PIXE Analyses of Byzantine Pottery from Hârşova - Carsium, Romania

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A selection of 36 Middle Byzantine ceramic shards excavated from Hârşova (Carsium), Constanţa county, Romania, were investigated using Particle Induced X-ray Emission (PIXE) technique. The analyzed pottery fragments were dated to the 11\textsuperscript{th} century A.D., period when the territory between the Black Sea and the Danube, and implicitly this settlement, was under Byzantine administration.

Micro-PIXE measurements were performed at the AN2000 accelerator of LNL, INFN Italy and led to the identification of the chemical composition of the analyzed samples – ceramic paste and decorations.

The shards chosen for this archaeometric study were divided into several categories (e.g. fine and coarse, decorated or un-decorated, fired in oxidizing or reducing atmosphere) by the archaeologist who discovered them. Some of the fine ceramic fragments, rare occurrences for the Middle Byzantine period, were covered with a very thin shimmering golden engobe, while others were decorated with a green-olive glaze. PIXE investigations were expected to answer the question if the differences in appearance of the ceramic pots can be connected to different compositional signatures.

The statistical analysis of the PIXE data performed using Hierarchical Cluster Analysis and Principal Component Analysis led to the identification of two main patterns in the compositional results. Thus, it was possible to distinguish a set of shards made from kaolinitic clays which was clearly dissimilar from the rest of the ceramic fragments. This finding suggested that the majority of the analyzed potteries were manufactured using local clays, but different working procedures (e.g. firing conditions, decorations). On the other hand, it was concluded that for kaolinitic potteries the Byzantine potters chose to employ raw materials from another location - most likely some 80 km far away from Hârşova - with the purpose of obtaining vessels with special properties (e.g. mechanical and/or thermal resistance, reduced porosity, etc.).

A remaining open question is the provenance of the golden engobe potteries. Similar finds dated to this period were only scarcely reported in the archaeological literature. Surprisingly, the determined chemical composition did not evidence any particular compositional signature for the ceramic paste. Consequently, only further mineralogical studies are expected to clarify if these potteries belong to a distinct category, possibly reflecting the employment of other raw materials and/or working techniques.

Micro-PIXE analyses scans on the interfaces between the decorated surfaces and the underlying ceramic bodies were performed in order to identify the compounds/minerals present in the golden engobe and the green glaze and to estimate the thickness of these decorations. Clear changes in the chemical composition were revealed only for the latter type of decoration, characterized by a strong enrichment in the lead oxide content as compared to the ceramic body. Most likely, the green color of the glaze was induced by a combination in different proportions of ferrous and ferric oxides. The PIXE analyses indicated that the main candidate for the yellow-golden engobe is the mineral called mica, ruling out the initial hypotheses that sub-micronic gold or copper particles were at the origin of this peculiar shine.

Based on these preliminary results, to be followed by other analyses by petrography and X-Ray Diffraction, some tentative conclusions regarding the ceramic manufacturing practices and raw materials employed in the Lower Danube region during the Middle Byzantine period were obtained.

This study on Byzantine ceramic will be continued with PIXE measurements on potteries excavated from three other nearby archaeological sites - Oltina, Valul lui Traian and Pantelimonu de Sus, as well as on golden engobe potteries from some Byzantine sites located on nowadays Bulgarian territory. Concluding, this archaeometric project based on micro-PIXE measurements is expected to provide hard science evidences for the vivid commercial exchanges between the Byzantine centers located along the Danube river flourishing during the 11\textsuperscript{th} century A.D.

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