Raman Microscopy: Application to the Identification of Pigments on Medieval Manuscripts

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1 Introduction

Our cultural heritage is intimately connected with writings and art, the analysis and interpretation of which embraces many disciplines within the Arts and Sciences. The identification of the materials used in the production of artefacts, *viz.* the pigments, binders, *etc.*, and the techniques for the construction of paintings and manuscripts have long been matters of great importance.[1–6] Not infrequently, such findings have provided insight into developments in chemical technology, in commerce, in trading routes, and in the spread of knowledge from country to country. As in all branches of chemistry, the techniques of analytical chemistry have seen great advances over the past few decades and those appropriate to the identification of pigments have been no exception in this regard. Most of these techniques, however, are either intrinsically destructive or are not amenable to *in situ* application. While the latter restriction might or might not be critical in the case of the identification of pigments on paintings, it certainly is so for those on medieval manuscripts, for which libraries almost invariably have non-sampling policies. The lack until recently of techniques for pigment analysis which can not only be carried out *in situ*, but are reliable, sensitive, and non-destructive has greatly restricted the number of significant studies which could be carried out on medieval manuscripts. Much important information of social and/or technological nature thus remains to be revealed.

It is contended that Raman microscopy[7] is the ideal analytical method for pigment analysis of the artefacts described above and that this technique combines the required attributes of reliability and sensitivity, and that it is non-destructive, largely immune to interference (from other pigments, binder, and fluorescence), and amenable to *in situ* application.[8–13] Furthermore, since the probe laser wavelengths used are in the visible region, usually 0.5—0.7 μm, the spatial resolution of the experiment is of this order and so individual pigment grains > ~ 0.7 μm across may be identified. These advantages are unique to Raman spectroscopy and are of enormous importance when, for example, the manuscript has undergone conservation treatment at different stages of its history or when a particular colour is made up from a mix of pigments, otherwise not identified.

Despite the above consideration, the use of Raman microscopy has been restricted in pigment analysis owing to difficulties to do with the measurement of the Raman signals (which may be weak in the absence of resonance effects), the use of lasers, the optimization of the optical and electronic components of the system for different laser wavelengths, and the possibility of sample heating on irradiation. Many of these problems have been solved with modern Raman microscopes and attachments and so the technique can now be used to provide new insight into the spread of culture and technology *via* art.

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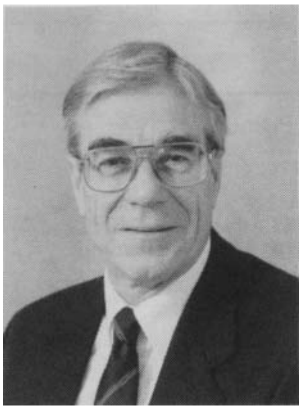

2 Purpose of the Examination of Pigments

There are several purposes behind the examination of pigments on, or removed from, paintings or manuscripts. These are[2–5,13]:

1. Characterization. The questions being addressed are ones such as
   (a) what were the pigments used by the artists?
   (b) were single pigments or pigment mixes used to achieve the same or closely similar hues?
   (c) was the final effect achieved by building up layers of paint, each differing in pigment composition or each differing in particle size?
2. Restoration, *i.e.* the repair of damaged areas and thus the matching to the original pigments, bearing in mind that there may [as with blue-green copper resinates and mercury(II) sulfide] have been changes in composition or structure, and hence in colour, with time.
3. Conservation, *i.e.* the care and preservation of works of art and the study of the effects of heat, light, and gaseous pollutants thereon.
4. Dating and authentication, *i.e.* the consideration as to whether or not the identification of the pigments used on a work of art may give an indication as to the date of the work and hence to its authenticity.

The characterization of a pigment may be required at different levels of sophistication. At one level, it may simply be a question of identification; at a higher level, it may be one of recognition of the crystal form of a pigment (*e.g.* the rutile or anatase form of titanium dioxide) or of the source of a mineral pigment (*via* for example, lead or tin isotope ratios).

The artist's concern in a pigment is with texture, permanence of colour, compatibility with other pigments, fastness in media, wettability, miscibility, oil absorption, stability of consistency, tinting strength, hiding power, transparency, drying effects, toxicity, and possible presence of adulterants or impurities.[4] The analyst, restorer, and authenticator will be concerned to learn whether the pigment identified is one normally found on a work of art executed at the particular time and place to which the artwork is attributed and whether the same pigment is used in other areas of the work.

It is obviously simplest to remove samples from paintings, manuscripts, or other artefacts in order to carry out the identification of the pigments present. In particular, such a procedure does not require the removal of the item from its permanent location, it need only be done once if done properly, and it involves less handling Moreover it may be possible either to excise pigment samples in such a way that the lacunae are not discernible to the naked eye or alternatively to remove them from offsets transferred onto (say) the opposite page of a manuscript However, although pigment sampling may be permitted from paintings, it is almost never allowed from manuscripts owing to the fragility of these items Thus the availability of *in situ* techniques is a matter of the utmost importance Raman microscopy is also very important as a means whereby reaction products may be identified when an inappropriate mix of pigments has been applied to a manuscript, *e g* cadmium sulfide and copper arsenoacetate, which yields black copper sulfide as an unintended product

3 Inorganic Pigments

The illustrators, even in medieval times, generally preferred to use inorganic pigments since these colours were known to be less fugitive and more stable than organic ones Many were available as minerals or by way of comparatively straightforward syntheses Early texts provide much information on this matter[2,5] The colour of a pigment arises as a consequence of absorption (*via* ligand-field, charge-transfer, or intervalence charge-transfer bands) and specular reflectance, it is modified by particle size, as is well known for $CuSO_4$ $5H_2O$ for example, since this affects the relative importance of diffuse and specular reflectance,[14,15] it is also obviously affected by the absorption coefficient and band width of electronic bands in the visible region The more common inorganic minerals and synthetic compounds or glasses which have been used as pigments at different periods of time are listed alphabetically in Tables 1—7 according to their colours blue, black, brown/orange, green, red, white, and yellow For each pigment is given the chemical formula, basis of the colour and, if not a mineral, the date of its first manufacture The basis of the possible dating of a manuscript is thus made clear

4 Organic Pigments

The principal dyes used by medieval dyers were indigo from woad for blue, alizarin and purpurin from madder for red, and luteolin from weld or crocetin from saffron for yellow, but all had been used long before the Middle Ages, weld was even known in the Stone Age[3,12,13] Many organic pigments have also been used on manuscripts, notably saffron and weld as yellows, indigo and woad as blues, Tyrian purple (mainly in fabric, as was indigo and woad), madder (and later, in paintings, carmine) as reds[16]

There were also many natural products extracted in the past from lichens and used to dye textiles Notable among these were orchil for purple and crottle for brown Other dye plants can yield greens, browns, and blacks (in the last case, for example, marble gall from oak *Quercus* trees with added iron sulfate)

As mentioned earlier, organic pigments are prone to both fluorescence as well as photochemical degradation Moreover

Table 1 Blue Inorganic Pigments

Pigment	Chemical Name	Formula	Date[a]	Transition[b]
azurite	basic copper(II) carbonate	$2CuCO_3$ $Cu(OH)_2$	min	LF
cerulean blue	cobalt(II) stannate	CoO $nSnO_2$	1821	LF
cobalt blue	cobalt(II)-doped alumina glass	CoO Al_2O_3	1775	LF
Egyptian blue (cuprorivaite)	calcium copper(II) silicate	$CaCuSi_4O_{10}$	3rd millennium B C /min	LF
lazurite (from lapis lazuli)	sulfur radical anions in a sodium aluminosilicate matrix	$Na_8[Al_6Si_6O_{24}]S_n$	min /1828	S_3 CT
manganese blue	barium manganate(VII) sulfate	$Ba(MnO_4)_2 + BaSO_4$	1907	LF
phthalocyanine blue (Winsor blue)	copper(II) phthalocyanine	$Cu(C_{32}H_{16}N_8)$	1936	π-π^*
posnjakite	basic copper(II) sulfate	$CuSO_4$ $3Cu(OH)_2$ H_2O	min	LF
Prussian blue	iron(III) hexacyanoferrate(II)	$Fe_4[Fe(CN)_6]_3$ 14—16H_2O	1704	IVCT
smalt	cobalt(II) silicate	CoO $nSiO_2$ $(+ K_2O + Al_2O_3)$	~ 1500	LF
verdigris	basic copper(II) acetate	$Cu(O_2CCH_3)_2$ $2Cu(OH)_2$	min	LF

[a] The pigment is either specified to be a mineral (min) and/or the date of its first manufacture is listed [b] LF = ligand field transition CT = charge transfer transition, IVCT = intervalence charge-transfer transition, π–π^* = electric dipole-allowed charge transfer transition of the phthalocyanine ring system

Table 2 Black Inorganic Pigments

Pigment	Chemical Name	Formula	Date
ivory black[a]	calcium phosphate + carbon	$Ca_3(PO_4)_2 + C + MgSO_4$	4th C B C ?
lamp black	amorphous carbon	C	~ 3000 B C
magnetite	iron(II,III) oxide	Fe_3O_4	mineral
mineral black	aluminium silicate + carbon (30%)	Al_2O_3 $nSiO_2 + C$	mineral
vine black	carbon	C	Roman

Bone black is similar to ivory black

Table 3 Brown/Orange Inorganic Pigments

Pigment	Chemical Name	Formula	Date
cadmium orange	cadmium selenosulfide	Cd(S,Se) or CdS (> 5 μm)	late 19th C (CdS *c* 1845)
ochre (goethite)	iron(III) oxide hydrate	Fe_2O_3 H_2O + clay, *etc*	mineral
sienna (burnt)	iron(III) oxide	Fe_2O_3 + clay, *etc*	antiquity?

Table 4 Green Inorganic Pigments

Pigment	Chemical Name	Formula	Date
atacamite	basic copper(II) chloride	$CuCl_2\ 3Cu(OH)_2$	mineral
chromium oxide	chromium(III) oxide	Cr_2O_3	Early 19th C
cobalt green	cobalt(II) zincate	CoO *n*ZnO	1780
emerald green	copper(II) arsenoacetate	$Cu(C_2H_3O_2)_2\ 3Cu(AsO_2)_2$	1814
green earth – a mix of celadonite and glauconite	hydrous alumino-silicate of magnesium, iron, and potassium	Variations on $K[(Al^{III}, Fe^{III})(Fe^{II},Mg^{II})],(AlSi_3,Si_4)O_{10}(OH)_2$	mineral
malachite	basic copper(II) carbonate	$CuCO_3\ Cu(OH)_2$	mineral
permanent green deep	hydrated chromium(III) oxide + barium sulfate	$Cr_2O_3\ 2H_2O + BaSO_4$	latter half 19th C
phthalocyanine green	copper(II) chlorophthalocyanine	$Cu(C_{32}H_{15}ClN_8)$	1938
pseudo-malachite	basic copper(II) phosphate	$Cu_3(PO_4)_2\ 2Cu(OH)_2$	mineral
verdigris (basic)	basic copper(II) acetate	$Cu(C_2H_3O_2)_2\ 2Cu(OH)_2$	mineral and synthetic (B C)
viridian	hydrated chromium(III) oxide	$Cr_2O_3\ 2H_2O$	1838 (?1850)

Table 5 Red Inorganic Pigments

Pigment	Chemical Name	Formula	Date
cadmium red	cadmium selenide	CdSe	*c* 1910
chrome red	basic lead(II) chromate	$PbCrO_4\ Pb(OH)_2$	early 19th C
litharge	lead(II) oxide	PbO	antiquity
realgar	arsenic(II) sulfide	As_2S_2	mineral
red lead (minium)	lead(II,IV) oxide	Pb_3O_4	antiquity
red ochre	iron(III) oxide + clay + silica	$Fe_2O_3\ H_2O$ + clay + silica	mineral
vermilion (cinnabar)[a]	mercury(II) sulfide	HgS	mineral and synthetic (13th C)

[a] Limited lightfastness (→ black form)

Table 6 White Inorganic Pigments

Pigment	Chemical Name	Formula	Date
anatase	titanium(IV) oxide	TiO_2	1923
barytes	barium sulfate	$BaSO_4$	mineral
bone white	calcium phosphate	$Ca_3(PO_4)_2$	antiquity
chalk (whiting)	calcium carbonate	$CaCO_3$	mineral
gypsum	calcium sulfate	$CaSO_4\ 2H_2O$	mineral
kaolin	layer aluminosilicate	$Al_2(OH)_4Si_2O_5$	mineral
lead white	lead(II) carbonate (basic)	$2PbCO_3\ Pb(OH)_2$	mineral and synthetic (500—1500 B C)
lithopone	zinc sulfide and barium sulfate	$ZnS + BaSO_4$	1874
rutile	titanium(IV) oxide	TiO_2	1947
zinc white	zinc oxide	ZnO	1834

Table 7 Yellow Inorganic Pigments

Pigment	Chemical Name	Formula	Date
barium yellow	barium chromate	$BaCrO_4$	early 19th C
cadmium yellow	cadmium sulfide	CdS	mineral (greenockite) + synthetic *c* 1845
chrome yellow	lead(II) chromate	$PbCrO_4$ or $PbCrO_4\ 2PbSO_4$	1809
cobalt yellow (aureolin)	potassium cobaltinitrite	$K_3[Co(NO_2)_6]$	1861
lead antimonate yellow	lead(II) antimonate	$Pb_2Sb_2O_7$ or $Pb_3(SbO_4)_2$	antiquity
lead tin yellow	lead(II) stannate	[I] Pb_2SnO_4 [II] $PbSn_{0\ 76}Si_{0\ 24}O_3$	antiquity? antiquity?
massicot	lead(II) oxide	PbO	antiquity
ochre	goethite + clay + silica	$Fe_2O_3\ H_2O$ + clay + silica	mineral (and synthetic)
orpiment	arsenic(III) sulfide	As_2S_3	mineral
strontium yellow	strontium chromate	$SrCrO_4$	early 19th C
zinc yellow	zinc chromate	$ZrCrO_4$	early 19th C

they often scatter only very weakly, perhaps due to their extremely fine grain size which may make them appear as a uniform wash rather than a fine dispersion or to the fact that they may have been made into lakes with a mordant such as alum,[17] hence they are difficult to identify uniquely on a manuscript owing to the lack of concentration of pigment at the sampling point The better known organic dyes and pigments are listed in Table 8 Pigments are defined as finely divided colouring materials which are suspended as 'discrete particles in the medium in which they are used as a paint' as distinct from a dye which is soluble in the medium [3] It should be borne in mind that dyes and pigments have usually been known by a very wide range of different names The Raman spectra of many organic pigments and dyes have now been recorded, including modern dyes such as methyl blue (a synthetic triarylmethane dye), methyl violet, perylene reds, *etc* ,[18] as well as medieval dyes, and these prove to be highly characteristic

5 Raman Microscopy

A detailed analysis of the strengths and weaknesses of a variety of different possible techniques for pigment analysis – some element specific, some chemical grouping specific, and some compound specific – including scanning electron microscopy

Table 8 Organic Pigments and Dyes

Colour	Pigment	Formula/Composition	Origin (Date)
blue	indigo	indigotin $C_{16}H_{10}N_2O_2{}^{a}$	plant leaf (B C) synthetic (1878)
black	bitumen	mixture of hydrocarbons	(B C)
brown	sepia	melanin^{b}	ink of cuttlefish (*c* 1880)
	van Dyck brown	humic acids allomelanins	lignite containing manganese (16th C?)
green	sap green	organic dye	buckthorn berry (14th C?) coal-tar dye
purple	Tyrian purple	6,6′-dibromoindigotin $C_{16}H_8Br_2N_2O_2{}^{a}$	marine mollusc (1400 B C) synthetic (1903)
red	carmine	carminic acid $C_{22}H_{20}O_{13}{}^{d}$ kermesic acid $C_{16}H_{10}O_8{}^{d}$	scale insect, cochineal (Aztec) scale insect kermes (antiquity)
	madder	alizarin $C_{14}H_8O_4{}^{d e}$ purpurin $C_{14}H_8O_5{}^{d}$	madder root (3000 B C) synthetic alizarin (1868)
	permanent red	various azo dyes	synthetic (after 1856)
yellow	gamboge	α- and β-gambogic acids $C_{38}H_{44}O_8$ and $C_{29}H_{36}O_6$	gum-resin (before 1640)
	Hansa yellow	various azo dyes	synthetic (1900)
	Indian yellow	magnesium salt of euxanthic acid $MgC_{19}H_{16}O_{11}\ 5H_2O$	cow urine (15th C)
	quercitron	quercitrin $C_{21}H_{20}O_{11}{}^{f}$	inner bark of *Quercus* oak
	saffron	crocetin $C_{20}H_{24}O_4{}^{g}$	crocus flower stigma (antiquity)
	weld	luteolin $C_{15}H_{10}O_6{}^{f}$	plant foliage (Stone Age)

Indigoid dye Mixture of polyacid polymers of the indole type Mixture of macromolecules having polymeric phenolic structures with the ability to chelate especially to iron Anthraquinoid dye (carminic acid is a glucosidal derivative) Turkey red is the calcium aluminium lake of alizarin $CaAl(OH)(Az)_3\ xH_2O$ where Az represents an alizarin molecule minus two hydrogen atoms and x = 3—6 (Ref 17) [f] A flavonoid dye [g] Carotenoid dicarboxylic acid

(SEM), *X*-ray fluorescence (XRF), *X*-ray diffraction (XRD), particle-induced *X*-ray emission (PIXE), particle-induced gamma-ray emission (PIGE), infrared spectroscopy, ultraviolet/visible spectroscopy, and optical microscopy has been made recently It was concluded[9] that Raman microscopy is the best single technique for this purpose This is in part because it is a vibrational technique and thus each pigment molecule has a potential $3N - 6$ markers, where N represents the number of atoms in the pigment molecule, each band having a particular wavenumber, intensity, and width It is thus a highly specific and sensitive technique which, moreover, has high spatial resolution (0 5—1 0 μm), is usually immune to interference, and can be operated *in situ*

Raman microscopy[7] involves the illumination of the sample with monochromatic light and the analysis of the components which are inelastically scattered, *i e* scattered with wavenumbers different from that of the light incident upon the sample Under the experimental conditions used, the exciting radiation is focused to a spot with a diameter of less than 1 μm and this defines the spatial resolution of the experiment The Raman spectrum (plot of the intensity of scattered radiation as a function of the wavenumber shift) is characteristic both of the composition and the structure of the sample and is sufficient, when observed with reasonable definition, to permit unambiguous identification of the sample Resonance Raman spectra are obtained when the wavenumber of the exciting radiation is close to, or coincident with, that of an electronic transition of the scattering species [1,9] Such spectra are usually characterized by a very large enhancement of the intensities of particular Raman bands, sometimes with the appearance of intense overtone and combination band progressions

In a typical set-up,[9] a microscope (*e g* Olympus B-H2) is coupled to a spectrometer (*e g* DILOR X-Y triple grating spectrometer) with an intensified photodiode array or CCD detector Laser radiation is brought to a focus on each pigment grain on the manuscript *via* the microscope objective (× 50 or × 100) The Raman scattering by the sample retraces the path of the incident beam, being collected by the same objective and directed to the monochromator and then to the detector The data may then be processed and displayed on screen or hard copy (Figure 1) Low laser powers (≤ 5 mW) are desirable in order to minimize the possibility of degradation of the pigment Different laser lines (low power) with wavelengths throughout the visible region may be used, and also 1064 nm excitation in the case of FT Raman spectroscopy (*e g* Nicolet 910 spectrometer)

The technique can usefully be complemented by reflectance spectroscopy in the near infrared, visible, and ultra-violet regions Light from a tungsten lamp may be focused onto the sample to produce an oval image, the dimensions of which (*ca* 1 × 1 2 mm) define the spatial resolution of the experiment Light reflected from the sample is then collected and focused onto the end of an optical fibre (*e g* Tech Optics SFS 105/125 Y) which is coupled to the entrance of the monochromator (*e g* Oriel 77200) The use of a single monochromator (spectrograph) in conjunction with a multichannel detector (*e g* Oriel Instaspec III) enhances the sensitivity of the spectrometer, this being important given the low intensity of the diffuse reflected light The exact profile of absorption bands, including those in the near infrared region, can often permit one to distinguish between pigments of similar hues The disadvantage of the technique is that the spectral features are broad and, in most cases, not sufficiently characteristic to permit unambiguous identification of a pigment in the absence of other more specific data In practice this limitation may not be serious when the range of possible pigments is restricted – as is the case for medieval manuscripts Likewise, the other techniques mentioned above may also be used to complement Raman spectroscopy and thereby provide confirmation of pigment identification

6 Examples of Pigments and Manuscripts Studied

The Raman spectra of a large number of pigments, both inorganic and organic, have been recorded and now form part of a data bank As mentioned above, although the organic pigments often yield poor spectra the inorganic ones are usually intense and well defined Indeed, in some cases the role played by Raman spectroscopy in defining or helping to define the nature of the chromophore has been critically important, this is particularly the case for lapis lazuli

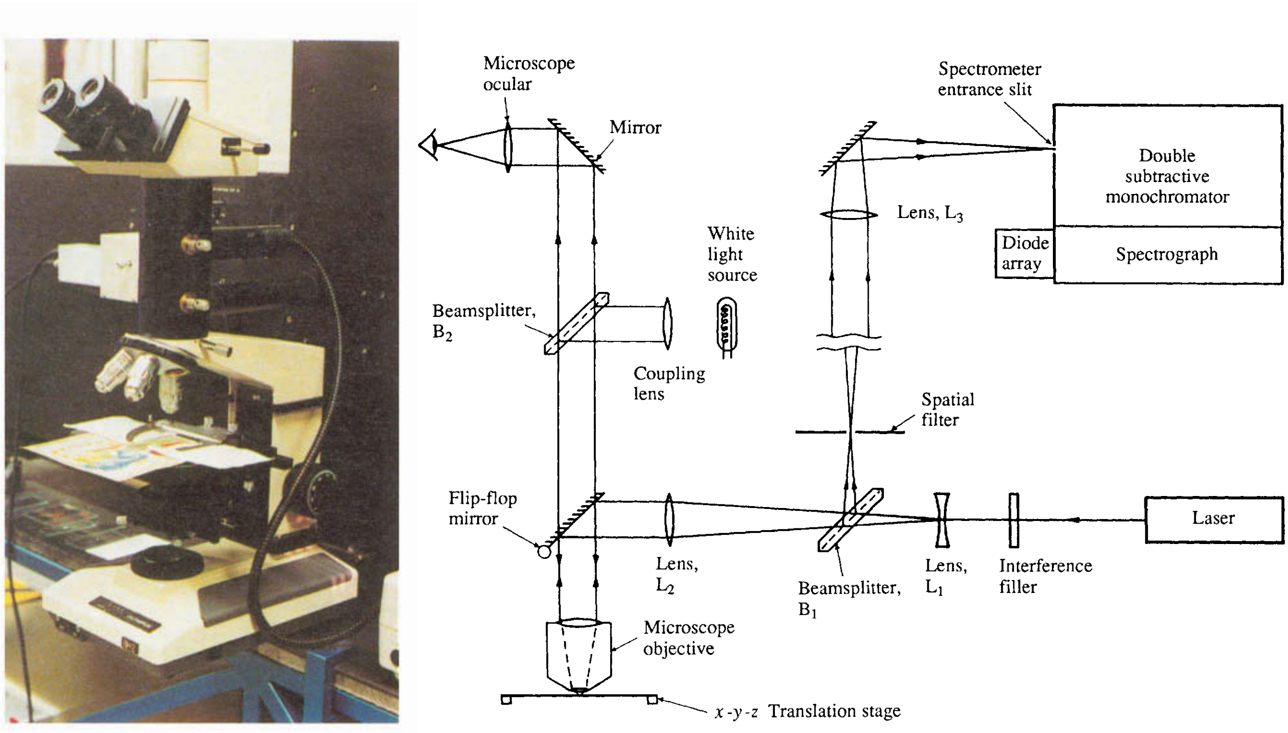

Figure 1 A Raman microscope together with an outline of its optical configuration. (The latter is reproduced by permission from *Chemistry in Britain*, 1993, 118—122.)

6.1 Lapis lazuli

The intense royal blue colour of the mineral lapis lazuli and its synthetic equivalent, ultramarine blue (the latter having been known since 1828), has been highly prized for at least 5000 years. Not only was the semi-precious gemstone admired as such, but the pigmentary properties of the material have been highly valued back through the middle ages to at least the eighth century (see the Lindisfarne gospels[20]). The origin of the colour was not understood until a combination of resonance Raman and electron spin resonance studies led to the identification of the chromophores as sulfur radical anions trapped (effectively matrix isolated) in the cubic holes of the host alumino-silicate (sodalite) cage, albeit present in very low ($\leq 1\%$) proportions.[21–25] The chromophores present were shown to be S_3^- ($\lambda_{max} = 610$ nm, $\omega_1 = 550.3$ cm^{-1}) together with some S_2^- ($\lambda_{max} = 380$ nm, $\omega_e = 590.4$ cm^{-1}). The key Raman observations on this pigment are the long resonance Raman progressions observed in the totally symmetric stretching mode of each radical anion, features which are characteristic of S_3^- and S_2^- when substituted into alkali halide matrices. Not all pigments, of course, have such intense and highly characteristic Raman spectra as ultramarine blue, but nonetheless these studies illustrate how important Raman spectroscopy has become in characterizing minerals and other pigmentary materials. The effective use of ultramarine in impressionist paintings is well known, *e.g.* Pissaro's 'Côte des Boefs', Monet's 'Gare Saint-Lazare' and Renoir's 'Les Parapluies', and has been discussed recently.[26]

6.2 Cadmium Sulfide

Although cadmium sulfide was first recommended as an artist's yellow pigment in 1818, the native minerals (greenockite and hawleyite)[27] were scarce and so not generally available. It was not until about 1846 that cadmium sulfide came on the market as part of the chemical revolution in the emergent paint industry, whereupon this pigment rapidly became popular among impressionist painters *e.g.* Claude Monet, 'Bordighera', 1884 and later ones *e.g.* Charles Demuth, 'Gladioli No.4', 1925.[5] Chemists discovered in the latter part of the 19th century that selenium could be made to substitute for sulfur, leading to the formation of cadmium seleno-sulfides with colours ranging from orange through to maroon depending upon the selenium content. This gave the impressionists a wider range of pigment hues to draw upon.[5]

6.3 Lead Tin Yellow

The usage of lead tin yellow as a pigment has a long and complicated history owing to the (not originally appreciated) existence of two forms, type I which is Pb_2SnO_4 (which has a tetragonal structure, isostructural with Pb_3O_4) and type II which is $PbSn_{0.76}Si_{0.24}O_3$ (which has a defect pyrochlore structure with 24% of the tin sites having been randomly substituted by silicon in the lattice).[28] Both synthetic pigments have been used at different periods over the past 2000 years. They have sometimes been confused with one another and sometimes also with lead antimonate yellow $Pb_2Sb_2O_7$ (Naples yellow). The Raman spectra of these two tin pigments are quite different from one another (Figure 2), and allow a ready distinction to be made between them.[28] For instance, a recent study of Titian's painting 'Death of Acteon' (National Gallery) shows clearly that the yellow bush in the foreground has been painted with lead tin yellow type I, whereas that of Paolo Veronese 'Allegory of Love', IV, (National Gallery) – the bright yellow of the man's cloak – has been painted with type II.

Several different case studies are now discussed and the key results of the Raman microscopy are outlined. Such work has resolved many ambiguities in the minds of art historians both quickly and definitively.

6.4 13th Century North Italian Antiphonal

This manuscript (Figure 3) shows Mary (on the left) being greeted by the mother of John the Baptist. Mary's cloak is

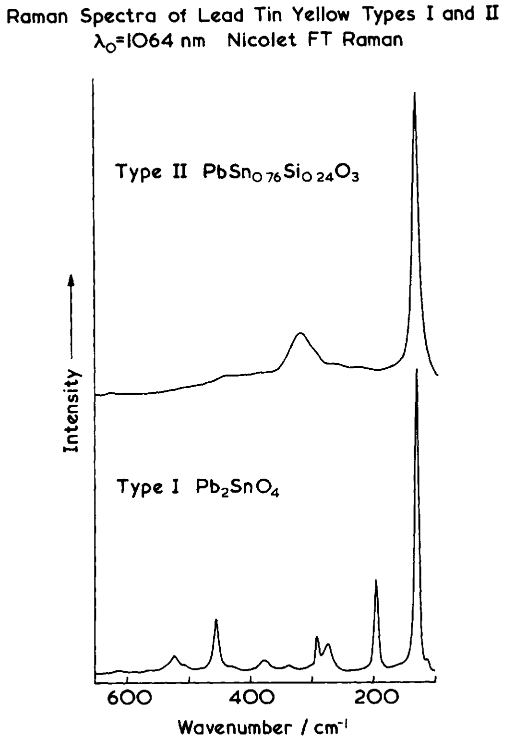

Figure 2 Raman spectra of lead tin yellow types I and II.[28]

painted in lapis lazuli and the mother's cloak in malachite.[9] It is curious that certain leaves at the bottom now appear blue rather than green, as originally painted. This is doubtless because the green was formed from a mix of lapis lazuli (easily identified by Raman microscopy) and a yellow pigment, presumably a fugitive organic one such as saffron or weld, which has now degraded.

6.5 13th Century North Italian Choir Book

The historiated capital letter 'O' (Figure 4) is shown to illustrate the technique of layering lapis lazuli over azurite.[9] This creates an interesting effect, and has the important economic consequence of minimizing the use of the more expensive mineral, lapis lazuli. The intriguing medieval practice of using the most valuable pigment for the most holy of the subjects, *i.e.* a saint, is often revealed in manuscripts.[29] Thus the hierarchy of pigment usage for blues would be lapis lazuli > azurite > woad.

6.6 16th Century German Choir Book

The elaborately historiated initial letter 'R' (Figure 5) has been extensively studied, and eight pigments – azurite, lead tin yellow type I, malachite, vermilion, white lead, red lead, carbon, and massicot – have been identified thereon.[9] Raman microscopy has demonstrated that in this case the two shades of blue on the garments of the right-hand woman arise from the same pigment, azurite, the illuminator having used less azurite and more binder to produce the lighter shade. The deeper blue arises from coarse grains of pigment (~ 30 μm diameter) whereas the lighter blue arises from fine grains (~ 3 μm diameter); this effect, as discussed earlier, arises from the different relative importance of diffuse and specular reflectance with differently sized grains.[14,15]

It is of particular interest that the dark grey colour of the pillar top is not obtained *via* a single pigment but by colour subtraction of a mixture of at least the seven pigments white lead, carbon, azurite, vermilion, red lead, massicot, and lead tin yellow type I. The mixture is evident at × 100 magnification in Figure 6; by Raman microscopy, each different pigment grain may be identified. Mixing of pigments was a common practice of medieval artists in order to achieve particular hues which were not available from a single pigment.

Figure 3 13th Century north Italian antiphonal (psalm book from which verses are sung alternately).

6.7 Paris Bible *ca.* 1275

Eight pigments have been identified on a bible known as the Lucka bible (see Figure 7), one of a very large number made in Paris *ca.* 1270.[10] Six of them were much used – white lead, vermilion, red lead, lapis lazuli, azurite, and orpiment – while two others – realgar and malachite – were found to be present only in trace amounts, possibly as unintended components of orpiment and azurite, respectively. The Raman spectra of these pigments are illustrated in Figure 8.

6.8 Skarð Copy of the Icelandic Law Book, the Jónsbók, *ca.* 1360

Three historiated initials and *ca.* 15 illuminated initials (see Figure 9) with associated background painting and embellishments from the Skarð copy of the Icelandic Law Book, the *Jónsbók*,[30] have been examined.[31] Six pigments were identified by Raman microscopy, *viz.* vermilion, orpiment, realgar, red ochre, azurite, and bone white. The pigments responsible for the various other green and blue colours could not be identified unambiguously, although the diffuse reflectance spectra of the lighter green and blue pigments appear to arise from verdigris or variants thereof. The dark green colours arise from verdigris, possibly mixed with green earth. Neither red lead nor white lead, pigments commonly used in Northern Europe, was found on this manuscript; this raises questions as to the availability of

Figure 4 Native lapis lazuli on quartz together with a 13th Century choir book illustrating in the historiated initial letter O the technique of layering of lapis lazuli over azurite
(The latter is reproduced by permission from *Endeavour* 1992 **16** 66—73)

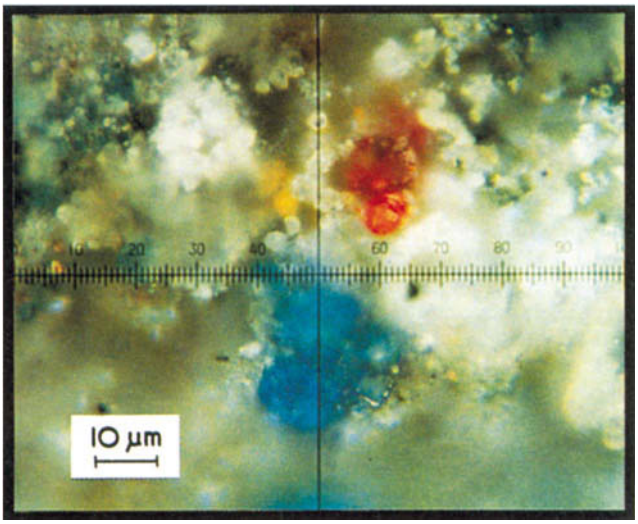

Figure 6 Magnified (× 100) portion of the top of the dark grey column in Figure 5 showing the individual pigment grains separately identified by Raman microscopy
(Reproduced by permission from *Endeavour* 1992 **16** 66—73)

Figure 5 16th Century German choir book (historiated initial letter R) Eight inorganic pigments have been identified within this letter
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Figure 7 Paris bible *ca.*1270; illuminated initial letter 'V' (of 'Verba Jeremiah'), on which eight inorganic pigments have been identified. (Reproduced by permission from *Chemistry in Britain*, 1993, 118—122.)

these pigments in Iceland, to which they are not native, and of the effectiveness of the trading routes (thought to be *via* Bergen).

7 Conclusion

Raman microscopy can clearly be used to perform identifications of a wide range of pigments on manuscripts without the need for the latter to be excised therefrom. It is therefore a valuable addition to the existing techniques used for this purpose, and arguably it is the best. The capability of dealing with the identification of mixtures of pigments at high spatial (≤ 1 μm) resolution is unparalleled. Moreover, a very high proportion of pigments on manuscripts, even in picogram quantities, may be identified by Raman microscopy. The main difficulty arises from certain organic pigments which either fluoresce (or their supports or binders do), are photosensitive, or fail to yield a Raman spectrum owing to their extremely low particle size and/or degree of dilution. The technique has thus become a very important means for the study of manuscripts[32] and of a wide variety of other coloured artefacts including wall paintings.[33]

The use of light pipes for remote sensing (particularly of pigments on paintings), the development of procedures for two-dimensional mapping of manuscript surfaces,[34] and depth profiling studies of manuscripts taking advantage of the large angle of collection (72° for a × 160 objective) can be expected to lead to more perceptive studies in the future.

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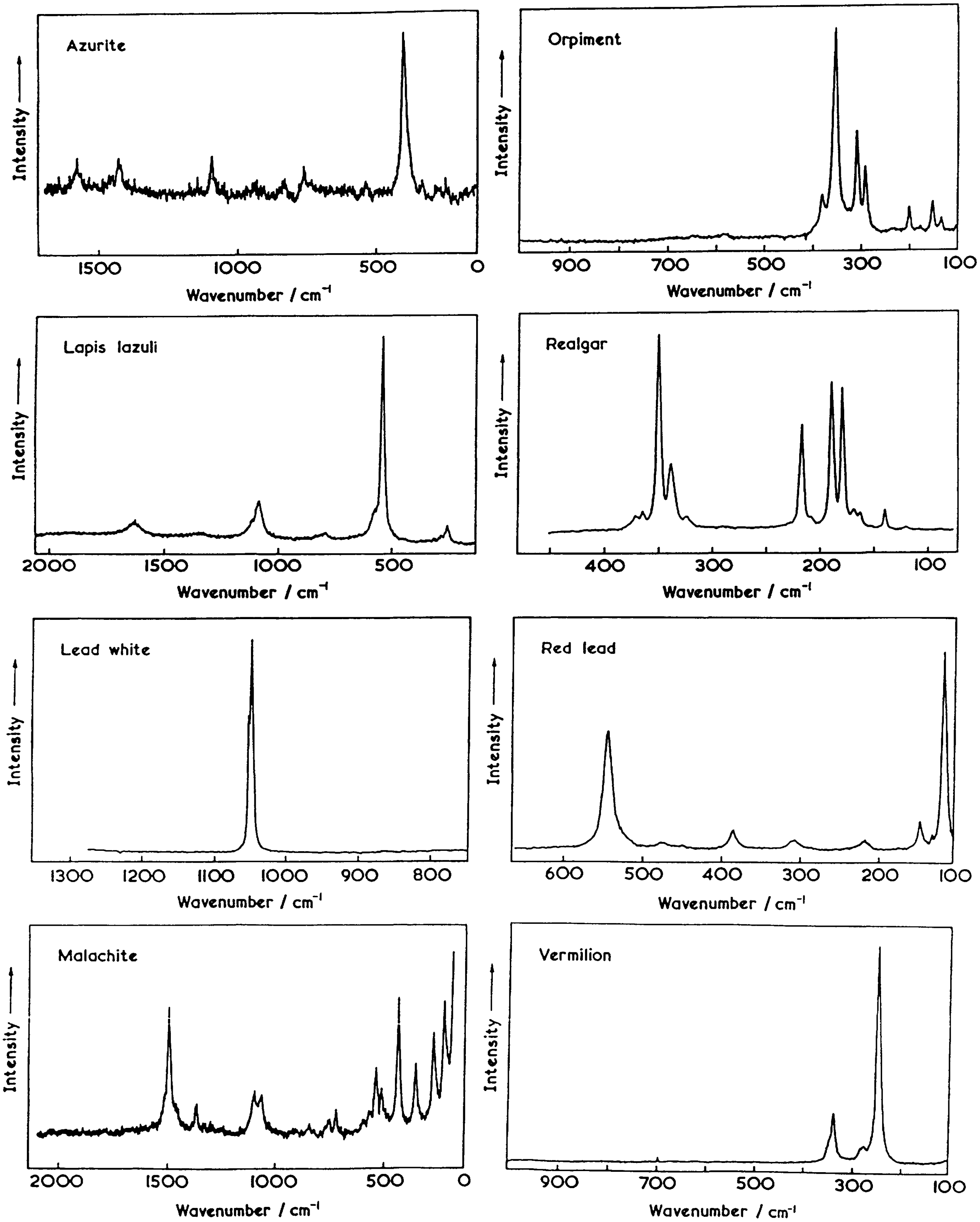

Figure 8 Raman spectra of eight pigments identified on the Paris bible. (Reproduced by permission from *Chemistry in Britain*, 1993, 118—122.)

(a)

(b)

(c)

(d)

Figure 9 Illuminated initials on the *ca* 1360 Skarð copy of the Icelandic *Jonsbok* (a) red ochre on an initial N (b) vermilion and red ochre on the hanged figure (c) mixture of bone white and azurite on the initial H and (d) vermilion on the initial N The use of bone white in Europe is unusual white lead being usually preferred
(Reproduced by permission from *Studies in Conservation* 1995 **40** 31—40)