

# Raman Spectroscopy of Ancient and Modern Ivories: Nondestructive Analytical Interrogation – An Appreciation.

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The Raman spectroscopic analysis of ancient and modern biomaterials can reveal the chemical composition of specimens non-destructively on the micro scale and without involving their chemical or mechanical pretreatment<sup>1,2,3</sup>. In the case of large objects the interrogation of small areas of interest using a fibre-optic probe is advantageous and particularly relevant for ivory inlays in wood and metal. However, the Raman effect is rather weak and depends upon the use of high powered lasers as excitation sources; care must therefore be taken in the illumination of the specimen so that the laser irradiance ( $\text{W cm}^{-2}$ ) to which the intensity of the Raman spectrum is related directly does not inflict damage to the object under study. Whereas this is not so important for modern specimens, it is particularly vital for archaeological specimens since the incorporation of materials from their depositional environment can result in laser beam absorption and consequent thermal damage caused by the dissipation of heat from the use of excessively large laser powers in the visible region focussed into very small specimen footprints. For example, 10 mW of a green argon ion laser focussed confocally into a cube of 2 micrometer dimensions yields an irradiance of  $1 \text{ GW cm}^{-2}$ , which gives Raman spectra of nice quality from minerals but can result in the “cratering” and carbonisation of more sensitive biomaterials especially where absorption of the laser beam occurs. Care should be taken, therefore, in the irradiation of sensitive biomaterials and expert analysis will involve the preliminary controlled assessment of the sensitivity of the specimen to the experimental conditions being employed.

A major problem associated with the Raman spectroscopic analysis of ivories is the onset of fluorescence emission, which is several orders of magnitude greater than the Raman effect, generated through the laser excitation of low energy excited electronic states of impurities or other associated materials in the sample; this is frequently encountered in the analysis of archaeological specimens and where specimens have been treated with exogenous substances and coatings for their enhancement or preservation. The adoption of long wavelength, low energy, near-infrared laser excitation which is insufficient to probe these electronic energy levels has provided an answer to this problem in many cases for the recording of Raman spectra from archaeological ivories. Despite this, the technique of “fluorescence burnout” has been employed with some success using visible laser excitation and biomaterials, in which the laser beam is focussed at relatively high power on the sample and remains there for a period of often an hour or more, during which the fluorescence emission background is significantly diminished, facilitating the observation of Raman spectral features which were previously hidden or “swamped” by the broad fluorescence emission. Although this procedure has been successful and there are reports in the literature of Raman spectra being obtained from otherwise recalcitrant specimens, care must be taken in its use to prevent possible thermal damage, as outlined above.

Nevertheless, the advantages of Raman spectroscopy for the analytical interrogation of archaeological and modern ivories outweigh the care that needs to be invoked in their examination:

- the ability to detect organic and inorganic signatures from the same specimen, important for an assessment to be made of the mineralisation of ancient ivory specimens in the burial environment, without the use of specialised instrumentation for detecting low wavenumbers;
- the low sensitivity of the Raman effect to water and glass means that it is possible to analyse ancient ivories from wet burial depositions without resorting to desiccative procedures which could cause mechanical stress cracks and specimen distortion, and to interrogate specimens under protective glass covers without exposing them to the atmosphere;
- it is possible to examine a wide range of specimens of different shapes and sizes from fragments of only a few microgrammes to whole tusks weighing several kilogrammes ; this might seem trivial at first but there are several instances where this aspect has assisted archaeologists in their interpretation of excavated fragments – in a recent Raman spectroscopic study<sup>4</sup> of a 2K year old example, some 23 ivory fragments from an excavation of Roman ivories showed that only 18 were actually ivory and the remainder were associated mineral deposits that had been stained in the depositional environment and resembled ivory;
- although ivory is a generic term for exoskeletal dental growth in mammalian species, from which therefore the Raman spectral signatures might be expected to be rather similar, there are several spectroscopic features which afford the possibility of identifying the particular mammalian species involved from the specimen under study and its discrimination from bone. This has been effectively undertaken with modern ivories, where the application of chemometric analytical procedures<sup>3,5,6</sup> to the Raman spectra have facilitated an unambiguous identification of ivory and its assignment to African and Asian elephant tusk, sperm whale tooth, narwhal tusk, hippopotamus tusk, walrus tusk, wart hog and pig tusk. However, the biodeterioration suffered by ancient ivories from excavation environments and in particular the preferential leaching out and degradation of the collagenic component of the ivory samples concerned results in often an only partial success being attained in this respect; despite this, it is still possible even in the worst cases to assign the specimen to a marine or terrestrial ivory –which is often sufficient to establish novel information to archaeologists about possible trade routes.
- the ability to identify minerals and organic components together in ivory specimens has resulted in unique information being provided about the mineralisation of specimens and also from databases of biological Raman spectral signatures, the presence of bacterial colonisation in the specimens which can alert conservators to potential ongoing degradation problems in the specimen being prepared for storage or display<sup>7</sup>.
- in a very recent development, the use of a special type of illumination known as spatially offset Raman spectroscopy ( SORS ) has facilitated the recording of Raman spectra of samples whose substrates have been concealed by the application of a surface coating that is impenetrable to light. The Raman spectra of African elephant ivory samples that were treated with paints and coloured varnishes were successfully obtained without necessitating the mechanical scraping or chemical removal of the surface coating<sup>8</sup>; clearly, this has application in the identification of ivories that have been concealed deliberately for contraband smuggling purposes.

- the detection of real and fake ivories, some of which were cleverly constituted in deliberate attempts to escape detection by law enforcement agencies, has also involved the use of Raman spectroscopy as a relatively rapid analytical provider of information around the concept of “is it or isn’t it ?” Again, the presence of spectral signatures of chemical components which are not part of genuine ivory provides a lead role in this respect for the identification of resins, mineral additives and synthetic analogues such as “gallalith” and “micarta”.

The literature on the Raman spectra of modern and ancient ivories is now quite extensive and the adoption of the technique as a first pass analytical interrogation of archaeological specimens is established. However, as the above account demonstrates, it is sometimes just not possible to acquire Raman spectra from ancient ivories, particularly where the degradation has been too severe. This obviously depends upon the particular burial environment and Raman spectral analyses of mammoth ivories over the age range spanning 120Ky to about 12Ky has demonstrated<sup>7</sup> that the extent of deterioration of the collagen varies considerably with the burial environment and is independent of the age of the specimen; for example, the most severe degradation of the organic component in mammoth ivories, as evidenced from the Raman spectrum and correlated with the visual examination and sample fragility, was shown to have occurred in a sample from a wet gravel pit dating from about 56Kya, whereas the collagen component from the 120Kya burial was as well preserved as that from the 12kya analogue. It transpires, therefore, that any allegation that attempts to suggest that Raman spectroscopy can be a prime indicator of the specimen’s age or antiquity *per se* is dangerous and must rather be treated “*cum grano salis*”!

## References

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