

MICRO-RAMAN STUDY OF PIGMENTS, CERAMICS AND MINERALS

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In the last decade, micro-Raman spectroscopy has proved invaluable for analyzing almost every kind of artefact, from gems to different painted materials, to dyed fibres and to ceramics and glasses. Its main advantages: non-destructiveness, possibility for analyzing very small samples, its high selectivity and sensitivity, opposed to very few disadvantages, mainly, high level of background fluorescence. We have focused our interest on the micro-Raman study of pigments in Byzantine icons and frescos and Byzantine glazed ceramics.

The identification of pigments by Raman spectroscopy is today well elaborated and is based on the comparison between their Raman spectra and a database of reference spectra. As part of the micro-Raman pigment analysis, we have analyzed six icons found in three different churches in the Skopje region, painted by the well known Macedonian painter, Dicho Zograph. Comparison was made between five pigments (blue, red, orange, pink and yellow) used for painting the icons in 1845/46 period with those painted in the year 1853. Another study of pigments in icons was made between three pigments (red, blue and green) in fifteen Byzantine and post-Byzantine icons painted in the period between 12th and 18th century. For the purpose of conservation, micro-Raman spectroscopy was also used to analysis the pigments taken from two different layers of paint (from 17th and 19th century) in fresco paintings in Sveta Bogorodica Church in Leshok (North-Western Macedonia).

In order to achieve some understanding and characterization of the materials and provenance as well as to achieve technological information on the manufacturing of the objects, fifteen fragments of the Byzantine glazed ceramic finds (all dated from 12th to 15th century) were analysed. All samples have an underglaze engobe and are characterized with sgraffito slip decoration. Characteristic Raman bands of ceramics 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 [1].

Finally, some examples of the use of micro-Raman spectroscopy in identification of minerals are presented. The example chosen is meteorite Struga, which fell 35 years ago in the Republic of Macedonia. Point by point micro-Raman spectra were recorded. It revealed several clear Raman spectra of minerals such as olivine, pyroxene, plagioclase and magnetite.

[1] Ph. Colomban, in Glasses, Glazes and Ceramics – Recognition of the Ancient Technology from the Raman Spectra. *In Raman spectroscopy in Archaeology and Art History*, H. G. M. Edwards and J. M. Chalmers (eds), Royal Society of Chemistry, London, 2005, p. 192, Chapter 13.