

# SPECTROSCOPIC STUDIES OF POTTERY FINDS FROM REPUBLIC OF MACEDONIA

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In order to increase the knowledge and understanding of ceramic archaeological finds in Republic of Macedonia, the study using micro-Raman and infrared spectroscopy in characterization of the pottery was undertaken. Additionally, data analysis using chemometric techniques, for specific purposes, was performed.

The pool of analyzed objects include Byzantine and Ottoman glazed ceramics, non-glazed simple pottery and early christian sacral terra cotta icons.

Micro-Raman spectroscopy was used for the study of the glazes, aiming to achieve technological information on the manufacturing of the objects. Characteristic Raman bands of ceramics glaze are identified and their relationships with the fluxing PbO are discussed. The procedure to identify different families of glassy silicate artefacts is based on the peak area ratio ( $A_{500}/A_{1000}$ ) related to symmetric Si-O-Si bending ( $\sim 500\text{ cm}^{-1}$ ) and Si-O stretching ( $\sim 1000\text{ cm}^{-1}$ ) modes. Based on the results from the Raman spectra, it was possible to enlighten firing temperature of the glaze. The glazes were found to be lead based or lead rich in all analyzed glazed samples, with firing temperature 600-800 °C. Additionally, the mineralogical composition of the ceramics was estimated using point to point Raman spectroscopy. Based on the identified specific minerals in the pottery, in some cases, an attempt is made to establish the provenance of the clay.

Infrared spectroscopy was used for assessing the firing temperature of the pottery bodies as well as to establish the basic mineralogical composition. The correlation of the  $\nu(\text{Si-O})/\delta(\text{Si-O-Si})$  bands in the infrared spectra was used in assessing the firing temperatures. For the analyzed ceramic bodies, the assessed firing temperature range between 600 and 800 °C.

Chemometric approach to the data analysis for identifying the clay origin of the terra cotta icons was performed, as well. The elemental analysis data of the terra cotta icons and of nine, nearby, clay pits determined by XRF were subjected to self-organizing maps (SOM). The analysis resulted with precise location of the used clay pit, Grnčarka, 2.5 km southeast from the Vinica Fortress, where the terra cotta icons were excavated.

Additionally, a target factor analysis (TFA) model for identification of efflorescence salts was developed. The development of the TFA model is based on infrared spectra database of salts commonly found in efflorescence. TFA allows simple approach in determining the composition of the salts efflorescence through comparison of the infrared spectra of the pure salts (stored in the database) with the ones reconstructed by TFA model.