Introduction

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The first chemical analyses of artworks and archaeological artefacts were accomplished historically and reported by Rene-Antoine Ferchault de Réaumur [1–4] in France in a series of publications between 1716 and 1739 and by Sir Humphry Davy [5] in the UK in 1815, respectively: the former appeared in the Memoires Academie de Sciences, Paris, on pottery, glass and porcelains and the latter on wall painting fragments from Pompeii was published in an issue of the Philosophical Transactions of the Royal Society in 1815. Both studies were directed at the identification of the pigments used by ancient artists and in both cases the complete destruction of the specimens was undertaken; Sir Humphry Davy especially commented on this undesirable although necessary aspect of his work. A classic review of Reaumur’s work and other early investigators has appeared in Colomban [6]. Even in 1922, the situation had remained unchanged and Eccles & Rackham [7] in their classic publication on the wet chemical analyses of English, Welsh, Chinese and Continental porcelains in the Victoria & Albert Museum’s collection had to destroy valuable and documentary pieces to achieve their objectives in the determination of the chemical composition of the selected specimens. The application of analytical spectroscopic and diffraction techniques in conjunction with microscopic interrogation to determine the elemental and molecular composition of artworks and archaeological specimens, usually with microsample region interrogation, is now well established and can be accomplished with minimal or no specimen sampling and additionally this can sometimes be performed in situ using portable instrumentation.

Raman spectroscopy was discovered by C. V. Raman in 1928, which gained him the Nobel Prize for Physics in 1930, hailed by Lord Rutherford as one of the four most important discoveries in physics made up to that time. Although initially having several advantages over infrared spectroscopy for molecular
characterization, the application of Raman spectroscopy to the analysis of art objects was not forthcoming until the advent [8] of the MOLE (Molecular Optical Laser Examiner) Raman microprobe in 1975 and reports of the determination of pigment composition on manuscripts in museum collections soon followed. It was several years before Raman spectroscopy was applied to genuine archaeological materials, when in 1991 the biodeterioration of exposed Renaissance frescoes [9,10] and later in the same year from biodeteriorated cave art [11] were reported. Then in 1995, Raman spectroscopic studies of archaeologically excavated biomaterials, specifically the mummified skin of Otzi the Alpine Iceman [12], dating from 5200 BC, were reported using a sample that would be later destroyed by accelerated mass spectrometry in a radiocarbon dating experiment. Since then the field has advanced rapidly [13] due to a wider selection of excitation wavelengths being made available, especially extension into the near infrared region where the competition of fluorescence emission is minimized, the use of microscopic examination to interrogate microgram and sub-microgram quantities of material, the availability of portable, transportable and, more latterly, hand-held instrumentation to effectively bring the laboratory to the specimen, art work or artefact and better detection systems and techniques to enhance the weaker Raman bands over often significant background emission which arises particularly from specimens taken from archaeological excavations and depositional environments [14–16]. Thus, several advantages of Raman spectroscopy are now manifest for the non-destructive or minimally destructive acquisition of materials identification from art works and archaeological objects which makes it an established technique of choice for researchers at the arts/science interface in association with historical provenancing—this has given rise to ‘forensic art’ investigations, which are now seen as an essential prerequisite for the establishment of a holistic analytical portfolio of an art work [17]. In this context, Raman spectroscopic data have been involved in several high-profile case studies.

In this special issue, published 201 years after Davy’s initial reports in an earlier issue of this same journal, some 14 research papers have been assimilated from 72 individual authors working in 13 countries and illustrate the diversity and range of objects and materials which all have a common theme of analytical Raman spectroscopy either used alone or in conjunction with other techniques. Some 11 of these papers are reporting studies of art works, in particular the composition of pigments and dyes in oil paintings, panel paintings, wall paintings, statuary and manuscripts. Other papers address the identification of gemstones, stained glass and the stratigraphic analysis of paint layers. Three other papers are specifically related to archaeological excavations and studies, on artefacts recovered from underwater excavations of a shipwreck, on tissue identification preserved in human skeletal remains and on the corrosion of gilded iron artefacts. Several papers reported in this issue address specific Raman spectroscopic techniques used to interrogate surface and subsurface deposits, such as SERS, HERAS and SORS and others report a combination of studies involving the combination of molecular Raman spectroscopic and elemental techniques such as TEM and XRF.

This special issue is not intended to encompass the whole range of applications in art and archaeology that are now accessible using Raman spectroscopy, but it will nevertheless give the reader a broad idea of the sort of information that can now be accessed using this powerful technique alone or in association with other techniques, either in situ using miniaturised instrumentation in museums or field locations or in the laboratory using standard bench-top spectroscopic apparatus.

References


3. Ferchault de Réaumur RA. 1729 *Second mémoire sur la porcelaine ou suite des principes qui doivent conduire dans la composition des porcelaines de différents genres et qui établissent les caractères des matières fondantes qu’on ne peut choisir pour tenir lieu de celle qu’on employe à la Chine*. Paris, France: Académie des Sciences.


