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Raman Spectroscopy in Art and Archaeology

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This paper gives a short overview of the Special Issue on *Raman Spectroscopy in Art and Archaeology* with the papers collected after the “3rd International Conference on the Application of Raman Spectroscopy in Art and Archaeology” held at the University Pierre et Marie Curie-Paris 6, Paris, France, August 31-September 3, 2005. The contributions present an extended view of works in the field, from technical developments, special analytical procedures to various applications.

KEYWORDS: Archaeometry; cultural heritage materials; biomaterials; minerals; SERS applications.

INTRODUCTION

Since the first conference of this series in London¹, 2001, the number of studies around cultural heritage involving Raman spectroscopy is in continuous increase as shown for example by the Journal of Raman Spectroscopy publications (20 articles between 2004 issue 10 and 2006 issue 7) or other journals²⁻³⁰ but also some specialised journals or publications in archaeometry, cultural heritage or conservation studies³¹⁻³⁵. As already mentioned³⁶ the instrumental improvements and the commercial availability of various devices are some keys of this success.

Among the devices abilities some are significant in these applications, as the opportunity to record spectra at very low laser power which respect sample integrity or the developments of mobile spectrometers. The latter seems actually to reach a maturity with at the technical point of view a clear feasibility demonstrated and the treatment of some specific investigations.

Since the first conference the audience continuously increases with in Paris about 120 participants and 88 abstracts selected for presentation representing 18 countries. This wide international representation is currently also notable. This underlines the Raman spectroscopists growing interest for ancient materials and the need of Raman characterisation ability in cultural heritage analysis.

Materials and questions diversify, furthermore Raman analyses are integrated in global analytical

strategies while established studies (as around pigments and minerals) continue their developments. This special issue introductory paper will present a brief overview of the papers collected after the “3rd International Conference on the Application of Raman Spectroscopy in Art and Archaeology” which reflect the present trends in the field. These 33 papers are classified in four topics chosen to underline these developments. In fact, some articles cover more than one topic with a certain degree of overlap, especially because studies are not first classified by materials, but rather by methodological originality or thematic investigations which advance the research in the field of cultural heritage.

TECHNICAL DEVELOPMENTS

Fluorescence emissions shading the Raman signal is a general limitation for Raman spectroscopy especially for studies dealing with “non-model materials”, which is chiefly the case with ancient materials. Hence different directions are explored, as the search for optimal excitation wavelength³⁷ or more non classic approaches with some mathematical spectra treatments³⁸.

An alternative way could be the increase of the Raman signal through Surface-Enhanced Raman Scattering (SERS). Actually widely used for weak Raman signal or low concentrated samples (especially in biology)³⁹, the developments of various SERS substrates and experimentalist’s skilfulness offer the opportunity to obtain Raman spectra from highly fluorescent materials and also from micro samples, allowing the application to

work of art dyes or lakes^{40,41}. It could thus offer an alternative to established techniques as High Performance Liquid Chromatography (HPLC), with the set up of specific non-extractive sample preparation and even direct SERS analysis on a single fibre sample⁴⁰. These experiments both exploit SERS specificities for low concentrated substances (and/or micro-sampling) and weak Raman signal against luminescence emission.

All these improvements also highlight the increasing interest for organic material studies. This uses the versatility of Raman spectroscopy among materials allowing to explore the large diversity of organic materials encountered in cultural heritage as presented by various papers of this special issue, with supports such as wood, textiles, paper, but also dyes, binders, colorants, etc. Previously the applications were limited by device efficiency (with degradation under laser irradiation) and/or material preservation state (low signal and high fluorescence signals).

Another specificity of the field is to develop analytical procedures which could be used by spectroscopy non-specialists. The devices and software offered by Raman companies are a first step, after to enlarge the community being able to manage spectra identification or treatment some automated or supervised procedures are developed. An example for spectra recognition is given by Castanys Tutzó *et al.*⁴².

MOBILE MEASUREMENTS

Examples given in this issue present the use of various commercial or prototype Raman devices. This technical opportunity reached by Raman spectrometers offer particular applications in the field of cultural heritage. The connection between Raman companies and end-users also generate some specific adaptations for our applications, like deported micro-analysis by optic fibre, visual control for sample and analysis, Laser power modulation, coupling with other technique, etc., or the development of prototypes/homemade devices for specific applications.

Mobile Raman spectroscopy is useful in several situations. On one hand, because each artefact is unique and because to achieve a meaningful level some problematic needs the examination of large sample collections, thus it is needed to reach some specific samples even in their environment. Sometimes it is easier to reach each object than to gather all in one lab. On the other hand, on-site measurements are requested for many objects which cannot be sampled and moved outside museums⁴³, or are none moving by nature because these are part of architectural monuments⁴⁴. In addition, progress in the studies of degradation processes will tend to propose alteration diagnosis procedures recurrently asked by conservators. It requires a simple operation which could be based on Raman spectroscopy because of its easy implementation and its mobile availability.

An important perspective for mobile Raman devices is offered by all other techniques actually developed to be also performed on site. It opens a larger object understanding and Raman spectra interpretation often not obvious with material complexity or heterogeneity. Additional to molecular information the opportunity to obtain chemical composition could be obtained with the coupling of X-Ray Fluorescence measurements (XRF) currently available as mobile. The work by Andrikopoulos *et al.*⁴⁵ present an original coupled XRF-Raman mobile device and its performances on Byzantine icons. To support the significance of on-site measurements Fremout *et al.*⁴⁶ show that conclusions obtained with on-site non destructive measurements could be compared with destructive laboratory experiments.

As a confirmation of its feasibility, even if it is not their main topic, other papers of this issue call upon on-site experiments.

COLOURS, PIGMENTS AND TECHNOLOGIES

The characterisation of pigments, binding media, etc., or generally the question of "colour" and techniques to obtain it, is a large field of investigation where Raman spectroscopy is regularly used.

Some work focuses on some pigments with the study of their synthesis and properties, as Sánchez del Río *et al.*⁴⁷ about the famous Maya blue pigment composed by a clay and indigo mixture with the question of its structure and stability.

Examples of studies concern a wide time span and diverse cultures, from rock art^{48,49} and wall paintings⁵⁰⁻⁵³ (which could also call for the use of mobile measurements), to various supports (paper⁵⁴⁻⁵⁶, wood⁵⁷). For numerous of these studies Raman analysis is involved in a general analytical strategy with complementary measurements as SEM-EDS, XRF, LIBS or XRD. Each technique with its performances or specific implementation will bring part of the answers.

The questioning about colour could also concern ceramics where aspects and colours are linked with their manufacturing technologies. From Mediterranean Antiquity⁵⁸, North America prehistory⁵⁹ to renaissance⁶⁰ and contemporary⁶¹, Raman spectroscopy could document technical history and production processes.

STUDIES DEALING WITH DEGRADATION PROCESSES

This field is under development, strongly linked with the conservation of cultural heritage, a technical and economical challenge (and probably social) for present and future societies. It is also on request for previsions over multi secular periods, with the use of ancient materials as analogues to provide experimental data for ageing numerical models. The next motivation is for partly or highly damaged materials and the attempt to get a better idea of the original object, as it is illustrated with a pigment identification⁶².

Degradation of numerous materials is explored from organic to mineral. Here are presented studies about waterlogged wood degradation and their conservation treatments optimisation^{63,64}. The diagnostic of degradation state is tackled for paper⁶⁵ or textile⁶⁶. The formation mechanism of patinas from long term natural alteration processes is explored with a case study on a stone object where raw material identification could be erroneous⁶⁷. With copper artefacts, patinas could not only come from natural processes but can be also the result of intentional artificial treatments for appearance modification which then emphasize technological performances. It is then necessary to make the share between these scenarios⁶⁸.

The questioning of alteration mechanisms through ancient artefacts and complementary techniques is presented for amber⁶⁹ with the complementarity of vibrational spectroscopies (IR and Raman) for a recovered molecular description of this fossil resin.

An additional specificity of Raman spectroscopy is exploited to revise iron atmospheric corrosion mechanisms⁷⁰. The Raman structural imaging gives access to a sharp description of material micro-heterogeneity and organisation. Because these features are closely related to degradation mechanisms these images, even obtained for low crystallised phases, bring statements to improve mechanisms descriptions.

FUTURE PROSPECTS

This field of research essentially multidisciplinary call for cooperation between historians, museum workers, conservation scientists and archaeologists on the one hand and spectroscopists, chemists, geologists, biologist, etc., on the other. Fruitful results are then obtain about cultural heritage but also some original by-products for other specialities via unusual experimental procedures/devices (because ancient material often offers challenges), weathering processes or material properties.

The role of Raman spectroscopy, thanks to instrumental improvements and its versatility among materials, will continue to develop in ancient materials studies. Its expansion is accompanied by devices which go out of the spectroscopy laboratory to museum conservation labs. Present researches also have to set up analytical strategies based on complementary methods where Raman spectroscopy is setting its role.

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