An approach for characterization of the mineral composition in pottery finds using point-to-point micro-Raman spectroscopy

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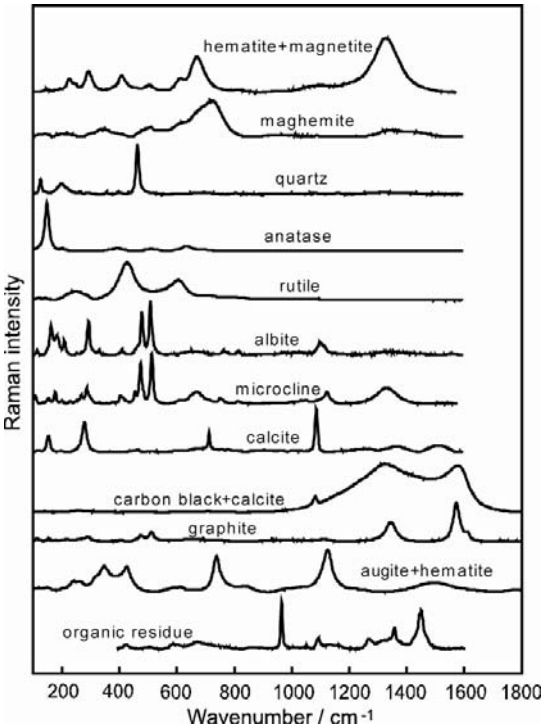
Micro-Raman spectroscopy has been frequently used in the studies of ancient pottery in order to gain information on the mineral composition of the clay, but also to study the production technologies by identifying the mineralogical phases produced by thermal transformation during the production process. Most of these studies were performed by focusing the laser beam on a clay matrix of the ceramics body on a selected spot [Marengo et al., 2005; Castriota et al., 2008]. This method is non-destructive, but it is time consuming and requires focusing the laser beam on many spots of the sample in order to obtain statistical representation of the minerals present in the sample.

In order to avoid this repetitive procedure, point-to-point micro-Raman spectroscopy was employed for characterization of the minerals present in the ceramics body. The Raman spectra were recorded using Horiba Jobin-Yvon LabRam 300 spectrometer with 532 nm laser line, with an average power on the sample of 3 mW and with the resolution of around 3 cm^{-1}. Pellets, prepared from 150–200 mg powder from the body of the ceramic shreds were placed under the microscope (100x) on an automatic XY mapping stage. Approximately 100 Raman spectra, with the step of 3 μm were acquired from a pellet, covering an area of around 0.03 x 0.03 mm to 0.05 x 0.05 mm.

In this study, we present Raman spectra recorded by point-to-point micro-Raman spectroscopy of 15 pottery shreds excavated at the Skopje Fortress in 2007. Twenty five different minerals of the analyzed ceramic bodies were identified by their Raman spectra. Depending on the surface that has been recorded, some of the spectra represent a pure mineral, while others are a mixture of two or more minerals (Fig 1). Besides quartz, iron oxides (hematite, magnetite and maghemite), plagioclases (microcline and albite), TiO_2 (anatase and rutile) and calcite, many other minerals were identified in the body of all the analyzed ceramic shreds, such as carbon black, graphite, but also titanite and hornblende. In some of the pottery finds, discriminative minerals were detected such as spessartine, diopside, siderite, dolomite, phlogopite, epidote, barite, augite, olivine, fayalite, enstatine and sphalerite. In one of the samples, a Raman spectrum of an organic residue was also detected (last spectrum on Fig.1).

In order to validate the mineralogical assessment of the pottery shreds obtained by point-to-point micro-Raman spectroscopy, the results were compared with X-ray powder diffraction measurements recorded on the same pellets used for the Raman analyses. The diffractograms were obtained using Rigaku-Rint 2200 diffractometer with Cu Kα radiation. A good correlation between the results of XRD and Raman spectroscopy was obtained, on the most abundant minerals in the pottery samples. The identification from the XRD data of the less abundant minerals in the clay matrixes, however, was very difficult, if at all possible.



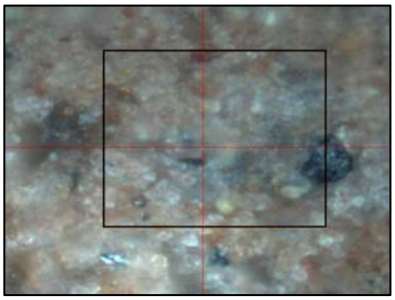


Fig. 1 (Top) Mapping area of the pellet used for recording point-to-point micro-Raman spectra.

(Left) Some Raman spectra of minerals and/or mixture of minerals obtained from this area.

In general, minerals identified by point-to-point micro-Raman spectroscopy are more numerous than those detected by XRD technique. The XRD measurements give one diffractogram for each sample containing summarized data for all the minerals present in the powdered pottery fragment. Sometimes, even for a very experienced crystallographer, it is difficult to interpret the XRD data and to assign a specific mineral in the clay matrix of many minerals, particularly if its abundance is under the detection limits of the instrument (in this case, less than 5 %). Point-to-point micro-Raman spectroscopy, on the other hand, provides clear evidence of the minerals present in the pottery body (even if they are present in small quantities). In one spectrum recorded from each spot on a mapping area, the Raman signature of one or a mixture of two/three minerals can be assigned by its/their characteristic bands and by comparison with the reference Raman spectra database of minerals [Spectral ID].

Since most of the studies of ancient ceramics have been made on pottery fragments obtained from many archaeological excavations, it is sometimes more convenient to take a small portion (150–200 mg) of the powdered ceramics body and make a pellet for recording point-to-point micro-Raman spectra. This approach is micro-destructive but effective. The Raman spectra are recorded automatically, the minerals are often good scatters and minor to trace minerals as well as polymorphs are readily identified in the pottery samples.

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References

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Spectral ID (3.02), Thermo Galactic (Horiba Jobin-Yvon Database of Raman Spectra).