

FTIR study of archaeological organic residues from ancient Upper Macedonia, northern Greece

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The aim of this study is the application of Fourier Transform Infra-Red spectroscopy (FTIR) to the characterization of archaeological organic remains, collected from Aiani archaeological site, northern Greece. FTIR spectroscopy is a widely used analytical method in the study of complex biological material, and is commonly used in art and archaeology for the initial identification of compound classes. Aiani is located approximately 20 km south of the city of Kozani, western Macedonia (Greece). Aiani was within the region of the ancient kingdom of Elimeia which, together with the rest of the Greek kingdoms (Tymphaia, Orestis, Lyncestis, Eordaia, Pelagonia) constituted the ancient Upper (i.e. mountainous) Macedonia. The systematic excavational research, which began in 1983, has revealed the architectural remains of both large and small buildings, rich in small finds, and groups of graves and organized cemeteries dating from the Prehistoric to the Late Hellenistic period. Amongst a variety of pottery residues provided by the local archaeological authorities, two types of organic residues dated from prehistoric (ca 5000 BC) to Hellenistic times (2nd century BC), were chosen for this study: carbonized particles (one from the interior of a vessel and another from the exterior of a different vessel) and a cream-coloured non-carbonized residue. Due to the inhomogeneous nature of the solid residues, samples were ground and intensely homogenised prior to use.

Specimens for FTIR were prepared using potassium bromide (KBr) pellet technique. The samples were measured as they are found and partly the samples were carefully extracted with methanol. Some drops of these extracts were poured on KBr and left in an oven (50 °C) for two days, and after grinding, KBr pellets were prepared. The insoluble matter left from the extraction was also analysed by FTIR. Fourier Transform Infrared Spectroscopy analysis was carried out on a Bruker Tensor 27, equipped with a DTGS-MIR-detector and controlled by Bruker's OPUS software. Spectra were recorded by co-adding 16 scans at a resolution of 4 cm⁻¹ for as well the background (just KBr) as the sample. The infrared signal was recorded between 400 and 4000 cm⁻¹. Bands were identified by comparison with published assignments.

IR spectra of the organic residue samples reveal an abundance of C=O and C-O-R structures (1800-1000 cm⁻¹ region), while clay and silicate minerals predominate in the 400-600 cm⁻¹ and 3600-3800 cm⁻¹ zone. There are distinct peaks in the aliphatic stretching region (3000-2800 cm⁻¹), attributed to symmetric and asymmetric -CH₂ stretching. The C-O groups in the 1115 cm⁻¹ and 1040 cm⁻¹ region are also obvious. The 1040 cm⁻¹ band may also result from silicate minerals (Si-O bonds). The intense bands at 3400 cm⁻¹ are attributed to -OH stretching from H₂O or phenol groups. The fairly sharp band at 1370-1490 cm⁻¹ and the sharp transmission at 870 cm⁻¹ are ascribed to the presence of precipitated calcium carbonate. Aliphatic (3000-2800 cm⁻¹) and aromatic (1600-1700 cm⁻¹) bands show higher intensities in the dried extract samples compared to raw organic residue and insoluble matter samples. The intensity of the mineral bands (in the 400-600 cm⁻¹ and 3600-3800 cm⁻¹ zone) was preferentially increased in the FTIR spectra of the insoluble material. FTIR spectra of the carbonized residues show the presence of aliphatic and aromatic moieties and confirm the aromatic nature and the degree of dehydration that has taken place. Cream-coloured residues have a much lower organic content than the carbonized ones, with an overwhelming presence of precipitated calcium carbonate, as well as the presence of silica. Despite the fact that FTIR spectroscopy is mostly limited to initial identification of compound classes of unknown solids, it gave valuable information in our study and helped us to schedule the ongoing research on archaeological food remains from this area.