

Raman techniques applied to Cultural Heritage objects

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1. Introduction

Raman spectroscopy, improved with recent advances in microscopy as well as with implementation of non-conventional techniques such as SERS (Surface-Enhanced Raman Spectroscopy), has become a very useful molecular diagnostic technique in the Cultural Heritage field. Like the more known Infrared Spectroscopy, Raman spectroscopy is a *molecular* technique. This means that it provides information about the molecular compounds present in the samples under study, then enlarging the elemental analysis information supplied by other spectroscopic techniques, such as XRF, SEM-EDX, PIXE, and LIBS, usually employed in analysis of artistic objects¹. Raman microscopy is nowadays present in the Conservation and Restoration departments of the most renowned Museums and Libraries all around the world, where it is used as a non-destructive technique for (even *in situ*) diagnostics of different materials, ranging from inorganic pigments to biomaterials, employed in artifacts so different as manuscripts, paintings, textiles, ceramics, glasses, sculptures, stone monuments, and even mummies or underwater cannonballs, where degradation products can also be assessed. The strengths and limitations of the Raman technique, as well as the recent approaches to overcome some of its weaknesses, will be presented.

2. Experimental

The initial developments of Raman microscopy were carried out by french researchers at Lille University in mid 1970s² and commercially produced as MOLE by a spin-off company (Lirinord)³. Another french researcher of the "Centre de Recherche sur la Conservation des Documents Graphiques" in Paris, working with the instrument existing at Lille, was the first one to apply the Raman microprobe to the analysis of inorganic pigments⁴ even in manuscripts and archaeological materials⁵. As a "spécialiste de la couleur" he was very much interested also in the analysis of organic pigments and dyes and tried not only the micro Raman for their detection⁶ but also the, at this time recently developed, SERS technique⁷. The goal of employing SERS was to identify alizarin, a natural organic dye reluctant to be detected with conventional Raman technique.

Although commercially available at 1980s, the use of Raman microscopy was not so much extended, as the overall efficiency of detection of the Raman signal from the older Raman spectrometers was still relatively poor, because it was based on double or triple spectrometers with a large number of optical surfaces, and on multichannel intensified diode arrays, which are relatively insensitive detectors. The advent in earlier 1990s of: a) two-dimensional CCDs with up to 80 percent quantum efficiency of detection, and b) holographic notch filters which are wavelength specific and have the property of blocking out the unwanted Rayleigh scattering (laser line), had a crucial contribution to the spreading out and popularization of Raman microscopy, as a Raman microscope could be built on a single stage spectrograph and provide enhanced sensitivity. The reasons are explained next. As the mentioned filters possess a cutoff that readily permits approach to within 50 cm⁻¹ or less of the excitation line, monochromators with the high dispersion previously required to filter out the Rayleigh line could be replaced by a spectrograph system with a single grating only, leading to much greater efficiency of throughput. The benefits of CCD detector/notch filter spectrographs are that (1) low-powered air-cooled lasers can be used, which both reduce the costs of purchase and operation and make the entire system portable (since elaborate and fixed water-cooling systems for the lasers are not required); (2) the spectrographs are much lighter and much easier to realign than earlier double or triple grating systems; and (3) the time required to acquire significant data is greatly reduced, in some cases even to seconds. Such spectrographs can also be used for remote Raman microscopy in which a probe head assembly both delivers the excitation beam to the sample and collects the scattered radiation from the sample by means of fiber optics. Additionally, it is possible to produce a Raman spectral map collecting data from many different sample points on an inhomogeneous surface. The method involves direct two-dimensional imaging of an inhomogeneous surface by analyzing one or more of the Raman bands characteristic of a given component on the surface. Since late 1990s, Confocal Raman microscopy is also commercially available, with spatial resolution up to 1 micron in X, Y and Z directions.

The two limitations of the Raman technique are its relatively low sensitivity, and the competence of the much more intense fluorescence, which can hide the Raman signals. Removing or reducing the fluorescent background is accomplished either employing a longer wavelength laser (1064 nm) and interferometric detection (FT-Raman)⁸ or applying changes in wavelength excitation with posterior mathematical procedures, as in SERDS (Shift-excitation Raman difference spectroscopy) and SSRS (Subtracted shifted Raman spectroscopy)⁹. If any of these two last approaches are used, then it is possible to work in resonant Raman conditions (532 nm) with the corresponding advantage of Raman signal increasing. This is what has recently been reported for the detection of organic dyes and lakes¹⁰. There is another, practically, 36 years-old Raman technique, Surface-Enhanced Raman Spectroscopy (SERS)¹¹ which overcome the intrinsic problems above mentioned, because, when the sample under study is in close proximity to nanostructured metal surfaces, its fluorescence is quenched and its Raman spectrum is enhanced several orders of magnitude. Our research group in Madrid has pioneered the application of such technique to the characterization of the two most important families of natural organic pigments (anthraquinones^{12,13} and flavonoids¹⁴) which, due to their high dyeing capacity, are used in minute quantities not detectable by conventional Raman. Besides, we have developed a method of production of silver nanoparticles "on the dyed textile", through laser photoreduction of a silver nitrate water solution in contact with the sample, which has allowed us to success in the extractionless non-hydrolysis SERS detection of historical mordant dyes on model textil fibers dyed according original

old recipes¹⁵, as well as on an archaeological Coptic textile (6th-8th AD) from Egyptian origin, where alizarin has been clearly identified¹⁶.

3. Results

The “boom” of the application of Raman techniques to art and archaeology really started at the beginning of the 1990s, when the group of R.J.H. Clark at the Department of Chemistry of the University College London, began to analyze pigments on illuminated medieval manuscripts^{17,18}. His interest developed via a chance encounter in the 1990s during which he became aware of the important role that Raman microscopy might play in the arts and heritage sector. He was approached by a library asking him if he could establish whether two pigments on a manuscript were azurite or lapis lazuli, an issue that he was able to resolve by Raman microscopy within half an hour: “I called the library back with the answer – that they were both azurite – and they seemed almost incredulous that this issue could be settled so quickly and definitively”¹⁹. Cheryl Porter²⁰ was the book conservator who “provides the artworks for analysis and background knowledge and enthusiasm for the project”¹⁷. Since then, the field has greatly grown up, with increasing number of groups in research institutions, museums and libraries applying (and improving) the different Raman techniques - largely Raman microscopy - to diagnosis of materials of interest in Cultural Heritage. There are many good recent reviews²¹⁻²³ where one can find exhaustive information about application of Raman techniques to different artistic artifacts and related materials, as well as about existing Raman databases.

4. Conclusions

In fact, we are dealing with a multidisciplinary area of study where Raman developers, Raman spectroscopists, chemists, conservators, restorers, art historians, archaeologists and others (even, forensic and/or policy scientists where forgeries are suspected), employing also other complementary techniques but Raman playing a very important role, form a team to “solve mysteries”. It is really a fascinating work!!

5. References

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- [19] <http://www.chem.ucl.ac.uk/people/clark/documents/bakerianlecturepiece.doc>. Prof. Clark was awarded in 2008 the prestigious Bakerian Lecture which is the Royal Society's premier lecture in the physical sciences and dates back to 1775. In 2009 he was the winner of the Sir George Stokes award “for his outstanding contribution to the application of analytical science to the arts and archaeology through his development of Raman microscopy for the identification of pigments”
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