

Application of Raman microspectrometry to art objects

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Raman microscopy is a powerful tool for the study of art objects. The analytical advantages and the specific experimental procedures are reported. Some examples are given for the identification of pigments and dyes on microsamples or *in situ*.

Introduction

The study of art objects by Raman microscopy [1] is a recent area of research since the first reports were published in 1984. They concerned the identification of pigments. The increasing number of papers during the last five years reflects the extension of this analytical technique. Consequently a session devoted to "Applications in Art and Archaeology" took place for the first time at the XVIth International Conference of Raman Spectroscopy (1998) [2].

The knowledge of the materials involved in our artistic and cultural patrimony, namely the pigments, allows a better understanding of our civilisation, and an improvement of the restoration and conservation methods. But, until recently, the study of works of art remained mainly the concern of research by art historians because the scientific techniques required a quantity of materials unacceptable for the integrity of the works. This limitation has been removed by the improvement of physicochemical microtechniques. Among them, Raman spectrometry is one of the most powerful, due to its characteristics.

Advantages and limitations of Raman microscopy for the study of art objects

Since Raman microscopy is an optical spectrometry, it has two main characteristics, which are very well suited to such studies. First, the analysis is non-destructive. It can be performed without sample preparation. Neither special coating or a controlled atmosphere is necessary. The analysis causes neither damage nor alteration, so it is possible to continue the investigation of the same sample, even on the same spot, with another laser wavelength or with another tech-

nique. The second advantage is the capability to focus the excitation beam on a very small spot, whose diameter depends on the selected laser wavelength and the aperture of objective, typically $\sim 1 \mu\text{m}$. Such a spatial resolution is required by the size of pigment grains embedded in pictorial layers. Besides, with the same optical microscope and the same focus point, it is possible to lighten the pictorial layer both with a white light, for observation and choice of grains seen with their true colours, and with a laser beam, for analysis of these grains.

The Raman analysis gives molecular information and leads to an unambiguous identification. For example, it is possible to distinguish between two green pigments with the same elementary analysis (copper, carbon and oxygen), like malachite and verdigris, copper carbonate and acetate respectively, or between two white pigments with the same stoichiometry (TiO_2) but different crystalline structures, such as anatase and rutile.

If the low sensitivity of Raman spectroscopy had long been a major limitation, the detectors have been tremendously improved and it is now possible to obtain the spectra of pigments on a microspot in a few tens of seconds. Besides, a clever choice of the laser wavelength may induce a resonance Raman effect and an enhancement, by sometimes several orders of magnitude, of the intensity of some bands. This effect appears when the excitation wavelength is close of that of an allowed electronic transition in the product. The coloured products, like pigments and dyes, absorb in the visible light and thus are good candidates for a resonance Raman effect.

The main problem is the high level of background fluorescence in many experiments on artefacts. It occurs often in impurities or organic materials of the sample. This problem is difficult to solve. The logical procedure would be to change the laser wavelength in order to separate the Raman and the fluorescence spectra since electronic fluorescence is excited by a specific wavelength, whereas the Raman spectrum varies in wavelength like the laser excitation. Sometimes, a prolonged exposure to the laser excitation may bleach the fluorescence and decrease its level. However, the easiest way is to investigate different points on the sample until finding a spot with a low fluorescence emission because materials, which give birth to fluorescence may not be evenly distributed. For example, archaeological samples of wall paintings found in excavations are usually contaminated by the surrounding soil, but differently according to their location. But none of these methods can be generalised

to any sample and with any spectrometer. Recently, interesting methods [3], based on mathematical treatment of data for suppression of background fluorescence, have been reported and applied to the Raman identification of dyes in ancient papers or pigments.

Identification of compounds and connected problems

The identification of compounds by Raman spectroscopy relies on the comparison between their Raman spectra and a database of reference spectra. Each compound is characterised by spectral fingerprint. The wavenumbers of the bands are constant whatever the experimental procedure, but their relative intensities in the spectrum may be affected by several factors. As mentioned above, the resonance Raman effect leads to an enhancement of some bands, those of chromophores, which modifies the visual features of the spectrum. Figure 1 shows spectra of indigotin (blue dye extracted from plants like weld or indigo), with two excitation wavelengths. Only a careful visual comparison reveals that these spectra come from the same product. Usually, spectrometers are equipped with Ar⁺ lasers ($\lambda = 0.459, 0.488, 0.514 \mu\text{m}$), or He-Ne lasers ($\lambda = 0.632 \mu\text{m}$). However, the new spectrometers have also laser diodes at $\lambda = 0.785$ or $1.06 \mu\text{m}$. An ideal database should contain the spectra of reference products obtained with these different excitation wavelengths.

Another phenomenon, which can affect the relative intensities in a Raman spectrum, is the orientation of a crystalline compound with respect to the direction of the electric field of the excitation laser. This physical parameter is not obvious for crystalline micrograins of pigments embedded in a pictorial layer. Figure 2 shows spectra obtained with two quadratic orientations of a microcrystal of malachite (green pigment of copper carbonate). A rapid comparison of these spectra, especially in the range $3\,300\text{--}3\,500 \text{ cm}^{-1}$, would lead to the conclusion of the presence of two compounds with different amounts. Therefore, a possible alteration of the band intensities should always be kept in mind when analysing Raman spectra.

Identification needs a Raman database. Materials for works of art are extremely various and concern as well pigments and dyes, also supports (textiles, wood, ivory, stone, parchment, paper...), media, and adhesives (resins, glue, lime, gums...). Concerning pigments, a useful reference library [4] has recently been published for more than 60 pigments, among the most common ones up to 1850, mainly mineral and natural. Very few Raman spectra of dyes are known. Other Raman libraries have been published on specific fields: gems or minerals [5]. Some reference spectra with laser excitation at $1.06 \mu\text{m}$ concern mainly natural materials [6]: waxes, resins, gums, etc. However the expansion of this technique is hampered by the lack of a large database.

Experimental procedure

The best procedure to analyse components of art objects is to obtain Raman spectra directly from them. Therefore the object has to be brought to the laboratory, put on the stage of the microscope and then analysed. That implies that the object is moveable, not too heavy nor too big for the stage. This procedure is possible for many objects, fragments of wall paintings, shards of pottery, miniatures, etc. For these investigations, it is better to use an objective with a long focal length. Its solid angle of collection is smaller than that of a classical one but the gap between the object and the lens allows moving the object and avoiding damaging shocks. The visual examination and Raman analysis of the object may be done for numerous points in order to control its homogeneity.

This procedure has been adopted for objects with a transparent cover, either external layers impossible to remove (glazes in miniature [7]), or a protective glass whose removal may be dangerous (for pastels [8]). The collected light contains the spectra of both the pictorial and transparent layers. The use of a confocal system allows the avoidance of recording the spectrum of the latter.

But it is often impossible to proceed in this way. The art object may be too fragile to be taken out of museums or libraries, or impossible to move out like wall paintings or heavy monuments. Then it is necessary to resort to microsampling. Raman microscopy allows to study the samples whose size is so tiny (tens of micrometers) that the removal does not mutilate the artefact and is approved by the curator. The sampling is done with a tungsten needle, under microscope (with a surgical scalpel for wall paintings). This procedure is approved by the *Bibliothèque nationale de France* for the study of its manuscripts. It needs one manipulation, without risks in contrast to the strong pressure that would need to be applied on the manuscripts leaf in order to prevent any motion of the leaf, so as to focus on the same point during the whole time of acquisition of the Raman spectrum.

Applications

A few fields of applications have been chosen in order to illustrate the wide potentiality of this technique.

Pigments in manuscripts

The main applications concern the identification of pigments on various kinds of supports. Pigments are the most significant part of pictorial layers and give important information about artists, artistic schools or technological evolution; mainly inorganic compounds, their Raman spectra are often strong and easily recorded. Therefore they are good candidates for Raman identification. On the other hand, manuscripts are also good candidates for these studies since

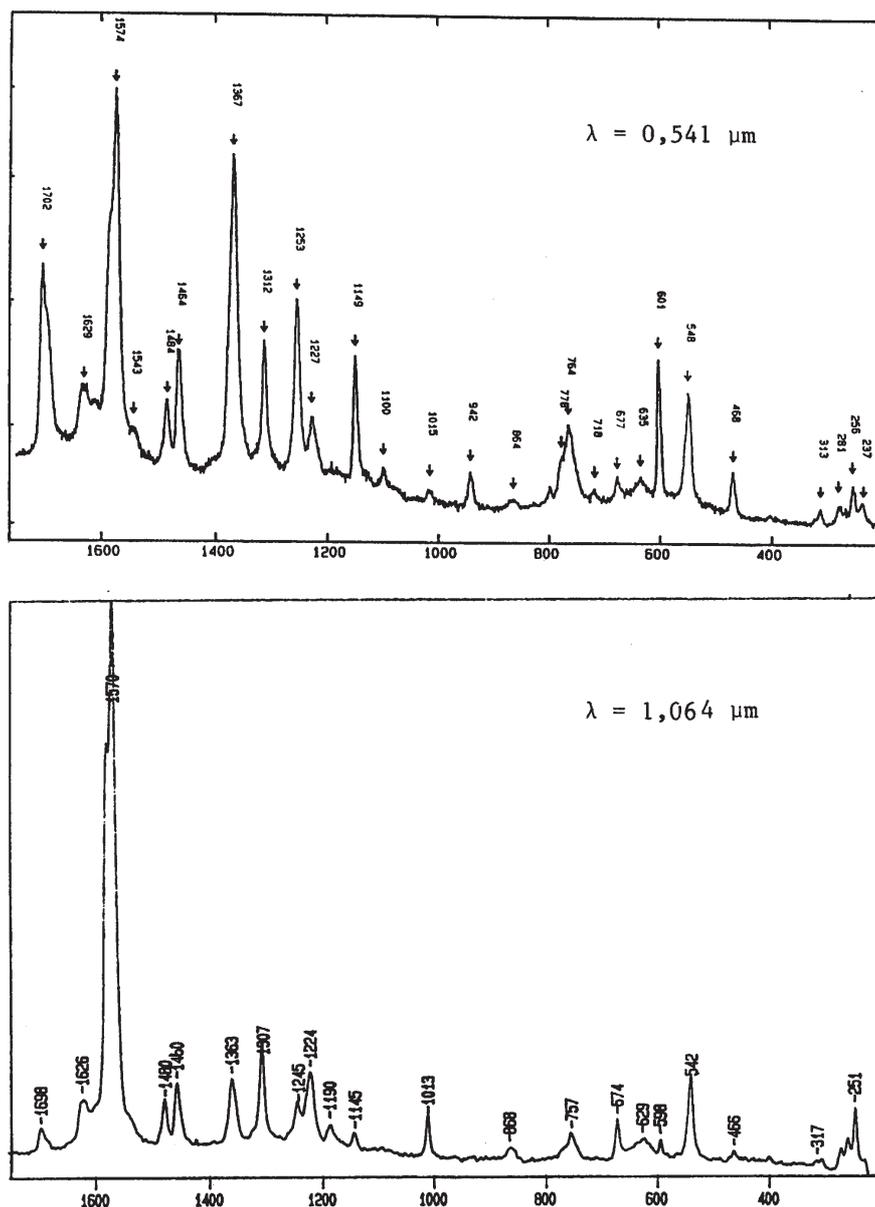


Figure 1. Raman spectra of indigotin obtained with laser excitation at two wavelengths.

the microsampling can be done on blots or offsets on the opposite page. Furthermore the pictorial layer contains little binder, hence the fluorescence is expected to be low. At least, the technical mediaeval literature indicates the products that the painter should use and these products are often mineral. But these advantages are not used enough and few studies [9] have been published, most of them concerning only single manuscript.

In contrast, our studies [10] of blue pigments concerned some thirty manuscripts, precisely dated and localised, of four French abbeys at Auxerre and Cîteaux (Burgundy), Fécamp (Normandy) and Corbie (Picardy), from the year 1000 to the end of the twelfth century. Two pigments have been identified. At the beginning of the eleventh century, the blue pigment changed from a vegetal product, indigotin,

from a local plant, weld, to ultramarine extracted from lapis lazuli, an expensive aluminosilicate coming from East Asia. Their Raman spectra are totally different (Fig. 3). Ultramarine is coloured by ions, S_3^- and S_2^- and its Raman spectrum exhibits only bands of these chromophores. At Auxerre, a miniature in a manuscript *c.* 1000 was decorated with the two products, with meaningful utilisation since the important person, saint Germain, deserved ultramarine, while the abbot was painted with less valuable indigotin. In the manuscripts studied for the other abbeys, we identified one product or the other. Different hues may be obtained, either by dilution in a medium to lighten the blue without addition of white pigment, or by mixing with black carbon to obtain a grey-blue. The picture on the front page of this issue shows Félix, one of the artists who used ultramarine at Corbie in the XIIth century. In the palette which he holds,

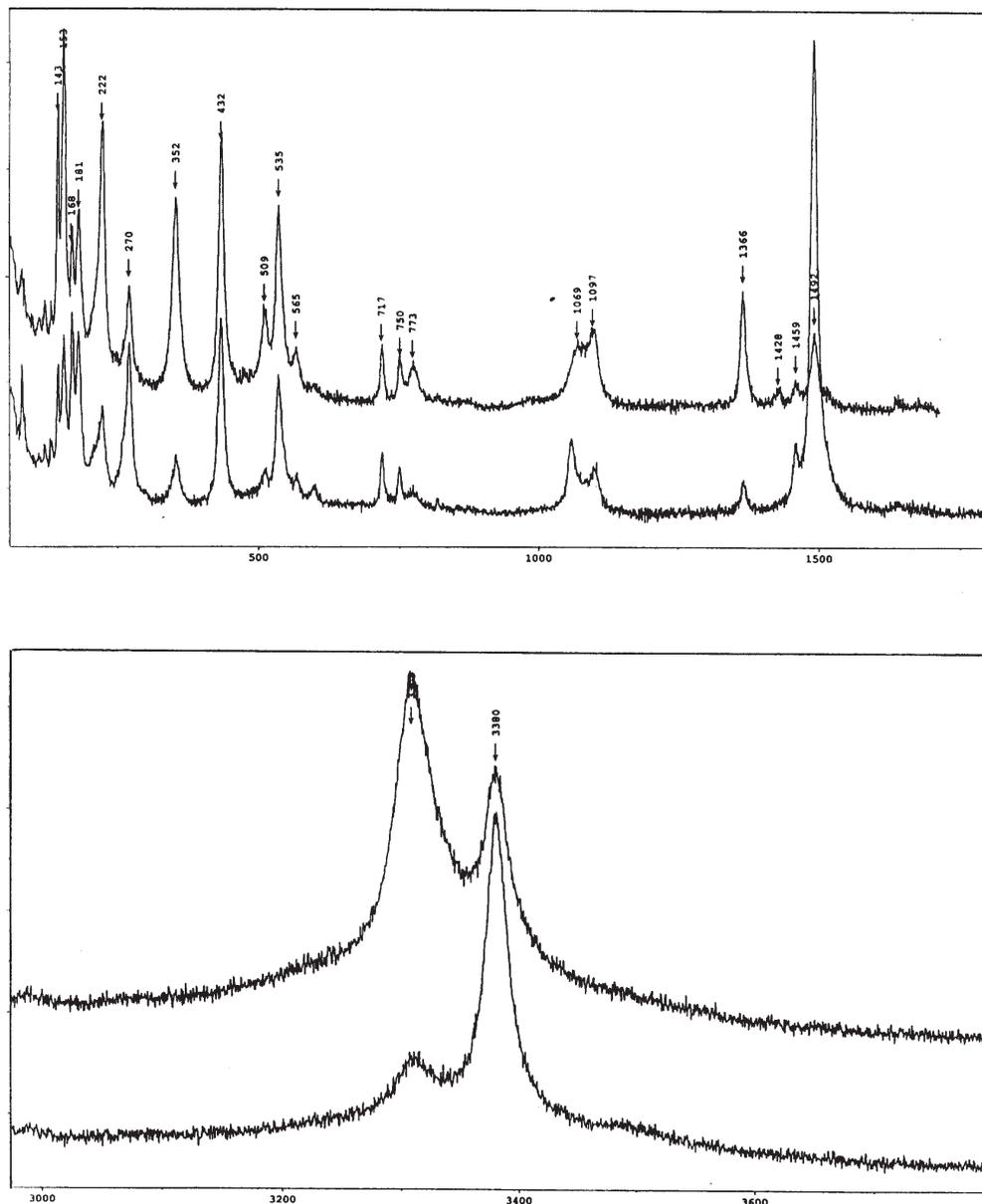


Figure 2. Raman spectra of malachite, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, with two quadratric orientations of laser excitation.

the blue pigment is only ultramarine, which he used to decorate this manuscript.

A similar study was performed on red pigments, but only for the Fécamp manuscripts. It revealed that, in the mid-XIth century, lead minium Pb_3O_4 (and/or PbO) was replaced by mercury sulfide, HgS , called vermilion by painters. The reason for the change is not understood yet.

Pigments in wall paintings

Iron oxygenated derivatives have been used as pigments since Neolithic paintings. Elementary analysis can indicate only the presence of iron and it is necessary to use Raman spectrometry to get some details about their composition. Spectra of brown-red samples from a Gallo-Roman *villa*

near Reims show a band around 650 cm^{-1} , assigned to magnetite, Fe_3O_4 , a brown compound, which changes the hue of red oxide Fe_2O_3 .

Some Chinese pictures of the beginning of our era have geometrical decoration with light and dark red lines. The pigment is everywhere red iron oxide, but with different degrees of quality seen on spectra (Fig. 4), perhaps an indication of several ways of preparation or various initial products.

Synthetic pigments

It is usually thought that pigments begin to be extensively synthesised in the mid-XIXth century. But the assumed first

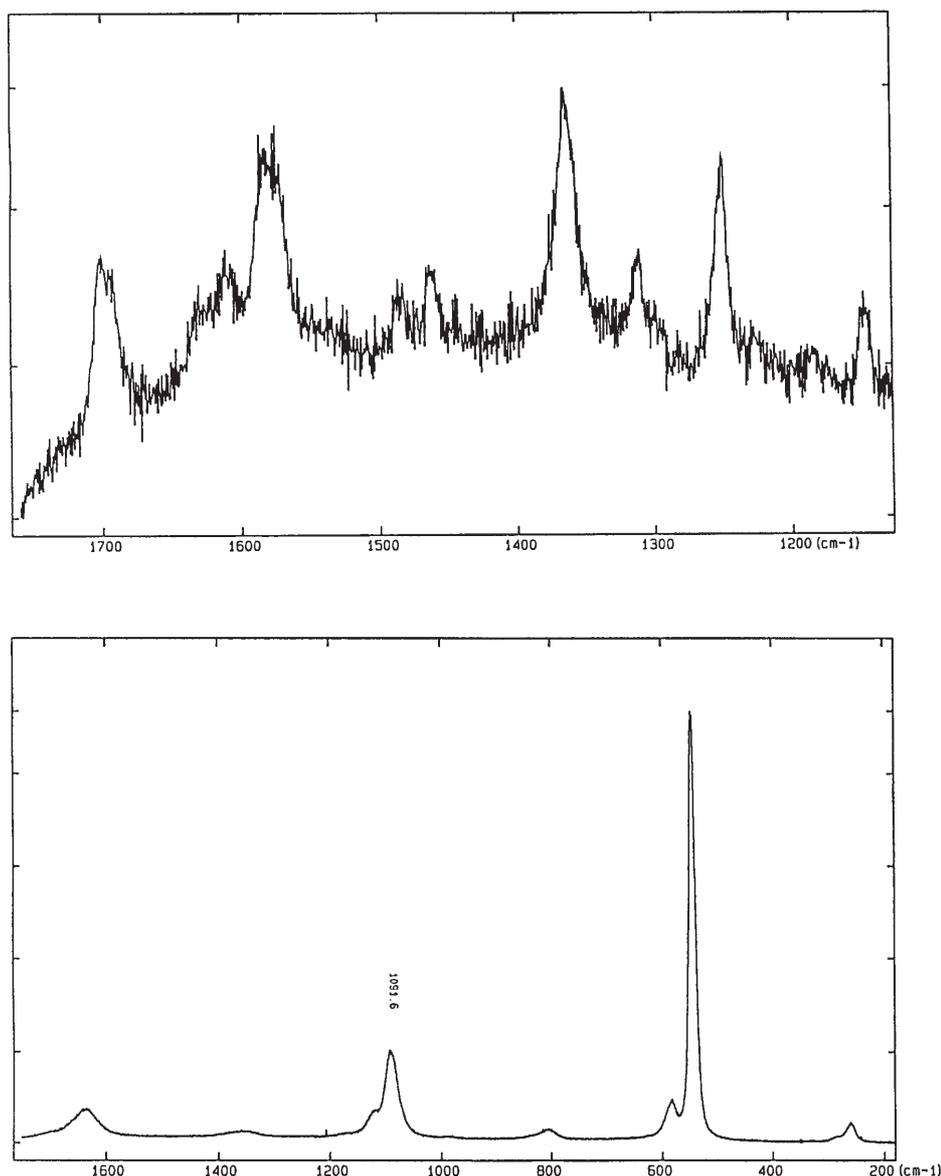


Figure 3. Significant ranges of Raman spectra of two blue pigments in manuscripts. Bottom: ultramarine; top: indigotin.

manufactured pigment is much older: the Egyptian blue, CaCuSiO_3 , was contemporaneous of the Great Pyramids, 2700 BC. Its Raman spectrum [11], now well-known (Fig. 5), allows to identify it in the pharaonic era, but also to follow its use in Roman, Gallo-Roman, and until Coptic wall paintings. Some questions were raised about the synthesis atmosphere. Samplings from raw pigment balls found in excavation were included in resin and analysed by Scanning Electronic Microscopy. In some micro-areas, only copper has been identified. Raman microscopy on these spots identifies copper oxide, CuO , and never Cu_2O . This result allows us to conclude that the Egyptian blue was synthesised in an oxidising atmosphere.

Synthetic pigments are useful to detect forgeries but one needs accurate knowledge of the date of the first synthesis, eventually confirmed by patents. Their identification in art objects assumed as older leads to a suspicious conclusion. The anachronistic presence of a pigment may have two explanations: either the object is a fake or it has been altered with products when restored. In a Roman painting [12], an art historian detected a contradiction between a floral ornament consistent with the Roman style, and a warrior with some very strange details. Analysis of pigments allowed to clarification of the matter. Pigments in the first part are Egyptian blue and iron oxides, typically Roman. In contrast, the warrior was painted with ultramarine, never identified in

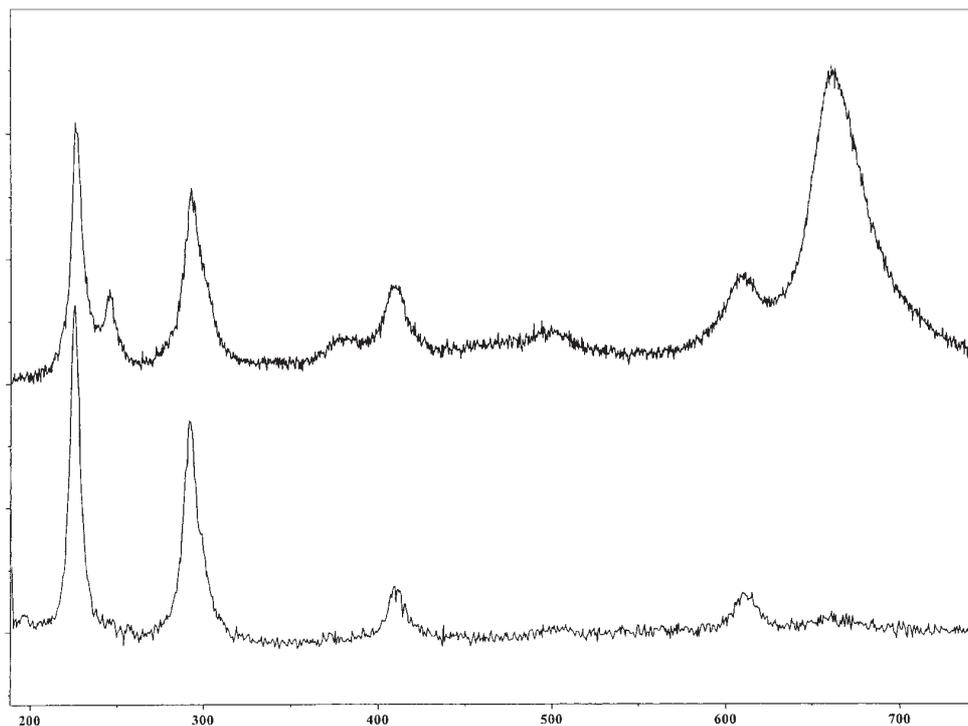


Figure 4. Raman spectra of red and red brown samples from Chinese wall-painting. Bottom: presence of Fe_2O_3 ; Top: presence of $\text{Fe}_2\text{O}_3 + \text{Fe}_3\text{O}_4$ (band at 660 cm^{-1}).

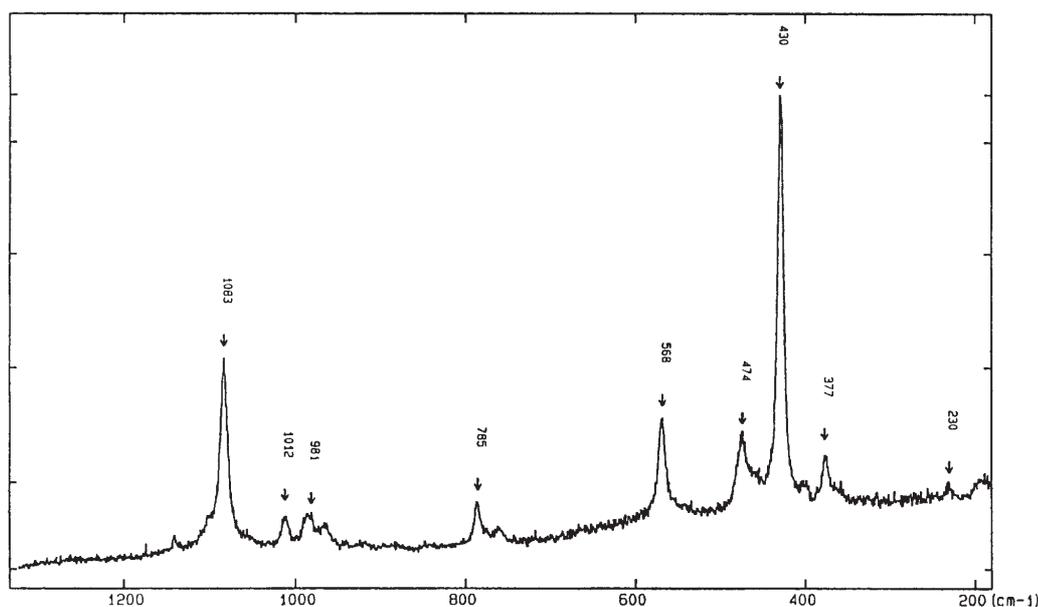


Figure 5. Raman spectrum of Egyptian blue, CaCuSiO_3 .

Roman civilisation yet, and titanium white and phtalocyanin, synthesised in XXth century. This clearly indicates a recent addition on an old painting with an unambiguously original location. Another example is the characterisation of Prussian blue, first synthesised around 1710, in the mantle of a Virgin painted in the XVth century.

Dyes on fibres

A new field of research concerns the identification of dyes, used in papers or textile fibres. The process of dyeing needs the presence of a metallic ion, the mordant, which links the dyeing molecule to the fibre. The nature of the metal affects

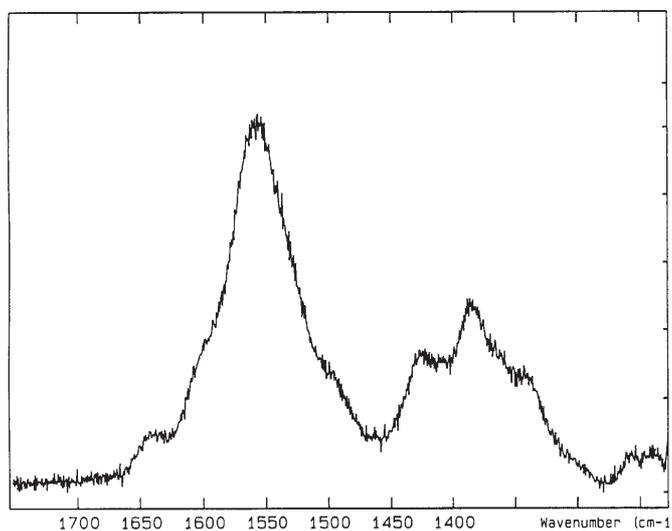
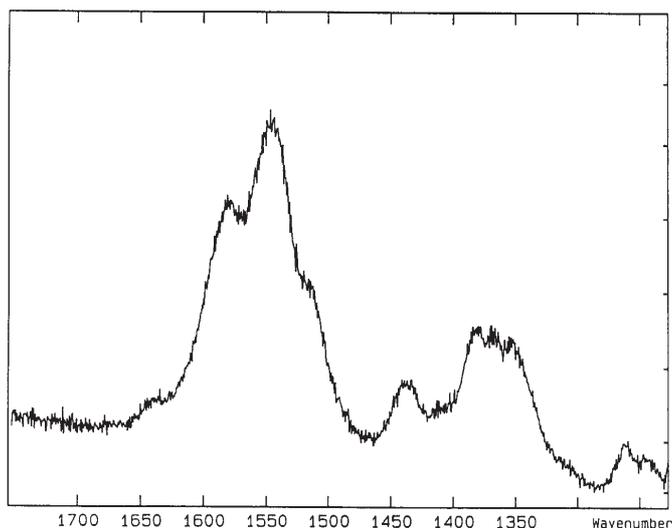


Figure 6. Significant ranges of Raman spectra of haemateine. Bottom: copper mordant; top: aluminium mordant.

the mode of fixation and hence the vibrational state of the molecule. For the same dye in papers [13], haemateine, and two mordants, copper and aluminium salts, the Raman spectra are different (Fig. 6). Similar studies have begun on textiles. The interpretation of Raman spectra of historical blue textiles [14] has allowed the identification of the dye indigotin, and proving the change in the planarity of the molecule when fixed.

The Raman results, along with other analytical methods [15], attain their full significance only when associated with specific investigations conducted by art historians.

Conclusion

The advantages of the Raman microscopy and its new technological advances should contribute to increase its applications to art objects. Two main improvements are the addition of an optical fibre to the spectrometer in order to analyse almost any part of objects in wherever location, and the use of near IR laser ($\lambda = 1.06 \mu\text{m}$) to eliminate fluorescence in most of the samples.

Raman microspectrometry allows a new approach of art objects without damaging them. The informations obtained at the molecular level shed light on fields as different as the making of an object, the mapping of the use of a compound according to the era or location, or even the detection of the alteration of an artefact.

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References

1. Coupry, Cl.; Brissaud, D. In: *Raman Microscopy* (Turrell G, Corset J, eds); Academic Press; London, 1996, chapter 10, 421-453.
2. Section 13. *Proceedings of the Sixteenth International Conference on Raman Spectroscopy* (Heyns A.M., ed) Cape Town (South Africa), September 6-11, 1998.
3. Bell, S.E.J.; Bourguignon, E.S.O. *Analyst* **1998**, *123*, 1729; Soneira, M.J.; Yuferra, J.M.; Ruiz-Moreno, S. *Applied Spectr.* **1999**, *53*, 365-371.
4. Bell, I.M.; Clark, R.J.H.; Gibbs, P.J. *Spectrochim. Acta* **1997**, *53A*, 2159-2179.
5. Schubnel, H.J.; Pinet, M.; Smith, D.C.; Lasnier, B. *Revue de Gemmologie* numéro hors série, **1992**.
6. Edwards, H.G.M.; Farwell, D.W.; Daffner, L. *Spectrochim. Acta* **1996**, *52A*, 1639-1648; Edwards, H.G.M.; Falk, M.J.; Sibley, M.G.; Alvarez-Benedi, J.; Rull, F. *Spectrochim. Acta* **1998**, *54A*, 903-920.
7. Derbyshire, A.; Withnall, R.; *J. Raman Spectrosc.* **1999**, *30*, 185-188.
8. Guineau, B. *Preprints of 7th Triennial Meeting ICOM Committee for Conservation*, Copenhagen (Denmark), September, 10-14 1984, 84.14.29-84.14.33.
9. Burgio, L.; Ciomartan, D.A.; Clark, R.J.H. *J. Mol. Structure* **1997**, *405*, 1-11; Clark, R.J.H.; Gibbs, P.J. *Chem. Commun.* **1997**, 1003-1004.
10. Guineau, B.; Coupry, Cl.; Gousset, M.T.; Forgerit, J.P.; Vezin, J. *Scriptorium* **1986**, *XL*, 157-171; Coupry, Cl.; Etude des pigments du manuscrit Paris, BN, lat. 12303, In: *L'école carolingienne d'Auxerre* (Iogna-Prat, D.; Jeudy, C.; Lobrichon, G.

- eds) Beauchesne, Paris, 1992, 119-126; Coupry, Cl. *In : Manuscrits et enluminures dans le monde normand (XI-XV siècles)* (Dosdat, M.; Boué, P. eds) Presses Universitaires, Caen (France), 1999, 69-79.
11. Pagès-Camagna, S.; Colinart, S.; Coupry, Cl. *J. Raman Spectrosc.* **1999**, *30*, 313-317.
12. Barbet, A.; Coupry, Cl.; Lautié, A. *In : Roman Wall Painting, Materials, Techniques, Analysis and Conservation* (Béarat, H.; Fuchs, M.; Maggetti, M.; Paunier, D. eds) University, Fribourg, 1997, 257-268.
13. Coupry, Cl.; Lautié, A.; Perkinson, R. *Technè* **1996**, 99-107.
14. Coupry, Cl.; Sagon, G.; Gorguet-Ballesteros, P. *J. Raman Spectrosc.* **1997**, *28*, 85-89.
15. Bussotti, L.; Carboncini, M.P.; Castellucci, E.; Giuntini, L.; Mando, P.A. *Stud. Conserv.* **1997**, *42*, 83-91; Bruni, S.; Cariati, F.; Casadio, F.; Toniolo, L. *Spectrochim. Acta* **1999**, *55A*, 1371-1377.