File S1

Methodological recommendation

General remarks

EDS and WDS analytical techniques are complementary and commonly applied in material studies. EDS analysis is precise enough for general studies. In turn, WDS analysis is more precise and should be used to refine localities selected during EDS analysis. The analyses should be made on a perfectly smooth thin section surface or fragment of the material. Of high significance in such analyses is the determination of the strict locality on the SEM image, which has impact the results. The presented images in previous papers are restricted to the glaze layer with a fragment of the body layer. Results of the analyses are typically presented recalculated to the content of oxides commonly occurring in nature, due to which the data are fragmentary and do not reflect the variability of the composition of faience material.

Polarized light microscopy

Observations of the large format scan indicate that the value of this parameter depend on the precise locality of the analysis. Areas with high and low packing are observed. Therefore, only studies of parameters which include the sample volume allowed for determining the actual porosity of the material; the body of the faience bowl is in almost 50 % composed of pores.

Physical properties

The value of parameter *n* obtained from image analysis is understated by 11 % in comparison to the calculated value. This results from the fact that the value obtained from image analysis refers to two dimensions of the sample (2D), whereas bulk density used for calculating parameter *n* was determined from a fragment of the faience bowl, i.e. using three dimensions (3D). Therefore an error was created at anisotropy of the faience material, when the quartz grains are strongly elongated. Such error will not appear in the 2D analysis when the material will be isotropic [38]. The smallest pores related with the clay mineral content, which were not preserved during thin section preparation, were also excluded from the image analysis (see Figure 5).

Based on studies of the physical parameters (bulk density and specific density) and calculations, only the general porosity value was obtained. Pore dimensions cannot be determined this way. SEM observations of the microstructure of the fracture surface have shown a large content of clay minerals in the material (Figure 5). Their content will increase the number of very small pores, i.e. ultra- and micro-pores (see Figure S8c,d and Table 1). However, SEM images of thin sections did not display such high content of clay minerals. This is related to the removal of these smallest structural elements during thin section preparation. Lack of the finest fractions, whose contribution was not included in the quantitative image analysis, caused an error in the obtained content of the smallest pores (Figure 9).

X-ray Powder Diffraction (XRD)

Among many technics used to analyse archaeological objects, such as old paintings or ceramics, the method of X-ray Powder Diffractometry (XRD) is commonly used. This method allows to identify the phase composition of the crystal structure. It is especially useful when different crystal phases with the same or similar chemical composition may be present in the sample, or when the analysed samples are microcrystalline. Undoubtedly, other advantages of the method include the possibility of identifying multicomponent mixtures, as well as its non-destructive nature (the sample might be reused for the purpose of other tests, for example the chemical composition analysis). Both the duration of the diffraction experiments and the sample preparation are fairly short.

In the case of the samples studied, the most important test was the one that intended to verify the colourant present in the glaze on the outer surface of the bowl. Three diffraction graphs are presented in Figure S9, registering two different modes, i.e. the Bragg-Brentano method (MS-BDY sample) and the DSH method (MS-GLZ_1h and MS-GLZ_3h samples). As seen in Figure S9a, quartz dominates in the samples. However, a closer look into the samples shows the presence of more phases, although their identification proved impossible for samples MS-BDY and MS-GLZ_1h. Cuprorivaite reflections can be seen in Figure S9b which is a scaled part of Figure S9a.

The test for colourant identification could not be conducted with the Bragg-Brentano method, because the colourant had been heavily diluted. However, this technique allows for a very representative (quantitative) analysis of the phase composition of the samples. Being extremely important in the case of the analysed example, the test approximates the firing temperature or the final composition of clay used for manufacturing ceramics. The major disadvantage of this method is the significant amount of the required powdered sample (~400 mg).

The DSH method is much more efficient for colourant identification. In the DSH method, the sample is placed in a thin-walled, non-reflective glass capillary. If very little of the analysed material is accessible (for example in the case of a very thin layer of the colourant inside the glaze), it is necessary to use a capillary with as small internal diameter as possible. Effectively, it is the diameter of 0.3 mm. Below that value, a problem with regard to the placement of the powder appears, and accordingly larger amounts of the powder need to be applied. Better filling of the capillary provides a shortened registration time, however a diffractogram with well-visible reflections can be acquired using a filling as high as a few millimetres. The amount of 20-30 μg of the material is enough to prepare the sample. The most important factor for the material to be acquired is to provide as high as possible concentration of the phase which is the subject of the conducted tests. The prolongation of the registration time up to 3 h resulted in flattening of the diffractogram (better statistics of the count for a radiation detector).

If the DSH method would not result in phase identification, Bontempi [78] recommend a micro diffraction technique. This method is advisable when the object of the tests is available in very small amounts or when the sample consists of many layers. Such tests must be conducted with the use of special X-ray optic elements and sensitive X-ray detectors. It requires precise targeting of the beam onto an uncrushed part of the sample. Because of the much larger duration of the analysis and the possibility that the mineral phases are oriented, it is advisable to use this method only when it is not possible to grind the sample or as the final measure when the DSH method will prove to be ineffective.

Simultaneous Thermal Analysis (STA): TG-DSC with Evolved Gas Analysis (EGA): FTIR-QMS

Two phases of carbon dioxide have been noted in the thermal analysis. Decrease of CO_2 emission and subsequent increase at 700 °C should be explained. It may be linked with opening of pores of different size. Explaining this issue would require studies at higher temperatures till the termination of the processes in the sample. The structure of the glaze layer would have to be tested again after the experiment in order to confirm the assumed interpretation. Detailed studies of the degassing process would also be helpful in reconstructing the temperature and number of firings in faience manufacturing.