Characterisation of the pigments on works of art and archaeological materials can be critical in finding solutions to problems in restoration, conservation, authentication and dating, and many techniques have been developed for this purpose. Over the past decade or so Raman microscopy has emerged in response to recent advances in optics and detectors, as one of the best of these techniques, on account of its high spatial (*c.* 1 micrometre) and high spectral (*c.* 1 cm^{-1}) resolution, together with its specificity, sensitivity (via CCD detectors) and the fact that many items may be examined *in situ*. The Raman effect will be discussed, together with the recent advances in instrumentation, and examples of items of high interest which have been studied recently, including Anglo-Saxon manuscripts, several Gutenberg Bibles, a series of medieval maps, postage stamps and a painting by Vermeer, as well as several items found to be forgeries, notably Egyptian papyri, maps and other philatelic materials.

Raman microscopy techniques for the characterisation of pigments

Tracey D. Chaplin & Robin J. H. Clark

Introduction

The identification of the pigments on works of art and archaeological materials is fundamental to furthering our understanding of an object's history or an artist's technique, solving certain conservation and restoration problems and providing evidence for the dating and attribution of artefacts. Many analytical techniques have been employed over recent years to achieve such aims. These include those which detect the elements present, such as scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX), X-ray fluorescence (XRF) and particle-induced X-ray or γ-ray emission (PIXE/PIGE) analysis, laser-induced breakdown spectroscopy (LIBS), and those which identify the compound present, such as infrared spectroscopy, Raman microscopy, X-ray diffraction (XRD) and polarized light microscopy (PLM).

Of these techniques, Raman microscopy may be considered as the single most effective tool in pigment identification, as it is non-destructive, non-invasive and can be used *in situ* on an object. All of these features are often essential when having to consider the ethical problems associated with conservation and restoration of objects such as manuscripts. Raman microscopy also has the advantages of high reproducibility, high sensitivity, high spatial resolution (≤ 1 μm) and high spectral resolution (≤ 1 cm^{-1}). These features allow the different components of pigment mixtures to be determined readily. The portability of certain Raman instruments which retain most of these features has enabled the technique to become even more important, the instrument being moved to the object rather than vice versa.

It was Raman who was awarded the Nobel prize for physics in 1930 for this discovery.

Here we will introduce the science on which Raman microscopy is based, the instrumentation currently in use, and recent applications of the technique to solving problems in the artworld. Other reviews of the application of Raman spectroscopy to the artworld are also available (for example, see Clark 2005; Clark 2002; Smith & Clark 2001).

The Raman Effect

Raman spectroscopy is an experimental technique which measures the change in energy of light scattered by a sample. The details of the technique will be treated briefly here and readers are referred to more in-depth explanations found in the wider literature such as Hendra *et al.* (1991), Turrell & Corset (1996) and Long (2002).

In brief, Raman spectroscopy involves illuminating a sample with a monochromatic beam of light (which is described as having frequency ν_0 and photon energy *E*). Most of the incident light, consisting of a stream of photons, is scattered by elastic collisions with the sample molecules, no change in energy being involved (known as Rayleigh scattering). However, a very small percentage of the incident photons (<<1%) is scattered *inelastically*, i.e. the incident photons gain or lose a small amount of energy, *e*, by interaction with the sample. This type of scattering is named Raman scattering after C.V. Raman, who discovered the weak effect during his research on molecular light scattering (Raman & Krishnan 1928). Almost simultaneously, Landsberg and Mandelstam independently reported the same effect in quartz (Landsberg & Mandelstam 1928). However, it was Raman alone who was awarded the Nobel prize for physics in 1930 for this discovery, with his name being permanently ascribed to the effect. The Raman effect describes the inelastic scattering of photons by a sample and it is by Raman spectroscopy that one is enabled to measure the energy (*E-e* or *E+e*) of these inelastically scattered photons.

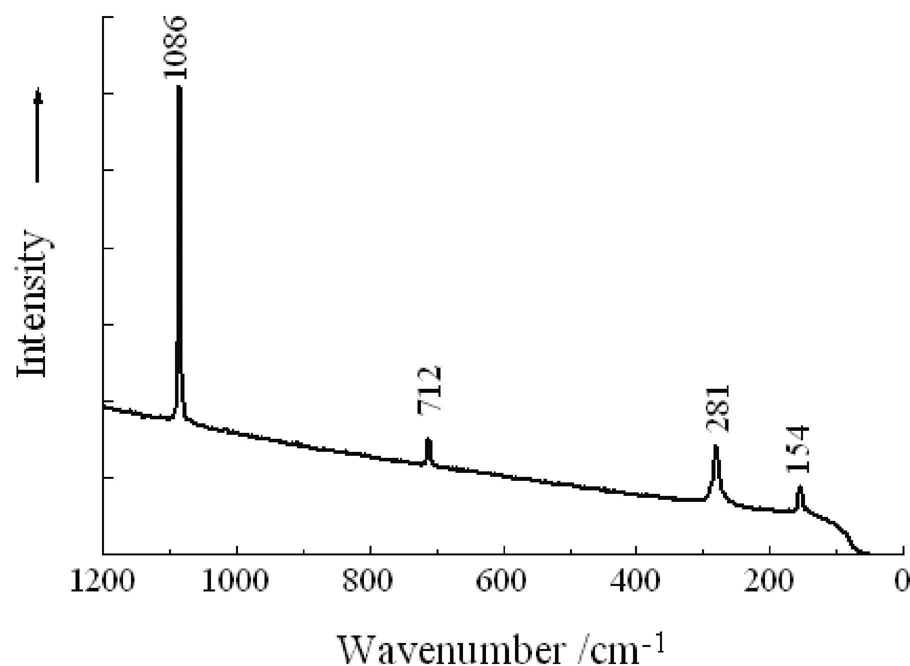

Fig 1. Raman spectrum of calcium carbonate (calcite, $CaCO_3$) showing bands at 1086 and 712 cm^{-1} related to the vibrational modes of the carbonate ion (CO_3) and bands at 281 and 154 cm^{-1} related to external modes (Porto et al. 1966; White 1974).

Each material is composed of a set of atoms bound together in a specific way which distinguishes it from any other material. The atoms in a material vibrate about their equilibrium positions in a number of particular ways at frequencies which are related to the masses of the constituent atoms and to the geometry and the strengths of the interatomic and intermolecular bonds. Thus each material is characterized by a particular set of vibrational frequencies unique to that material. The change in energy of a photon scattered inelastically by the material is associated with the transfer of energy to or from the material. By measuring the energy changes of a set of scattered photons, i.e. the Raman spectrum, we can determine the characteristic vibrational frequencies of the sample. The Raman spectrum is unique to each material, and can therefore be treated as a 'fingerprint', thereby allowing characterisation of that material.

For example, Figure 1 shows the Raman spectrum of calcium carbonate (calcite, $CaCO_3$), in which four of the bands are clearly observable at 1086, 712, 281 and 154 cm^{-1}. The Raman spectra collected have to be compared with those obtained previously from reference materials. Published libraries of spectra are now widely available in the literature on historical pigments (Bell *et al.* 1997; Burgio & Clark, 2001), enamel and glazing pigments (Colomban *et al.* 2001), modern synthetic pigments (Vandenabeele *et al.* 2000a), modern inks (Claybourn & Ansell 2000), gums, waxes, varnishes, resins and other binders of historical and archaeological importance (Burgio & Clark 2001; Edwards *et al.*, 1998, 1996; Edwards & Falk 1997; Vandenabeele *et al.* 2000b), minerals (Griffith 1987; Coleyshaw *et al.* 1994; de Faria *et al.* 1997) and plant fibres (Edwards *et al.* 1997a).

Modern instrumentation for Raman spectroscopy

As already mentioned, Raman scattering is a very weak phenomenon which requires an intense monochromatic light source to generate a readily detectable effect. Historically, mercury arc lamps were used to provide a relatively intense light source, although they were a slow and inefficient method of generating Raman scattering. In the 1960's the newly discovered laser was first applied to Raman spectroscopy. Lasers, which emit intense and coherent beams of monochromatic light, have a much greater power flux density than traditional sources (for example, the power flux density of a Hg lamp is *c.* 1 W cm^{-2} whereas that for a typical continuous-wave argon ion laser is *c.* 10^5 W cm^{-2}). For this reason significantly more intense Raman spectra can be obtained by the use of an incident laser rather than a mercury lamp as the excitation source. Also, the use of lasers has allowed a wider choice of excitation lines, with wavelengths ranging from 351.1 to 1064 nm.

The Raman spectrum is unique to each material, and can be treated as a 'fingerprint', thereby allowing characterisation of that material.

The use of lasers on works of art may be thought to be possibly hazardous to the work of art. However, for Raman spectroscopy the laser power is kept to a minimum, never exceeding 4 mW at the object or sample surface, thus minimizing any potential risk of laser-induced degradation. To reduce any potential risk further, laser wavelengths are selected where possible to match the colour of the pigment being analysed, thereby minimizing any possible heating of the pigment by absorption of

the laser light. The most commonly used laser lines are 488.0 nm (blue) and 514.5 nm (green) emitted by an argon ion (Ar+) laser, and 632.8 nm (red) emitted by a helium-neon (HeNe) laser.

Fluorescence in addition to Raman scattering may be generated by an irradiated sample, in particular from certain organic compounds. This is caused by electronic absorptions by the sample which generate a broadband emission that may be far more intense than the Raman scattering. Problems arising from sample fluorescence can usually be circumvented by using a laser beam of longer wavelength, such as that from a gallium-aluminium-arsenide (GaAlAs) diode laser (782 nm) or neodymium-doped yttrium-aluminium-garnet (Nd^{3+}:YAG) laser (1064 nm). However, it must be borne in mind that Raman scattering intensity is proportional to the fourth power of the excitation frequency so that excitation lines of longer wavelength will produce much less intense Raman scattering than those of shorter wave length.

Lasers are now established as a fundamental part of a Raman instrument. Further recent technological advances have led to the rapid development of Raman spectroscopy over the past 15 years as a powerful analytical tool; in this respect it has emerged as the single most effective method of characterising the pigments found on decorative surfaces. In particular, the development of highly sensitive photon detectors has significantly improved the detection rate for Raman scattered photons and thereby the quality of any Raman spectra; consequently the time taken to collect a spectrum has reduced dramatically, in some cases to a matter of seconds.

Modern Raman spectrometers typically consist of four fundamental parts: a laser excitation source, an optical microscope, a monochromator or interferometer, and a photon detector (Turrell & Corset 1996). The basic system is shown

> *Raman spectroscopy has emerged as the single most effective method in characterising pigments found on decorative surfaces.*

schematically in Figure 2; the laser source (not shown) is typically positioned behind and parallel to the system. The excitation beam is steered into the lower right-hand corner of the spectrometer by the use of two adjustable mirrors; an additional mirror is used to direct the laser beam to the beam

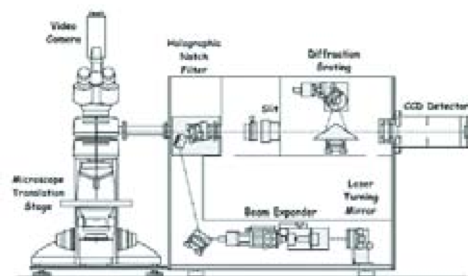

Fig. 2. Schematic diagram of a modern Renishaw Raman spectrometer with major parts indicated; the positions of the lasers are not shown, but these would sit directly behind and parallel to the system. The complete instrument measures 168 cm (l) x 65 cm (d) x 75 cm (h).

expander which reduces the power density of the beam, thereby protecting the optical components from damage. The laser beam is then passed down the optical train of a standard microscope where it is focused onto the surface of an object or sample on the microscope stage via an objective of suitable magnification (typically x5, x10, x20, x50 or x100). The laser spot diameter at the object surface varies according to the objective used; a x50 lens typically providing a spot of *c.* 1 μm across. Such a small spot size allows samples of this dimension to be readily analysed, and the individual components of pigment mixtures to be identified. This advanced use of the microscope for pigment characterisation has enabled artists' materials to be examined in great detail *in situ* on small objects.

Using the microscope system, the light scattered by the sample (both Rayleigh and Raman) is collected back through the same focusing objective (180° back-scattering geometry). The Rayleigh scattered light is rejected by the use of a monochromator or interferometer. In the new generation of movable instruments (e.g. as shown Figure 2), a small, narrow-band holographic notch filter is used to achieve this. Although smaller and more efficient than the heavier monochromator/interferometer counterparts, systems involving notch filters usually prevent useful information from being obtained below 50 cm^{-1}. Although a separate (and expensive) notch filter assembly is required for each laser wavelength, this problem has been overcome somewhat by the development of tunable filters such as the Renishaw near-excitation-tunable (NexT) filter which allows the collection of spectra within *c.* 5 cm^{-1} of the excitation line. After passing through the notch filter, the Raman scattered light is passed onto a diffraction grating which spatially separates out the inelastically scattered photons. These are subsequently recorded as a Raman spectrum using a photovoltaic detector. The more recent technological advances have enabled the use of thermoelectrically cooled, highly sensitive charge-coupled device (CCD) detectors which obviate the need for liquid nitrogen cooling systems. This is another feature which has enabled portable instruments to be developed.

For larger objects, remote probe heads are used instead of the microscope to direct the laser light to the object and to collect the Raman data (Figure 3). Such heads are attached to the spectrometer via optic fibre cables and can be used to access all areas of large and complex objects such as statuary. The probes require only a steady mount which allows some degree of translation to aid focusing of the laser beam onto different parts of the surface of the object under study.

Advantages and limitations of Raman spectroscopy

The advantages of Raman spectroscopy in the characterisation of pigments are that it is a non-destructive, non-invasive technique in which the sample or object is not harmed during the analysis;

Fig. 3. Remote probe head used to deliver the laser beam onto the surface of an object which cannot be accommodated under the microscope; the probe is held on a specially constructed support which includes a book cradle. (Reproduced with permission, Elsevier Masson, Clark, 2002).

no sampling is required as measurements can be performed *in situ*. If separate samples are analysed, no sample preparation is required; the analysis may be also performed directly on dispersion and cross-section samples. Raman spectroscopy is a rapid and effective technique for characterising materials, giving essentially unambiguous results for inorganic and organic materials. It gives both structural and chemical information and can therefore be used to distinguish between polymorphs. In a pigment context this is useful for distinguishing between, for example, the three polymorphs of titanium(IV) dioxide (rutile, anatase and brookite) which may be encountered in modern white paints, pastels, paper and ceramic glazes (Laver 1997; Braun *et al.* 1992), as well as natural minor impurities in earth pigments (Duval 1992); or between litharge and massicot, both forms of lead oxide, PbO (Bell *et al.* 1997).

Raman microscopy enables the user to target very small sample areas (<1 μm^2), with high spatial (≤ 1 μm) and high spectral resolution (< 1 cm^{-1}), whilst remote probes provide non-destructive access to inhomogeneous and complex objects commonly encountered in museums, galleries and restoration studios. Further, the designed portability of many of the modern instruments means that the equipment can be taken to the object rather than vice versa (Best *et al.* 1992).

Raman spectroscopy, however, does have a number of limitations which means that it is not suitable for all forms of analysis required in conservation and restoration. In particular, it cannot be used in the analysis of metals or metal alloys, or for elemental fingerprinting. Also, it is a surface technique so it cannot always be used to analyse the layer structure of an object *in situ*. That said, the technique may be used to investigate the materials present beneath clear layers of varnish, plastic or glass, by focusing the excitation beam down through these materials, and the presence of any craquelure can be exploited by examining the layers revealed by the cracks.

Application of Raman Spectroscopy to the Characterisation of Pigments

The characterisation of pigments on works of art is usually undertaken as part of a conservation or restoration effort, for the advancement of historical knowledge or possibly to probe questions as to authenticity. Many studies have been carried out on pigments and binders found on manuscripts, paintings, frescoes and philatelic materials, using Raman spectroscopy either as a single technique or in conjunction with other analytical methods. There are also now many examples of how Raman spectroscopy has been used to understand observed degradation processes. The following provides a selection of examples from each of these fields so that the reliability and widespread use of the Raman technique can be appreciated.

Manuscripts

The palette of a wide range of manuscripts has been established in large part by the use of Raman spectroscopy. In terms of Western manuscripts, various published studies on pigments include those found on the Lindisfarne Gospels (Brown & Clark 2004a) and other Anglo-Saxon manuscripts (Brown & Clark 2004b), a 13th Century Paris Bible (Best *et al.* 1993), a 13th Century north Italian antiphonal (Clark 1995), selected mediaeval manuscripts (Burgio *et al.* 1997; Vandenabeele *et al.* 1999; Bicchieri *et al.* 2000), Flora Danica (Burgio *et al.* 1999), a 14th Century Icelandic Book of Law (Best *et al.* 1995), the Vinland Map (Brown & Clark 2002), and recently on seven Gutenberg Bibles (Chaplin *et al.* 2005). The last study allowed the illuminations on the King George (III) Gutenberg Bible held at the British Library to be examined *in situ*, and the palette established as consisting of: vermilion (or its mineral equivalent, cinnabar), a red lake, azurite, malachite, verdigris, lead tin yellow (type I), chalk, lead white, carbon-based black and gold leaf.

Fig. 4. Folio 27b-28a ('Circular World Map') from The Book of Curiosities of the Sciences and Marvels for the Eyes, examined using Raman spectroscopy (Chaplin et al. 2006; image reproduced by permission of the Bodleian Library, University of Oxford).

Technical examinations using Raman spectroscopy on a wide selection of Eastern manuscripts have also been published, including those on ancient Egyptian papyri (Burgio & Clark 2000), ancient Chinese manuscripts (Clark *et al.* 1997; Bell *et al.* 2000), a c.13th Century Qur'an (Clark & Huxley 1996), Persian manuscripts (Ciomartan & Clark 1996) including a 16th Century Qazwini manuscript (Clark & Gibbs 1998a), as well as Javanese, Thai, Korean, Chinese and Uighur manuscripts (Burgio *et al.* 1999). Recently several important 13th Century maps from the Arabic world contained within *The Book of Curiosities of the Sciences and Marvels for the Eyes* acquired by the Bodleian Library have been examined with regard to establishing the palette (Figures 4 & 5), knowledge of which will be used to govern conservation treatments (Chaplin *et al.* 2006).

Raman spectroscopy has been used to solve conservation and restoration problems on manuscripts. For example, the observation of widespread pigment darkening on an important lectionary was considered to arise from the degradation of lead white into black lead(II) sulphide (Clark & Gibbs 1997, 1998b) by hydrogen sulphide or other sulphur-bearing species. The latter may have been generated by atmospheric pollution or bacterial activity involving the break-down of adjacent pigments and/or binding media. The black degradation product was confirmed to be lead(II) sulphide by Raman microscopy on the highlights (originally lead white) of a now blackened German (1585) watercolour, the Jamnitzer Manuscript (Smith *et al.* 2002, Figure 6).

Paintings

Raman spectroscopy is now in regular use for the identification of pigments used on paintings and its use in analysing fine art objects has been discussed by Davey *et al.* (1993) and elsewhere (Clark 2005).

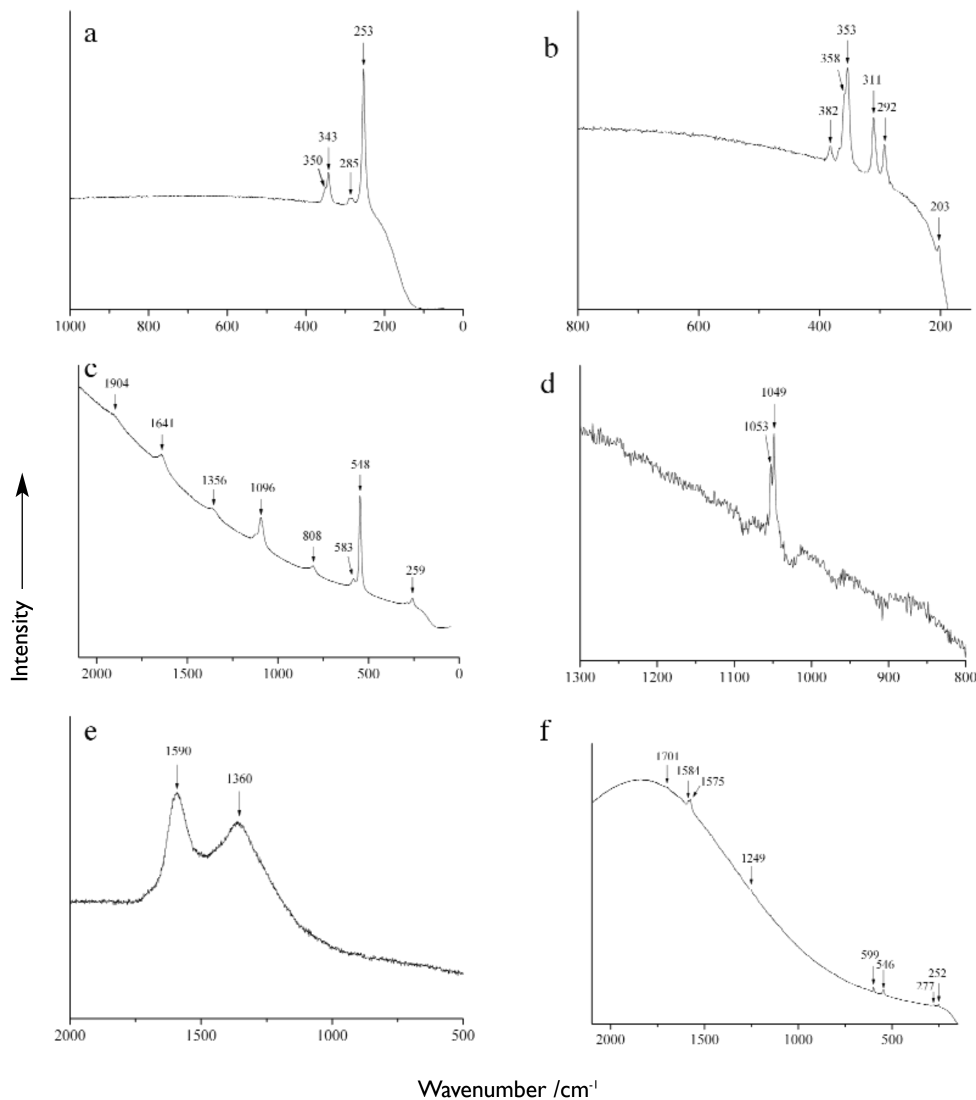

Fig. 5. Raman spectra of pigments identified on Folio 27b-28a from The Book of Curiosities of the Sciences and Marvels for the Eyes (cf. Figure 5): a) vermilion/cinnabar, b) orpiment, c) lazurite, d) lead(II) carbonate hydroxide, 'lead white', e) carbon-based black and f) indigo (see Chaplin et al. 2006).

With prices of fine art realising up to £48 million at auction, the provision of spectroscopic data consistent with authenticity is of paramount importance. Pigment analysis can be used to check that no materials of inappropriate dates of first manufacture or usage are present. Recently, Raman microscopy has been used as part of the study to examine the "Trionfo d'Amore" attributed to Botticelli (Andalò *et al.* 2001), Candido Portinari's *Portrait of Murilo Mendes* (de Oliveira *et al.* 1998), and more recently to support the attribution of *Young Woman Seated at a Virginal* to Vermeer (Burgio

Fig. 6. Detail of the illumination in volume 1, folio 33v of the Jamnitzer manuscript at the Victoria & Albert Museum, London, in which the original lead white highlights have degraded to black lead sulphide (reproduced with permission, International Institute for Conservation; Smith et al. 2002).

With prices of fine art realising up to £48 million at auction, the provision of spectroscopic data consistent with authenticity is of paramount importance.

et al. 2005; Sheldon & Costaras 2006). Raman spectroscopy has also been employed to examine the pigments used at several rock art sites in France, North America and Australia (e.g. Edwards *et al.* 1998, 1999, 2000) and Spain (Hernanz *et al.* 2006).

Frescoes

The pigments used on frescoes have also been studied by the use of Raman spectroscopy and examples of studies include mediaeval frescoes from Spain (Edwards *et al.* 1999a; Perez *et al.* 1999), frescoes from King Herod's Palace at Jericho (Edwards *et al.* 1999b), Byzantine wall paintings from Mount Athos, Greece (Sister Daniilia *et al.* 2000) and English mediaeval wall paintings (Edwards *et al.* 1997). Biological-induced deterioration of frescoes has also been investigated with this technique (e.g. Edwards *et al.* 1997b).

Philatelic materials

Raman microscopy has also recently been applied to the analysis of pigments used on stamps. With the rarest of these objects being valued at up to £1 million, philatelists have required the use of scientific equipment to distinguish forgeries from authentic items. Being small, uncoated and with no possibility of samples being taken, Raman microscopy provides the most appropriate analytical tool for this type of analysis. The blue pigments used on original 19th Century Hawaiian Missionary Stamps (1851, Figure 7) and the first Mauritian stamps (1847) have been identified as Prussian blue, with ultramarine blue optical brighteners in the paper, and have allowed these stamps to be distinguished from later reproductions and forgeries (Chaplin *et al.* 2002, 2004).

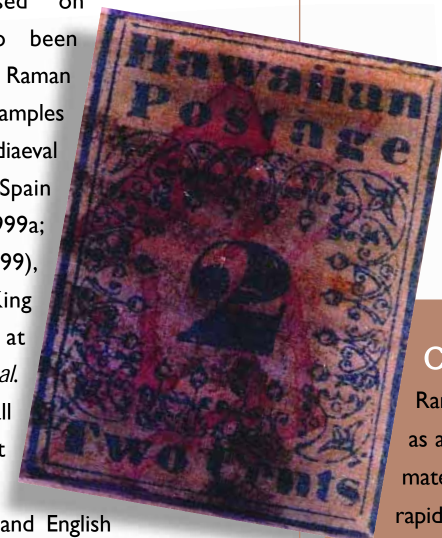

Fig. 7. Photograph of an 1851 2c Hawaiian Missionary stamp from the Tapling Collection at the British Library (reproduced with permission of the British Library): the blue pigment used for printing the stamp was determined to be Prussian blue and that for the black cancellation mark to be carbon black (reproduced with permission, John Wiley and Sons Ltd, Chaplin et al. 2004).

CONCLUSIONS

Raman spectroscopy is now established as a powerful tool in the examination of materials used for works of art, allowing rapid and unambiguous characterisation of the materials present, *in situ*, with no consequential damage to any surface. Recent technological advances have led to the development of compact, lightweight and portable Raman instruments which can be taken to the objects of interest. The use of remote probes in addition to the microscope can allow access to a wide range of otherwise inaccessible objects of any shape or size. A survey of publications over the last 15 years has shown that Raman spectroscopy is being increasingly used in conservation institutes, galleries, libraries and museums, as its effectiveness is now becoming fully appreciated.

Dr Tracey D Chaplin
Christopher Ingold Laboratories
University College London, 20 Gordon Street, London WC1H 0AJ
t.chaplin@ucl.ac.uk

Dr Tracey Chaplin is an honorary research fellow in the Department of Chemistry at UCL. Having been awarded a PhD in geology (1998, UCL), which involved the theoretical and practical application of Raman spectroscopy to geological materials, Chaplin has since applied this knowledge to the study of artists' pigments. Chaplin is also an independent scientific consultant specialising in the analysis of painted surfaces and is employed part-time as a lecturer in conservation science at the London Metropolitan University. .

Professor R J H Clark
CNZM FRS
Christopher Ingold Laboratories
University College London, 20 Gordon Street, London WC1H 0AJ
r.j.h.clark@ucl.ac.uk

Robin Clark is the Sir William Ramsay Professor and the former Head of Chemistry and Dean of Science at UCL. His research focused on inorganic chemistry, spectroscopy and the development of Raman and resonance Raman spectroscopy into powerful structural tools. He later pioneered the application of Raman microscopy to the characterisation of pigments on artwork and archaeological objects. His work is embodied in c. 500 scientific papers, 3 books and 36 edited books, and he has acted as visiting professor to 13 universities and lectured in over 350 institutions in 35 countries. He was appointed a Companion of the New Zealand Order of Merit in 2004 for services to Science.

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