Towards a multi-analytical methodology based on molecular spectroscopy techniques for the detection and characterization of organic residues in archaeological findings

Maria Eleni Konstantinou*[1,2], Evangelia Ralli[2], Ioanna Misyri[2], Maria Roumpou[1], Aggelos Philippidis[1], Sophia Sotiropoulou[1], Apostolos Spyros[2], and Demetrios Anglos[1,2]

[1]Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (IESL-FORTH), 700 13 Heraklion, Crete, Greece – Greece

[2]Department of Chemistry, University of Crete, 700 13 Heraklion, Crete, Greece – Greece

Abstract

Systematic sampling and analysis of organic residues, found typically, yet not exclusively, as material remains adsorbed in the walls of archaeological ceramic containers, have enabled archaeologists, over the past three decades, to obtain significant information concerning the use and processing of natural products in antiquity, also allowing reflections on the implications of the data generated. Chromatographic techniques utilizing different detection schemes (GC, GC-MS, HPLC, LC-MS), often combined with isotopic analysis (GC-c-IRMS, IRMS) have been widely applied in the context of archaeological residue analysis, given their high sensitivity and selectivity, which help analysts to achieve reliable analysis of complex and even highly degraded archaeological samples. Nonetheless, these techniques are destructive and moreover require copious and time-consuming sample preparation steps, eventually limiting the number of samples amenable to analysis. Molecular spectroscopic techniques, on the other hand, could offer alternative, faster approaches to chemical analysis that would enable efficient screening and characterization of organic remains found either as amorphous deposits or trapped in inorganic matrices. The complexity of organic matter preserved in various archaeological contexts necessitates multi-analytical approaches. The implementation of spectroscopic techniques could ensure in many ways availability of samples for future analysis, as well as allow assessment of their state of preservation, guiding further analytical steps. The work presented in this paper outlines a case study focusing on archaeological resinous materials, known to have been used for a range of purposes since prehistory. Our primary aim is to work out a multi-analytical methodology utilizing FTIR, micro-Raman, Fluorescence and NMR spectroscopies for the characterization of molecular species that are reported as biomarkers in archaeological resins. It has been demonstrated that these biomarkers survive in the archaeological record and in various burial environments primarily because of their hydrophobic nature and they exhibit specific spectral features that can be assessed through molecular spectroscopy techniques. Samples from modern resins, distributed across the Mediterranean region, have been examined, with the purpose to propose a refined residue analysis protocol for resin samples, including the generation of spectral libraries for specific compounds and plant species. Spectroscopic results of archaeological ceramic samples preserving resin residues, according to GC-MS analysis, are used for validation

*Speaker

purposes. Model samples are also submitted to artificial ageing to develop suitable reference spectra and provide insights into the degradation pathways and how these might be reflected in the spectra produced. The selected spectroscopic techniques complement each other and we hope that our study will address, furthermore, issues of portability, highlighting the potential of routine utilization of spectrochemical analysis tools in archaeometry laboratories, also facilitating analysis of residues that cannot be sampled off of archaeological objects or excavation sites.

Keywords: organic residue analysis, resins, spectroscopic techniques