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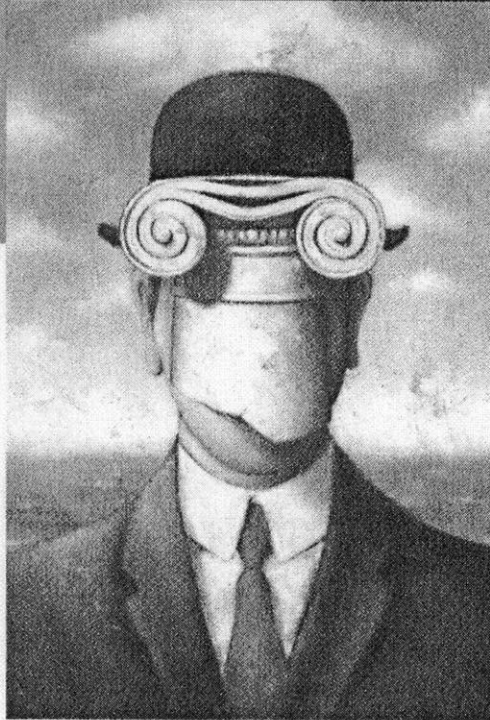
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MRM (MOBILE RAMAN MICROSCOPY): A POWERFUL NON-DESTRUCTIVE POLYVALENT IN SITU ARCHÆOMETRIC TOOL FOR MICROSPECTROMETRICAL ANALYSIS OF CULTURAL HERITAGE IN THE NEXT MILLENNIUM (ARCHÆORAMAN): GEOMATERIALS, BIOMATERIALS & PIGMENTS

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INTRODUCTION

Although of great potential for research in archæometry *sensu lato*, Mobile Raman Microscopy (MRM) is unfortunately still little-known amongst archæologists, art historians and many other researchers in the field of Cultural Heritage. A mini-symposium and workshop on this non-destructive technique, polyvalent *par excellence*, was organised by the first author for this 2nd International CNR/CNRS Congress on: "Science and Technology for the Safeguard of Cultural Heritage in the Mediterranean Basin". The topics presented are summarised here along with a few selected references.

THEORY AND APPLICATIONS OF MRM TO THE CULTURAL HERITAGE

The "Raman effect" spectroscopic technique, discovered by C.V.Raman in 1928, has only recently become *mobile*. Many archæologists, curators and administrators may not yet be aware that they can now analyse precious artefacts non-destructively, whether geomaterials, biomaterials or pigments, *in situ* on a micron scale without any sample preparation. Hence it may no longer be necessary to take risks to transport samples to a laboratory or to destructively extract samples, or even microsamples, for analysis elsewhere.

Most crystalline, molecular or amorphous materials,

whether solid, liquid or gaseous, change the wavelength of visible (or UV or NIR) light which impinges upon them. This concerns the vibrations of atoms and hence of the bonds between them. Different kinds of bond vibrations have different energies, and when transformed electronically the diffused light produces a spectrum where each peak (band) corresponds to a specific vibration. Like human fingerprints, a particular unique combination of peaks provides an unequivocal identification of the inorganic or organic species present by comparison with standard spectra in a database.

The "Raman effect" technique has been called by many different names and symbols. Here we use MRM to emphasise that the material can be observed through a Microscope objective for a 3-d microcartographical observation of all the different phases present *before* choosing the specific micron-sized particle to which the laser source light will be directed. The Mobility is manifested in two distinct ways. Optical fibres from 5 to 500 m long allow a remote "head" to be positioned in any orientation in order to analyse *in situ*: e.g. pigments: in Rock Art inside a cave; in frescoes on a temple ceiling; or in stained-glass windows on a cathedral wall. Likewise for almost any kind of artefact still inside Museum drawers. The fibres are connected to a Raman spectrometer which may be "portable" by one person or "transportable" by several people. Thus it is now even possible, with an MRM in a boat and fibres held by a diver, to

envisage analysing corroded metals in shipwrecks or gemstones embedded in statues still under water at Alexandria.

MRM is already established as a major powerful technique for archaeometry and ethnology as it provides, simultaneously, both chemical and physical characterisations (particularly helpful for provenancing). It has yet other advantages as it can even identify material *under* water, glass or mineral (e.g. microinclusions). It is especially useful to rapidly detect fakes, imitations or substitutes (e.g. drugs, gems, ivories, paintings).

Smith and Edwards (1998)¹ defined the term *ARCHAEO-RAMAN*[®] as denoting "Raman Spectrometry for the physical/chemical characterisation of geological or biological materials of importance in Archaeology", where the last term is used *sensu lato* to include Art and Architecture, as well as Anthropology and Ethnology, from prehistory through to the beginnings of the Industrial Revolution. Nine subjects were defined and denoted by a similar acronymic codename. The mini-symposium demonstrated examples from many of these subjects, ranging from Palaeolithic or Neolithic pigments through Egyptian mummies, Greek or Roman paintings and Celtic or Mudejar artefacts, to Medieval manuscripts and Renaissance glass:

- *GEMMORAMAN*: gemstones (rough, cut or mounted), cameos, corals, intaglios, jewellery².
- *CERAMORAMAN*: china, earthenware, faience, glass, porcelain, pottery, slags, tiles³.
- *PETRO-RAMAN*: axeheads, building columns, ceremonial stones, inlaid rock, millstones, mosaics, necklaces, sculptures, vitrified forts⁴.
- *METALLORAMAN*: corroded bracelets, coins, cutlery, necklaces, statues, swords, tools⁵.

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- *RESINORAMAN*: amber, glue, gum, oil, putty, wax⁶.
- *TISSUERAMAN*: papyrus, parchment, cotton, linen, wool, wood, bone, feather, fur, hair, horn, ivory, leather, nail, silk, skin, teeth^{7,8}.
- *FRESCORAMAN*: pigments on or in brick, ceramic, plaster, stone, stucco^{9,10}.
- *ICONORAMAN*: pigments/inks/dyes on or in bone, canvas, paper, skin, textile, wood^{11,12}.
- *VITRORAMAN*: pigments on or in enamel, glass or glaze¹³.

One may add *CLIMATORAMAN* as the study of the climatic deterioration of any of these materials. Indeed MRM can provide valuable information concerning the original materials, the corrosive agents involved, and the intermediate and final products; this may be of considerable assistance for the planning of restoration and conservation work.

CONCLUSIONS

Although many analytical techniques can be used to examine cultural heritage items, and some of these are indeed non-destructive and/or micron-scale and/or *in situ*, or share some other key feature with MRM, the combination of the advantages of MRM is surely unique. Directly identifying the species, and not only the chemical composition, is of immense benefit. Its polyvalence makes it appropriate for almost any type of scientific investigation of geomaterials, biomaterials or pigments with no spatial or temporal limitations. MRM may thus be expected to become one of the major *mobile* techniques for the cultural heritage in the next millennium.

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