

Application of Molecular Spectroscopy to Study the Composition of Prehistoric Pigments from Excavations (Argentina)

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Determination of prehistoric pigments composition was performed by two molecular spectroscopy methods – infrared (IR) and micro-Raman spectrometry (MRS). Infrared spectra were obtained by IR spectrometer Spectrum BX-II (Perkin Elmer). Raman spectrometric measurements were carried out by Renishaw InVia micro-Raman spectrometer with laser excitation at 785 nm.

The objects of investigation were pre-historic pigments from Carriqueo rock shelter (North Patagonia, Argentina). The pigment samples of orange, red and brown shades were collected from archaeological sites.

Usually the natural yellow, orange or red pigments, composed of yellow and red ochres are frequently detected in prehistoric pigments. The main components of ochre are iron (hydro)oxide (haematite or goethite), clay and silica.

Several yellowish, reddish and red-brown pigments demonstrated Raman spectra corresponding to haematite, goethite, gypsum, quartz, oxalates. In some cases huge fluorescence caused by the presence of clay in the pigments disturbed the Raman signal to such an extent that made it not informative. Therefore we used infrared spectrometry to analyse their composition. A thin layer of the pigments was put on BaF₂ substrate and IR absorption was measured. For reddish pigments, we detected absorption bands typical for natural red earth, consisting of iron oxides in hydrated and anhydrous forms. Yellowish pigments consist of amber yellow (a kind of yellow ochre) and satin ochre as main components. Green pigment was recognized as green earth by typical absorption bands.