagipar technológiája (Technology of clay industry), Természettudományi Könyvkiadó-vállalat, Budapest, 240 p.

Wilson, T., 2007. Le maioliche, in: Franceschi, F., Goldthwaite, R., Mueller, R. (Eds), Il Rinascimento italiano e l'Europa, IV, Commercio e cultura mercantile. Fondazione Cassamarca - Angelo Cola Editore, Treviso - Costabissara, 217-245.

Zucchiatti, A., Bouquillon, A., Castaing, J., Gaborit, J. R., 2003. Elemental analyses of a group of glazed terracotta angels from the Italian Renaissance, as a tool for the reconstruction of a complex conservation history. Archaeometry 45, 391-404.

Zucchiatti, A., Bouquillon, A., Katona, I., D'Alessandro, A., 2006. The Della Robbia blue: a case study for the use of cobalt pigments in ceramics during the Italian Renaissance. Archaeometry 48, 131-152.

Zucchiatti, A., Bouquillon, A., 2011. Les glaçures: atout maître des Della Robbia, in: Bouquillon, A., Bormand, M., Zucchiatti, A. (Eds.), Della Robbia: dieci anni di studi – dix ans d'études. Sagep Editori, 32-43.


Web reference

RRUFF Project database: http://rruff.info

Table and figure captions


Table 1. Chemical composition (in wt%) of the ceramic body of the studied Hutterite faience artefacts (average of area measurements for 'bulk' composition by EDS, standard deviation in parenthesis, n: number of analyses, results are normalised to 100%, original analytical totals are also indicated).


Table 2. Chemical composition (in wt%) of the white and blue tin glaze of the studied Hutterite faience artefacts (average of area measurements for 'bulk' composition and spot measurements for matrix composition by EDS, standard deviation in parenthesis, n: number of analyses, results are normalised to 100%, original totals are also indicated, na: not analysed).

Table 3. Chemical composition (in wt%) of the ceramic colours of the studied Hutterite faience artefacts (average of area measurements for 'bulk' composition and spot measurements for matrix composition by EDS, standard deviation in parenthesis, n: number of analyses, results are normalised to 100%, original totals are also indicated, na: not analysed).

Fig. 1. Location of Sárospatak in Hungary.

Fig. 2. The studied Hutterite faience artefacts, (a) sample 1: fragment of a jug, (b) sample 2: fragments of a bowl, (c) sample 3: fragments of a bowl, (d) sample 4: fragments of a bowl, (e) sample 5: fragment of a bowl?, (f) sample 6: fragment of a tazza, the inlet shows it from the lateral view.

Fig. 3. (a) X-ray diffraction patterns of the ceramic body of the studied samples (st: standard, $SnO_2$ derives from the tin glaze). BSE images showing the microstructure of the ceramic body of sample 1 (b) with a void due to dissociation of carbonate and (c) with a non-dissociated (residual) carbonate (calcite). Q: quartz, M: matrix, CC: calcite, V: void (tiny bright crystals on fig. a are Pb±Sb particles).

Fig. 4. The microstructure and inclusions of the tin glaze (BSE images). (a) white tin glaze with high concentration of tin oxide (bright inclusions) and quartz and feldspar particles (dark inclusions) (sample 4), (b) tin oxide (abbreviated as cass) particles and aggregates of needles in white tin glaze (sample 1), (c) blue tin glaze with tin oxide and small amount of quartz and feldspar particles (sample 6), (d) calcium-lead arsenate needles and prisms in a rounded pore in the blue tin glaze (sample 6).

Fig. 5. Yellow, blue and black colours over white glaze (sample 2, BSE image).

Fig. 6. The microstructure and inclusions of the colours (BSE images). (a) bright lead antimonate particles and aggregates and dark quartz particles in the yellow colour over white glaze (sample 1), (b) bright lead antimonate and dark quartz particles in the yellow colour (sample 2), (c) blue colour over white glaze (sample 1), (d) tiny, bright arsenate crystals and dark quartz and silica particles in the blue colour (sample 2).

Fig. 7. Raman spectra of the colour pigments. (a) lead antimonate identified in yellow colour of (i) sample 1 and (ii) sample 2, (b) braunite identified in the black colour of (i) sample 1, (ii) sample 2, (iii) sample 6 and (iv) the reference spectrum of braunite from the RRUFF database (R050385); (v) hausmannite identified in sample 2 and (vi) the reference spectrum of hausmannite from the RRUFF database (R060512).

Fig. 8. The microstructure and inclusions of the colours (BSE images). (a) green and black colours over white glaze (sample 6), (b) idiomorphic manganese silicate (braunite, br) crystals in the black colour (sample 6), (c) idiomorphic manganese silicate (braunite, br) crystals in the black colour over yellow colour (sample 1), (d) manganese pigment particles in the black colour: hausmannite (h) and braunite (br) (sample 2).

Fig. 9. Variation diagram PbO vs. $SnO_2$ for the white glaze of the studied Hutterite faience artefacts (see Table 2) compared with the white glaze of the Archaic, Early and Late Renaissance Italian maiolica (data from Viti et al., 2003, Tite, 2009, Amato et al., 2010) and white glaze of della Robbia sculptural ceramics (data from Kingery and Aronson, 1990, Zucchiatti et al., 2003, Gianoncelli et al., 2008, Tite, 2009, Barbour and Olson, 2011). The chemical compositions as measured by SEM-EDS analyses for maiolica glaze, and SEM-EDS, microprobe and portable XRF analyses for della Robbia glaze, respectively. Explanations: ●: studied Hutterite faience, ▲: Archaic maiolica, ◆: Early Renaissance maiolica, ◇: Late Renaissance maiolica, ■: della Robbia terracotta.

Table 1

| Sample | n | SiO$_2$ | Al$_2$O$_3$ | Na$_2$O | K$_2$O | MgO | CaO | TiO$_2$ | FeO | Orig. total |
|---|---|---|---|---|---|---|---|---|---|---|
| sample 1 | 3 | 53.14 | 13.80 | 1.04 | 2.27 | 2.99 | 21.23 | 0.63 | 4.91 | 71.89 |
| | | *(3.22)* | *(0.62)* | *(0.36)* | *(0.29)* | *(0.22)* | *(1.59)* | *(0.19)* | *(0.34)* | *(4.21)* |
| sample 2 | 3 | 53.63 | 12.77 | 1.03 | 2.20 | 2.85 | 22.46 | 0.44 | 4.62 | 69.76 |
| | | *(1.20)* | *(0.66)* | *(0.40)* | *(0.35)* | *(0.32)* | *(0.77)* | *(0.06)* | *(0.28)* | *(3.11)* |
| sample 3 | 3 | 55.08 | 16.50 | 1.36 | 2.68 | 3.77 | 14.51 | 0.70 | 5.40 | 73.35 |
| | | *(1.06)* | *(0.59)* | *(0.15)* | *(0.10)* | *(0.25)* | *(0.43)* | *(0.07)* | *(0.41)* | *(5.26)* |
| sample 4 | 4 | 57.61 | 15.04 | 1.26 | 2.70 | 2.93 | 15.99 | 0.58 | 3.91 | 71.87 |
| | | *(1.02)* | *(0.62)* | *(0.29)* | *(0.13)* | *(0.17)* | *(0.70)* | *(0.07)* | *(0.19)* | *(4.51)* |
| sample 5 | 4 | 56.05 | 15.84 | 1.33 | 2.75 | 4.11 | 14.16 | 0.68 | 5.08 | 74.88 |
| | | *(0.22)* | *(0.31)* | *(0.14)* | *(0.27)* | *(0.26)* | *(0.37)* | *(0.08)* | *(0.27)* | *(0.63)* |
| sample 6 | 6 | 54.58 | 16.32 | 0.78 | 2.50 | 2.82 | 17.91 | 0.62 | 4.48 | 72.10 |
| | | *(1.27)* | *(0.98)* | *(0.13)* | *(0.25)* | *(0.28)* | *(0.45)* | *(0.11)* | *(0.15)* | *(2.57)* |

Table 2

| Sample | | n | SiO$_2$ | PbO | SnO$_2$ | Na$_2$O | K$_2$O | CaO | MgO | Al$_2$O$_3$ | FeO | CoO | NiO | As$_2$O$_3$ | Cl | Orig. total | SnO$_2$/ PbO | K$_2$O/ Na$_2$O | K$_2$O+ Na$_2$O |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Tin-opacified white glaze | | | | | | | | | | | | | | | | | | | |
| Sample 1 | Bulk | 4 | 46.33 | 23.14 | 20.34 | 4.15 | 2.58 | 1.04 | 0.12 | 1.27 | 0.34 | na | na | na | 0.69 | 98.40 | 0.88 | 0.62 | 6.73 |
| | | | *(1.09)* | *(2.34)* | *(0.73)* | *(1.00)* | *(0.55)* | *(0.31)* | *(0.15)* | *(0.22)* | *(0.12)* | | | | *(0.14)* | *(3.29))* | | | |
| | Matrix | 24 | 55.21 | 28.66 | 5.48 | 3.09 | 3.15 | 1.67 | 0.12 | 1.26 | 0.44 | na | na | na | 0.91 | 99.00 | | | |
| | | | *(2.84)* | *(4.53)* | *(2.08)* | *(0.76)* | *(0.42)* | *(0.92)* | *(0.23)* | *(0.65)* | *(0.70)* | | | | *(0.30)* | *(2.43)* | | | |
| Sample 2 | Bulk | 8 | 44.06 | 26.49 | 16.87 | 3.70 | 3.68 | 1.34 | 0.13 | 2.50 | 0.18 | na | na | na | 1.05 | 94.79 | 0.64 | 0.99 | 7.38 |
| | | | *(0.36)* | *(0.73)* | *(0.66)* | *(0.46)* | *(0.29)* | *(0.44)* | *(0.11)* | *(0.36)* | *(0.19)* | | | | *(0.19)* | *(1.13)* | | | |
| | Matrix | 28 | 52.55 | 31.90 | 4.18 | 2.54 | 3.77 | 1.63 | 0.15 | 2.04 | 0.15 | na | na | na | 1.09 | 97.06 | | | |
| | | | *(1.87)* | *(3.17)* | *(0.85)* | *(0.51)* | *(0.41)* | *(0.95)* | *(0.27)* | *(0.57)* | *(0.23)* | | | | *(0.26)* | *(2.72)* | | | |
| Sample 3 | Bulk | 5 | 43.41 | 27.69 | 19.30 | 3.79 | 2.02 | 0.58 | 0.03 | 2.12 | 0.20 | na | na | na | 0.87 | 94.30 | 0.70 | 0.53 | 5.81 |
| | | | *(1.86)* | *(1.30)* | *(0.96)* | *(0.13)* | *(0.16)* | *(0.17)* | *(0.13)* | *(0.24)* | *(0.17)* | | | | *(0.04)* | *(4.37)* | | | |
| | Matrix | 7 | 51.26 | 36.73 | 2.80 | 2.20 | 2.44 | 0.75 | 0.08 | 2.40 | 0.15 | na | na | na | 1.19 | 94.50 | | | |
| | | | *(0.83)* | *(1.16)* | *(0.78)* | *(0.31)* | *(0.36)* | *(0.10)* | *(0.15)* | *(0.36)* | *(0.25)* | | | | *(0.19)* | *(2.36)* | | | |
| Sample 4 | Bulk | 3 | 49.53 | 17.88 | 20.21 | 2.89 | 2.94 | 2.41 | 0.27 | 3.10 | 0.38 | na | na | na | 0.39 | 95.01 | 1.13 | 1.02 | 5.83 |
| | | | *(0.53)* | *(1.14)* | *(1.60)* | *(0.24)* | *(0.15)* | *(1.17)* | *(0.11)* | *(0.45)* | *(0.18)* | | | | *(0.07)* | *(3.18)* | | | |
| | Matrix | 22 | 54.46 | 26.68 | 6.09 | 3.00 | 3.89 | 2.17 | 0.18 | 2.55 | 0.32 | na | na | na | 0.68 | 99.44 | | | |
| | | | *(1.69)* | *(2.53)* | *(1.86)* | *(0.50)* | *(0.52)* | *(0.61)* | *(0.18)* | *(1.02)* | *(0.20)* | | | | *(0.16)* | *(2.83)* | | | |
| Sample 5 | Bulk | 3 | 44.63 | 26.22 | 19.27 | 3.26 | 2.50 | 0.85 | 0.07 | 2.19 | 0.11 | na | na | na | 0.88 | 94.27 | 0.73 | 0.77 | 5.77 |
| | | | *(0.38)* | *(0.95)* | *(1.15)* | *(0.23)* | *(0.39)* | *(0.16)* | *(0.08)* | *(0.40)* | *(0.16)* | | | | *0.09* | *(1.42)* | | | |
| | Matrix | 19 | 52.74 | 32.49 | 3.85 | 2.60 | 3.28 | 1.17 | 0.09 | 2.22 | 0.24 | na | na | na | 1.31 | 97.92 | | | |
| | | | *(2.04)* | *(2.51)* | *(0.72)* | *(0.43)* | *(0.37)* | *(0.66)* | *(0.19)* | *(0.32)* | *(0.21)* | | | | *(1.09)* | *(2.69)* | | | |
| Sample 6* | Bulk | 3 | 48.57 | 22.05 | 17.10 | 2.54 | 4.47 | 1.08 | 0.18 | 2.32 | 0.31 | 0.15 | -0.03 | 0.23 | 1.02 | 96.18 | 0.78 | 1.76 | 7.02 |
| | | | *(2.16)* | *(0.86)* | *(0.84)* | *(0.09)* | *(0.28)* | *(0.20)* | *(0.16)* | *(0.09)* | *(0.11)* | *(0.07)* | *(0.24)* | *(0.19)* | *(0.11)* | *(2.87)* | | | |
| | Matrix | 18 | 56.96 | 25.78 | 4.13 | 1.77 | 5.03 | 1.56 | 0.21 | 2.77 | 0.46 | 0.13 | -0.03 | 0.20 | 1.15 | 96.01 | | | |
| | | | *(2.30)* | *(3.53)* | *(1.59)* | *(0.45)* | *(0.63)* | *(0.67)* | *(0.22)* | *(1.19)* | *(0.31)* | *(0.25)* | *(0.26)* | *(0.15)* | *(0.77)* | *(4.40)* | | | |
| Tin-opacified blue glaze | | | | | | | | | | | | | | | | | | | |
| Sample 6 | Bulk | 9 | 46.50 | 28.10 | 11.06 | 3.07 | 4.94 | 0.85 | 0.04 | 1.94 | 0.74 | 0.68 | 0.16 | 0.86 | 1.06 | 97.76 | 0.39 | 1.61 | 8.02 |
| | | | *(0.93)* | *(0.71)* | *(1.44)* | *(0.30)* | *(0.38)* | *(0.17)* | *(0.13)* | *(0.38)* | *(0.24)* | *(0.26)* | *(0.10)* | *(0.12)* | *(0.08)* | *(2.35)* | | | |
| | Matrix | 57 | 53.07 | 30.65 | 2.76 | 2.03 | 4.55 | 1.29 | 0.20 | 1.57 | 0.98 | 0.80 | 0.17 | 0.78 | 1.15 | 98.91 | | | |
| | | | *(2.17)* | *(2.77)* | *(0.96)* | *(0.40)* | *(0.57)* | *(0.68)* | *(0.23)* | *(0.72)* | *(0.41)* | *(0.24)* | *(0.29)* | *(0.38)* | *(0.91)* | *(4.00)* | | | |

*white glaze partly below blue colour

Table 3

| Sample | | n | SiO$_2$ | PbO | SnO$_2$ | Na$_2$O | K$_2$O | CaO | MgO | Al$_2$O$_3$ | FeO | CoO | NiO | As$_2$O$_3$ | Sb$_2$O$_3$ | CuO | MnO | Cl | Orig. total | K$_2$O/ Na$_2$O | K$_2$O+ Na$_2$O |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Yellow** | | | | | | | | | | | | | | | | | | | | | |
| Sample 1 | Bulk | 3 | 43.66 | 37.01 | 0.34 | 4.00 | 2.53 | 0.71 | 0.20 | 2.95 | 2.08 | na | na | na | 6.11 | na | na | 0.41 | 96.53 | 0.63 | 6.53 |
| | | | *(1.26)* | *(1.35)* | *(0.33)* | *(0.48)* | *(0.21)* | *(0.02)* | *(0.02)* | *(0.43)* | *(0.07)* | | | | *(1.08)* | | | *(0.14)* | *(3.03)* | | |
| | Matrix | 9 | 51.73 | 35.23 | 0.37 | 2.24 | 2.75 | 0.35 | 0.19 | 3.38 | 2.10 | na | na | na | 1.16 | na | na | 0.50 | 96.09 | | |
| | | | *(1.16)* | *(1.65)* | *(0.53)* | *(0.34)* | *(0.30)* | *(0.13)* | *(0.14)* | *(0.85)* | *(0.34)* | | | | *(0.67)* | | | *(0.24)* | *(1.89)* | | |
| Sample 2 | Bulk | 4 | 50.09 | 25.49 | 0.86 | 3.59 | 3.43 | 0.75 | 0.23 | 3.41 | 2.81 | na | na | na | 8.87 | na | na | 0.47 | 95.02 | 0.96 | 7.03 |
| | | | *(2.06)* | *(1.22)* | *(0.66)* | *(0.31)* | *(0.41)* | *(0.10)* | *(0.13)* | *(0.30)* | *(0.41)* | | | | *(0.44)* | | | *(0.15)* | *(1.93)* | | |
| | Matrix | 10 | 58.36 | 25.10 | 0.33 | 1.91 | 3.39 | 0.35 | 0.29 | 3.00 | 3.87 | na | na | na | 0.33 | na | na | 0.48 | 96.22 | | |
| | | | *(2.39)* | *(1.48)* | *(0.43)* | *(0.43)* | *(0.46)* | *(0.10)* | *(0.18)* | *(0.81)* | *(1.20)* | | | | *(0.43)* | | | *(0.24)* | *(1.93)* | | |
| **Blue** | | | | | | | | | | | | | | | | | | | | | |
| Sample 1 | Bulk | 3 | 51.40 | 31.95 | 2.01 | 5.39 | 3.57 | 0.96 | 0.05 | 1.19 | 1.12 | 0.77 | 0.48 | 0.71 | na | na | na | 0.39 | 92.77 | 0.66 | 8.96 |
| | | | *(0.26)* | *1.01* | *(0.31)* | *(0.80)* | *(0.21)* | *(0.08)* | *(0.02)* | *(0.07)* | *(0.14)* | *(0.21)* | *(0.04)* | *(0.32)* | | | | *(0.09)* | *(5.54)* | | |
| Sample 2 | Bulk | 2 | 56.06 | 25.69 | 1.20 | 4.80 | 3.61 | 0.81 | 0.11 | 1.57 | 1.40 | 1.10 | 0.95 | 1.62 | na | na | na | 1.08 | 92.23 | 0.75 | 8.41 |
| Sample 6 | Bulk | 2 | 47.96 | 33.40 | 3.51 | 3.40 | 4.81 | 0.70 | -0.13 | 0.80 | 1.42 | 1.38 | 0.34 | 1.71 | na | na | na | 0.69 | 94.74 | 1.42 | 8.21 |
| **Green** | | | | | | | | | | | | | | | | | | | | | |
| Sample 1 | Bulk | 4 | 40.49 | 30.82 | 13.78 | 5.44 | 2.56 | 0.85 | 0.26 | 2.39 | 0.61 | na | na | na | 0.20 | 1.82 | na | 0.77 | 96.55 | 0.47 | 8.00 |
| | | | *(0.83)* | *(0.67)* | *(0.54)* | *(0.07)* | *(0.04)* | *(0.10)* | *(0.10)* | *(0.30)* | *(0.17)* | | | | *(0.43)* | *(0.17)* | | *(0.06)* | *(0.86)* | | |
| | Matrix | 8 | 47.78 | 36.18 | 3.05 | 3.09 | 2.59 | 0.85 | 0.27 | 2.65 | 0.60 | na | na | na | na | 2.02 | na | 0.91 | 90.44 | | |
| | | | *(1.16)* | *(0.99)* | *(0.41)* | *(1.19)* | *(0.22)* | *(0.24)* | *(0.13)* | *(0.54)* | *(0.22)* | | | | | *(0.36)* | | *(0.26)* | *(1.58)* | | |
| Sample 6 | Bulk | 6 | 47.81 | 24.47 | 10.97 | 3.75 | 5.15 | 0.91 | 0.38 | 3.94 | 1.16 | na | na | na | na | 0.66 | na | 0.81 | 98.37 | 1.37 | 8.89 |
| | | | *(1.48)* | *(2.64)* | *(1.92)* | *(0.31)* | *(0.36)* | *(0.09)* | *(0.12)* | *(1.04)* | *(0.44)* | | | | | *(0.22)* | | *(0.17)* | *(1.72)* | | |
| | Matrix | 9 | 53.16 | 30.01 | 3.48 | 2.12 | 4.18 | 1.26 | 0.35 | 2.17 | 0.94 | na | na | na | na | 1.19 | na | 1.13 | 95.43 | | |
| | | | *(1.43)* | *(2.17)* | *(1.74)* | *(0.22)* | *(0.35)* | *(0.26)* | *(0.12)* | *(1.00)* | *(0.59)* | | | | | *(0.27)* | | *(0.26)* | *(1.93)* | | |
| **Black** | | | | | | | | | | | | | | | | | | | | | |
| Sample 1* | Bulk | 1 | 38.83 | 24.46 | 16.75 | 5.25 | 2.94 | 1.51 | 0.38 | 2.48 | 1.30 | na | na | na | na | 0.33 | 5.36 | 0.42 | 87.89 | 0.56 | 8.19 |
| | Matrix | 2 | 48.89 | 28.06 | 4.23 | 2.88 | 3.29 | 1.94 | 0.35 | 2.76 | 1.12 | na | na | na | na | 0.56 | 5.40 | 0.51 | 88.48 | | |
| Sample 1** | Bulk | 1 | 38.29 | 21.62 | 0.68 | 4.88 | 2.14 | 1.28 | 0.59 | 2.50 | 3.20 | na | na | na | na | na | 24.61 | 0.20 | 91.13 | 0.44 | 7.02 |
| | Matrix | 2 | 48.01 | 31.48 | 0.50 | 3.41 | 3.15 | 1.47 | 0.28 | 3.61 | 2.57 | na | na | na | na | na | 5.35 | 0.17 | 92.12 | | |
| Sample 2*** | Bulk | 1 | 41.30 | 33.84 | 6.74 | 5.05 | 3.73 | 0.73 | 0.19 | 2.62 | 0.71 | na | na | na | na | na | 4.05 | 1.05 | 100.33 | 0.74 | 8.78 |
| | Matrix | 3 | 46.58 | 34.65 | 2.78 | 3.00 | 3.84 | 0.59 | 0.40 | 2.32 | 0.78 | na | na | na | na | na | 4.22 | 0.85 | 96.42 | | |
| | | | *(1.47)* | *(2.52)* | *(1.13)* | *(1.53)* | *(0.35)* | *(0.01)* | *(0.16)* | *(0.33)* | *(0.18)* | | | | | | *(0.25)* | *(0.13)* | *(0.85)* | | |
| Sample 2** | Bulk | 3 | 42.54 | 25.67 | 1.63 | 5.61 | 3.15 | 0.70 | 0.04 | 2.81 | 1.45 | 0.89 | 0.72 | 1.52 | na | na | 12.49 | 0.78 | 95.16 | 0.56 | 8.76 |
| | | | *(3.07)* | *(0.59)* | *(0.22)* | *(0.26)* | *(0.36)* | *(0.12)* | *(0.14)* | *(0.24)* | *(0.17)* | *(0.08)* | *(0.17)* | *(0.31)* | | | *(4.44)* | *(0.10)* | *(1.35)* | | |
| | Matrix | 4 | 48.81 | 30.30 | 0.29 | 2.32 | 2.91 | 0.80 | 0.25 | 3.88 | 1.51 | 0.70 | 0.50 | 1.33 | na | na | 5.64 | 0.76 | 92.36 | | |
| | | | *(1.73)* | *(1.71)* | *(0.93)* | *(0.31)* | *(0.18)* | *(0.13)* | *(0.12)* | *(0.96)* | *(0.08)* | *(0.41)* | *(0.36)* | *(0.28)* | | | *(0.43)* | *(0.24)* | *(1.25)* | | |
| Sample 6* | Bulk | 4 | 44.91 | 23.63 | 12.24 | 4.11 | 4.87 | 1.14 | 0.24 | 3.58 | 1.11 | na | na | 0.13 | na | 0.63 | 2.53 | 0.89 | 96.03 | 1.18 | 8.98 |
| | | | *(1.70)* | *(1.61)* | *(1.58)* | *(0.68)* | *(0.51)* | *(0.28)* | *(0.21)* | *(0.82)* | *(0.23)* | | | *(0.26)* | | *(0.35)* | *(1.36)* | *(0.24)* | *(2.92)* | | |
| | Matrix | 13 | 50.44 | 28.22 | 2.12 | 2.36 | 4.60 | 1.56 | 0.28 | 3.27 | 1.41 | na | na | 0.42 | na | 0.76 | 3.77 | 0.80 | 95.12 | | |
| | | | *(2.63)* | *(1.81)* | *(0.82)* | *(0.29)* | *(0.39)* | *(0.32)* | *(0.18)* | *(0.69)* | *(0.42)* | | | *(0.50)* | | *(0.39)* | *(1.38)* | *(0.28)* | *(1.94)* | | |

* black colour over green colour, ** black colour over yellow (sample 1) or blue colour (sample 2), *** black colour over white glaze,

cass

a   yellow   white   20 μm

b   10 μm

c   blue   white   20 μm

d   10 μm

a

138
139

intensity

202
204
300
302
341
332
364
382
458
459
508
512
640
644
774
751
(i) sample 1
(ii) sample 2

Raman shift (cm⁻¹)

b

220
248
214
217
202
337
330
331
330
476
475
474
513
509
510
506
575
577
572
575
618
614
608
617
688
689
681
687
957
954
950
954
(i) sample 1
(ii) sample 2
(iii) sample 6
(iv) reference

intensity

655
658
316
317
364
371
(v) sample 2
(vi) reference

Raman shift (cm⁻¹)