PAPER

Characterisation of colourants on illuminated manuscripts by portable fibre optic UV-visible-NIR reflectance spectrophotometry

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The use of ultraviolet and visible diffuse reflectance spectrophotometry as a preliminary technique in the investigation of illuminated manuscripts is discussed. Because ancient manuscripts are amongst the most fragile and precious artworks, characterisation of the materials used in their decoration should be performed using non-invasive analytical methods. Ultraviolet and visible reflectance spectrophotometry with optical fibres (FORS) allows non-invasive identification of several colourants used by ancient illuminators, causing no damage or mechanical stress to the artworks subjected to analysis. Identification is usually based on the comparison of analytical data with a spectral database built from painted areas on parchment, created by preparing paints according to ancient recipes as described in medieval technical treatises. Such database and the spectral features of the colourants analysed are discussed, along with the benefits of extending the spectral range of analysis into the shortwave infrared (to 2500 nm). FORS can be best appreciated as a rapid preliminary tool that offers an overview on the main colourants employed and guides the selection of painted areas of manuscripts on which more selective techniques, such as X-ray fluorescence or Raman spectroscopy, can be employed for a more complete and accurate identification.

Introduction

Illuminated manuscripts are among the most precious artworks. The palettes used by ancient illuminators included many different colourants, meaning with this term both *pigments*, which are of inorganic (mineral or synthetic) origin,

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and *dyes*, which are of organic (animal or vegetal) origin. Manuscripts, however, are also fragile and the characterisation of their palette is an interesting task for conservation scientists but with no doubt a challenging one. Sampling is usually not allowed (though micro-sampling has demonstrated its efficiency), the same holds true for the application of techniques that require coming into contact with miniatures, such as FT-IR in ATR mode. Exposition of ancient codices to analytical instruments must neither cause damage to miniatures nor induce mechanical stress by forcing them to stay wide open, when still bound in books. Another difficulty is due to the natural tendency of the support, be it parchment or paper, to warp when it is exposed to heat or to electromagnetic beams from the analytical facilities, as this causes additional stress to miniatures. It is therefore clear that data acquisition times must be reduced to a minimum. All this explains the need for rapid, non-invasive techniques. Moreover, the availability of portable analytical devices also plays a role in limiting the stress undergone by these fragile artworks through allowing them to be analysed in the facilities where they are normally housed.

Among the many available non-invasive analytical techniques, Raman spectroscopy already established itself as the most efficient in the identification of colourants used in manuscript illumination. Thanks to the availability of portable systems, several studies have been published in the past few years concerning the characterisation of the palette used in

illuminated manuscripts.[1-4] Raman spectroscopy, though, has some drawbacks that limit its application: dyes and lakes are generally poor Raman scatterers and their identification is very difficult or even impossible, at least through a non-invasive approach. When long exposure times are requested, local heating on the parchment, induced by laser irradiation, can cause small, unperceivable movements of the support and consequent loss of focus. Among other techniques with good diagnostic power, X-ray fluorescence spectrometry (XRF) has been frequently applied to manuscript analysis[5,6] with some limitations due to the fact that X-rays go right through the parchment foils, and that it is an elemental technique which does not provide unique pigment identification. Additionally, XRF cannot be used to identify most organic compounds. The same holds true for PIXE spectrometry which has been sparely applied on miniatures[7] and mostly not in portable version but carrying the manuscript under study[8] into the laboratory. PIXE has been applied more frequently in the characterisation of inks in historical manuscripts.[9,10] Finally, FT-IR spectrophotometry[11] and X-ray diffraction spectrometry,[12] though both available in portable version, are at present still difficult to use routinely as *in situ* techniques; nevertheless, FTIR can be used to identify alteration products and binders.[13,14]

None of the cited techniques, therefore, has fully satisfying features nor can be used as self-consistent analytical tools. The optimal strategy to recognise colourants used in miniatures should therefore provide for a multi-technique approach,[15] as generally required when dealing with diagnostic in cultural heritage.[16]

Ultraviolet and visible (UV-Vis) spectrophotometry in diffuse reflectance mode, with particular reference to the variant with optical fibres or FORS (Fibre Optic Reflectance Spectrophotometry) has some characteristics that make it particularly suitable for the analysis of ancient illuminated manuscripts, at least as a preliminary technique with fast response times before the application of more sophisticated techniques, in order to limit the number of sites analysed. FORS is relatively easier to use in comparison with some of the other methods mentioned, it requires short times of analysis (each spectrum is collected in a few seconds), it causes no physical and chemical alteration to the area subjected to analysis, it can be applied in any geometrical condition due to the availability of different probes, and finally there is large availability in the market of truly portable and relatively not expensive instrumentation.

UV-Vis reflectance spectrophotometry in FORS configuration is a well-established technique for the characterization of colourants in works of art; early publications on the topic, without using fibres, date back to the 1930s.[17,18] Since then, FORS has been widely used for the identification of colourants in paintings and frescoes,[19-23] but its application in the study of manuscripts still appears to be relatively limited.[6,24-28] Despite its many advantages, some drawbacks prevent the reliable use of FORS as a self-consistent analytical tool for the analysis of miniatures. In particular, reflectance spectra of colourants in the UV-Vis range have few broad bands and therefore they have an intrinsically lower *fingerprinting* ability when compared with spectra obtained with other molecular spectroscopic techniques

such as FT-IR or Raman spectroscopy. In some cases, therefore, reflectance spectra cannot allow unambiguous identification, in particular when two or more absorbing species are present in a mixture. Identification with FORS can nevertheless rely on the fact that in miniature painting the range of possible colourants is likely to be restricted by taking into consideration colour, availability, period and geographical zone of production of the manuscript under examination.[29,30] The presence of unusual and unexpected colourants can obviously never be excluded, which is why a multi-technique analytical approach is always preferable, as already noted.

In this work advantages and limitations of UV-Vis FORS in the characterisation of miniature paintings are critically discussed. Firstly, a database of reflectance spectra has been created from analysing mock-ups made with colourants used by medieval illuminators. The mock-ups have been analysed in three labs (Università degli Studi del Piemonte Orientale in Alessandria, Italy; IFAC-CNR in Sesto Fiorentino, Italy; National Gallery of Art in Washington, USA) with different instrumentation, some of which included analysis in the shortwave infrared (SWIR) range. The benefits of extending the range analysed into the SWIR are discussed here using azurite as an example. FORS analyses have also been carried out on numerous manuscripts, and the results were compared with parallel analysis performed using XRF and Raman spectroscopy. The analysis of a *Graduale* from the Museo di San Marco in Florence is reported here as a case study.

Experimental

Instruments

FORS analysis at the Università degli Studi del Piemonte Orientale (UPO) was performed with an Avantes (Apeldoorn, Olanda) AvaSpec-ULS2048XL-USB2 model spectrophotometer and an AvaLight-DH-S-BAL balanced deuterium–halogen light source; the detector and light source were connected with fibre optic cables to an FCR-7UV200-2-1.5×100 probe. In this configuration, both the incident and detecting angles were 45° from the surface normal, in order not to include specular reflectance. The spectrophotometer may operate in the 200–1160 nm range. Depending on the features of the monochromator (slit width 50 μm, grating of UA type with 300 lines per mm) and of the detector (2048 pixels), the best spectral resolution was 2.4 nm calculated as FWHM (Full Width at Half Maximum). Diffuse reflectance spectra of the samples were referenced against the WS-2 reference tile provided by Avantes and guaranteed to be reflective at 98% or more in the spectral range investigated. The investigated area on the sample had a 1 mm diameter. In all measurements the distance between the probe and the sample was kept constant at 1 mm. To visualise the investigated area on the sample, the probe contained a Framos (Agrate Brianza, Italy) WEB1315SI model digital micro camera, connected to PC *via* USB. The instrumental parameters were as follows: 30 ms integration time, 50 scans for a total acquisition time of 1.5 s for each spectrum. The whole system was managed by means of AvaSoft v. 8 dedicated software, running under Windows 7. The probe was mounted on a mobile

arm fixed on a tripod, in order to carry out analyses in all geometrical situations.

FORS was performed at IFAC-CNR using two portable Zeiss spectra-analysers, the models MCS 601 UV-Vis and MCS611 NIR 2.2 WR, which are mounted on the same chassis. They operate in the 200–2200 nm range. The standard configuration of the devices made it possible to acquire reflectance spectra in the 350–2200 nm range. The acquisition step was 0.8 nm per pixel in the 350–980 nm range and approximately 5 nm per pixel in the 980–2200 nm range. The sampling area was about 2 mm in diameter. A hemispheric probe-head (designed at IFAC-CNR) was used to collect the FORS spectra with a 0°/45°/45° geometry. The acquisition time for each spectrum was about 2 seconds. Each spectrum was the average of three acquisitions. Additional spectra on the same reference paintouts were also acquired at IFAC-CNR by using a Lambda 900 Perkin Elmer (Waltham, MA, US) spectrophotometer equipped with a PELA-1017 fibre optic remote accessory (total reflection integrating sphere) and operating in the 200–2500 nm range. The spectral resolution of the measurements was 2 nm in the 199–860 nm range and variable (from 1 to 20 nm, depending on the different wavelength and analysed sample) in the 861–2500 nm range. In both cases the instruments were calibrated using a white Spectralon® standard (99% reflectance).

At the National Gallery of Art (NGA), FORS analyses were carried out with an FS3 fibre optics spectroradiometer (ASD Inc., Boulder, Colorado). The spectrometer operates in the range 350–2500 nm, with a spectral sampling of 1.4 nm from 350 to 1000 nm and 2 nm from 1000 to 2500 nm. The spectral resolution is 3 nm at 700 nm and 10 nm at 1400 and 2100 nm. The optic fiber was held fixed normal to the sample, and the ASD high intensity light probe was set on a tripod at a 45° angle. The fibre was placed about 1 cm from the samples, so that the analysed area was about 3 mm in diameter. Typically 64 spectra were averaged for each sample and the total acquisition time was 10 seconds for each spectrum. The spectrometer was calibrated against a white Spectralon® standard.

Reference spectra

The spectral database was created by measuring reflectance upon paints laid on parchment. Materials and recipes of production were selected following the indications contained in medieval texts, such as *De Arte Illuminandi*,[29] *Manoscritto di Lucca*[31] and *Il libro dell'arte*.[32] Colourants were purchased by Kremer Pigmente GmbH & Co (Aichstetten, Germany). Parchment was purchased from La Pergamena Antica s.n.c. (Sona, Italy).

To simulate the painting technique used by ancient illuminators, paints were laid down on parchment in pairs, once bound with egg white tempera and once with gum arabic. The resulting palettes are shown in Fig. 1.

Nearly 70 different colourants were chosen; their complete list is available in Table 1, together with reflectance/absorbance band positions (average values) and characteristics which will be thoroughly discussed in the following paragraphs. The identification of pigments was confirmed by means of XRF and

Fig. 1   Palettes of paints on parchment.

Raman analysis, while for dyes it was not possible to have further diagnostic information from other analytical methods. Reflectance spectra of all these colourants were collected at UPO, IFAC-CNR and NGA.

Spectra of real artworks

Analyses on artworks were performed on a large set of medieval and Renaissance manuscripts held in various institution throughout Italy, such as the Museo Civico di Arte Antica, the Biblioteca Nazionale Universitaria and the Biblioteca Reale in Turin; the Archivio e Biblioteca Capitolare in Vercelli, the Biblioteca Nazionale Braidense in Milan; the Biblioteca Palatina in Parma; the Museo Nazionale del Bargello, the Museo di San Marco and the Biblioteca Medicea Laurenziana in Florence.

Results and discussion

Reflectance spectra can be used to discriminate between colourants of similar hue by the identification of maximum peaks and inflection points, the latter corresponding to maxima or minima in the first derivative spectrum. However, these spectral features can vary greatly as a consequence of the addition of another colourant, be it a differently coloured one or even simply a white one, as described by Gargano *et al.*[33] It is therefore more reliable to look for *absorption* features, whose wavelength positions are known to remain more constant. Moreover, while reflectance features are hard to identify in a mixture, the absorbance features of the individual components of a mixture can sometimes be singled out because of the additivity of absorbance. The *apparent absorbance* spectrum can be obtained

Table 1 List of colourants analysed for the spectral database

Category	Colourant	Band position (nm) and characteristics
Red, orange & brown pigments	Cinnabar	600[a]
	Minium	565[a]
	Realgar	530[a]
	Armenian bole	580,[a] 875[b]
	Hematite	580,[a] 875[b]
	Red ochre	580,[a] 875[b]
	Burnt sienna	580,[a] 875[b]
	Burnt umber	580,[a] 875[b]
Red dyes	Madder	510,[b] 540[b]
	Red safflower	530[b]
	Brazilwood	560[b]
	Kermes	520,[b] 555[b]
	Armenian cochineal	520,[b] 555[b]
	Mexican cochineal	520,[b] 555[b]
	Dragon's blood	—[c]
Yellow pigments	Orpiment	480[a]
	Litharge	455[a]
	Lead–tin yellow type I	480[a]
	Lead–tin yellow type II	500[a]
	Lead antimonate	500[a]
	Mosaic gold	530[a]
	Yellow ochre	545,[a] 640,[b] 900[b]
	Goethite	545,[a] 640,[b] 900[b]
	Natural umber	545,[a] 640,[b] 900[b]
	Natural sienna	545,[a] 640,[b] 900[b]
Yellow dyes	Weld	410[b]
	Yellow safflower	400[b]
	Saffron	435[b]
	Stil-de-grain	420[b]
	Turmeric	420[b]
Green colourants	Malachite	800[b]
	Verdigris	720[b]
	Green earth	760[b]
	Copper resinate	695[b]
	Iris juice	605[b]
	Sap green	605[b]
Blue colourants	Lapis lazuli	600[b]
	Azurite	640[b]
	Indigo	660[b]
	Woad	660[b]
	Smalt	545, 600, 640[b]
	Egyptian blue	629[b]
Violet and purple dyes	Elderberry	555, 590[b]
	Tyrian purple	630[b]
	Folium	545, 580[b]
	Orchil	545, 595[b]
Metallic pigments	Silver	330[a]
	Gold	510[a]
	Brass	535[a]
	Bronze	570[a]
	Copper	580[a]
White, grey & black pigments	Lead white	—[c]
	Bone white	—[c]
	Gypsum	—[c]
	Lampblack	—[c]
	Vine black	—[c]
	Bone black	—[c]
	Iron-gall ink	—[c]

[a] Inflection point. [b] Apparent absorbance maximum. [c] No clear spectral feature detectable.

via Kubelka–Munk or $\log(1/R)$ conversion, in order to highlight spectral features due to absorbing species. The golden rule is that the reflectance maximum gives an indication of the colour of the paint, while the reflectance minimum, *i.e.* the apparent absorbance maximum, gives an indication of the colourant.

As fully discussed elsewhere,[20,34–36] the absorption of visible light in the substances used as colourants occurs due to the following main mechanisms of electronic transition:

- charge transfer;
- transition among d–d orbitals due to the ligand field;
- transition from valence to conduction band;
- delocalised molecular orbitals.

It must be pointed out that identification of inorganic colourants by FORS is relatively straightforward, but the same does not hold true for dyes. The main difficulties in unambiguous identification of dyes arise both from the procedures used in their extraction from raw materials and from the two ways in which they were employed in miniature painting: either as *juices* or as *lakes*. Juices were obtained by dissolving in an aqueous medium the dyes obtained from vegetables or animals; in order to fix the dye to the parchment, a mordant, *i.e.* inorganic cations such as Al(III), was added. Lakes were instead obtained by fixing the natural dyes onto an inorganic substrate in order to obtain a pigment. Different preparations of the dyes may produce very different hues depending on the mordant used (aluminium, iron, tin, *etc.*) and on the conditions employed in their extraction, with pH playing a major role. As an example, the hue of turnsole, a dye extracted from *Chrozophora tinctoria*, can be red, purple or blue following, respectively, acid, neutral or basic extraction from the plant. The measured reflectance spectrum changes accordingly. In addition, because of the low hiding power of juices and lakes, the reflectance spectra of dyes can show a significant contribution from underlying layers, such as the pictorial support or other painted areas, so that it can be difficult to single out the contribution of the dye. Clearly, then, identification of dyes by FORS is strongly bound to the availability of an extensive database of reference spectra, including most, if not all, possible variants in terms of preparation and application of each dye on parchment.

We will discuss the performance of FORS in the 200–1100 nm range for the analysis of illuminated manuscripts according to the different hues used in the palette of illuminators; in this sense, the present article aims to work as a reference study for anyone using FORS in the identification of colourants on illuminated manuscripts (similar work was presented by Montagner *et al.*[37] concerning modern organic dyes). Then special cases will be discussed such as the discerning ability of the technique for mixtures of colourants, as well as the improved diagnostic ability following the extension of the range of analysis into the SWIR (to 2500 nm).

To allow a better comparison of reflectance spectra in the various figures, offset was applied along the *Y* axis according to needs.

Red, orange and brown pigments

Four pigments were usually employed by illuminators for red and orange painted areas: cinnabar (HgS, either natural from

the homonymous mineral or the synthetic vermillion), minium (Pb_3O_4), realgar (As_4S_4), and iron oxide-based pigments in their several variants (*e.g.* ochres and earths). As occurred for other colours, these pigments were used with a definite 'hierarchy' by miniature painters, in which their symbolic meaning was correlated with their material value. In this view, cinnabar was considered the most prised red pigment. There is a well-defined difference in the mechanism that determines the absorption of UV-Vis radiation by these compounds in that minium, cinnabar, and realgar are semiconductors, while pigments containing iron oxides owe their colour to the ligand field and charge transfer mechanisms, the latter among Fe^{3+} and O^{2-} or OH^- ligands.[38] In the 300–800 nm range these four pigments show a sigmoid-shaped spectrum (Fig. 2) with an inflection point that becomes a maximum peak in the first derivative reflectance spectrum.

Spectra of semiconductors show a sigmoid with a steeper rise around the inflection point. In terms of energy the valence-to-conduction gap is fairly different among the three semiconductors and this allows discrimination among them: in the first derivative spectrum realgar shows a maximum peak around 530 nm, minium at 560–570 nm and cinnabar and vermillion at 590–605 nm. The relative uncertainty in the position of the inflection points can be justified by the presence of impurities in the semiconductor possibly influencing the energy gap, by decreasing or increasing its value and consequently causing respectively a bathochromic or a hypsochromic shift of the spectral edge. Other important factors causing shift could be the particle size distribution and concentration of pigments in the paint layer. All the red iron oxide pigments show similar spectral features, due to the presence of hematite, α-Fe_2O_3 as chromophore: the maximum peak in the first derivative spectrum lays in the 575–590 nm range and it is therefore distinguishable from semiconductors; moreover their spectra show a characteristic positive slope in the region above 600 nm which generates a less pronounced inflection point around 700 nm. Finally, an absorption band due to ligand field transition, centred around 850–900 nm, is usually present. These features can be well recognised in the different red iron oxide pigments (Fig. 3), such as red ochre, hematite, Armenian
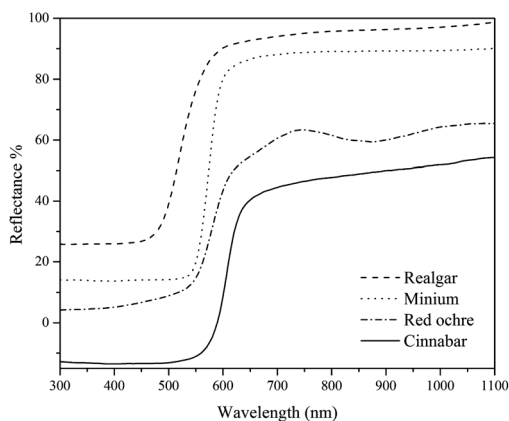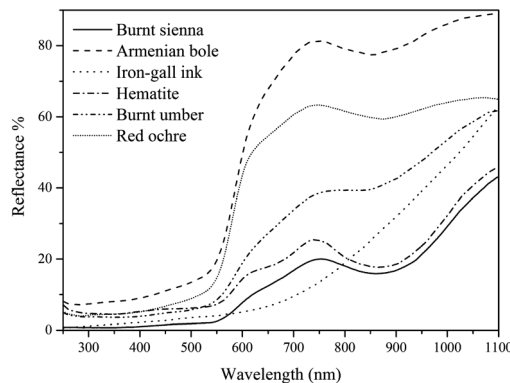

Fig. 3   Spectra of red and brown iron-based colourants.

bole (a red clay frequently added by illuminators to the preparatory layer under the gold leaf), and in pigments obtained by roasting goethite-containing earths, such as burnt sienna and burnt umber. It is not possible, however, to discriminate among the different red iron oxide pigments cited only on the basis of their FORS spectra, due to the overlapping of their spectral features which are all determined by the presence of the same chromophore.

The same red pigments could be used to obtain pink and brown hues, by adjusting their saturation and/or brightness with a white and a black pigment respectively. In the case of pink hues, the resulting reflectance spectra are similar in terms of spectral features to those of the pure red pigments. Brown, however, has always been a troublesome colour from the diagnostic point of view. Miniature painters used mostly iron oxide pigments to obtain brown, which in some cases yield a spectrum typical of red iron oxide pigments; in cases where very dark pigments are used, a less defined and therefore hardly recognisable spectrum is obtained.

Another brown iron-based colourant is iron-gall ink, prepared by addition of Fe(II) sulphate to an aqueous extract from gallnuts. Iron-gall ink, apart from being extensively used in writing since early medieval times, was sometimes used as a colourant in miniature painting[15,39] with shades ranging from brown to black. Iron gall ink is easily discriminated from carbon black ink on the basis of its FORS spectrum, due to its shape with a typical slow rise in the red region; it is not possible, however, to define accurate spectral features as no maximum, minimum or inflection points are present.

Red dyes

The identification of red organic compounds is more difficult, due to the previously mentioned issues. The most common dyes used in manuscript illumination, with hues ranging from red to purple and violet, were madder from *Rubia tinctorum*; brazilwood from *Caesalpinia* plants; kermes, cochineal and Indian lac from Coccid scale insects; Dragon's blood from *Dracaena draco*; red safflower, *i.e.* the red component of the juice obtained from flowers of *Carthamus tinctorius*. These colourants were applied as such (either in juice or lake form) or as finishing layers (glazes) on other painted areas, in both cases

Fig. 2   Spectra of red and orange pigments.

with little or no hiding power. Similar to red inorganic pigments, red dyes show a sigmoid-shaped reflectance spectrum with a typical inflection point, although with a less steep rise in the red region. Moreover, a small maximum band in the blue region is usually present, which explains their hues different from pure red. When turned into apparent absorbance coordinates, their spectra highlight one or more absorption bands which are useful for their identification (Fig. 4).

The mechanism of absorption of light in natural dyes differs from that of red pigments, which is due to transitions among delocalised molecular orbitals. Dyes with anthraquinonic structures (madder, insect dyes) can be detected as they show an absorption band structured into two sub-bands in the 500–580 nm range, with dyes of vegetal origin (madder) ideally peaking at 510–515 and 540–545 nm, while dyes of animal origin (kermes, cochineals and Indian lac) showing bands at 520–525 and 550–565 nm. FORS spectra do not allow us to distinguish among kermes, Indian lac and the different types of cochineals, *i.e.* Armenian, Polish and Mexican cochineal. Brazilwood shows a single absorption band centred at 560 nm, while that of red safflower can be found around 530 nm. Dragon's blood has less distinct spectral features and it is therefore more difficult to identify.

Absorption energies can vary in the presence of different mordanting ions, which promote the formation of ion-dye chelates. While it is usually possible to broadly classify red dyes as of animal or vegetal origin, in the analysis of real artworks their exact identification can be complicated by the presence of other pigments, by the nature of their application, and by the effects of natural ageing. Many of the absorption features can vary depending on the preparation of the dye into a lake[40] as well as the preparation of the paint. Nevertheless, in our experience, the signals obtained from the real manuscripts analysed usually showed bands that were comparable to those obtained from the reference palettes where alum was present. Some studies have recently investigated in detail the spectral features of red dyes as determined by FORS.[41–43] To date however, to the best of the authors' knowledge, there have been no systematic studies of the exact effect of preparation, ageing, and type of lake on the reflectance spectrum.
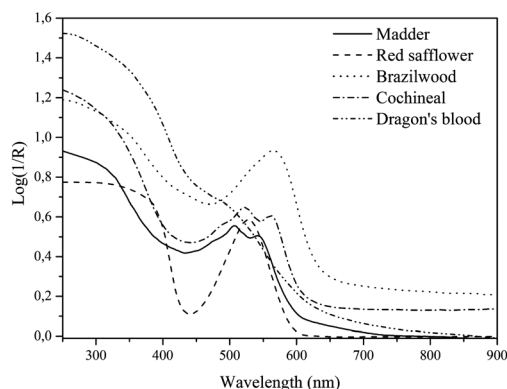
Yellow pigments

There is a limited set of yellow pigments that one can expect to find in medieval manuscripts. In the early Middle Ages, orpiment and yellow ochre were mostly used. These pigments were still in use in the Late Middle Ages and the Renaissance, with the addition of some synthetic materials: the most important were lead-containing pigments (lead–tin yellow types I and II, lead antimonate also known as *Naples yellow*) and, from the 13th century onwards, a tin(IV) sulphide known as *mosaic gold* because of its resemblance to pure gold. Other less used alternatives were Pb(II) oxides known as litharge and massicot. The reflectance spectrum for yellow pigments is sigmoid-shaped, similar to reds (Fig. 5).

The spectrum is generated by different mechanisms of light absorption: yellow ochres and other yellow iron oxide pigments absorb light similar to red ochres, while orpiment, mosaic gold and lead-containing yellows are all semiconductors. Apart from the iron-based pigments whose spectra are richer in spectral features, the inflection point in the spectrum is again the characteristic feature to be used for the identification of yellow pigments. It can be found around 455 nm for litharge, in the 470–490 nm range for lead–tin yellow type I and orpiment, at 490–510 nm for lead–tin yellow type II and lead antimonate. Mosaic gold has its inflection point in the 525–535 nm range and the rise in the yellow region is less steep, so that the whole spectrum appears to be less sigmoid-shaped than that of other yellow pigments, resembling more the spectrum of gold (see below). It must be kept in mind, though, that the inflection points can vary greatly when these pigments are mixed with a white pigment,[33] so that the values cited must be seen as indicative only.

Yellow iron oxide pigments share similar spectral features to red ones; in this case the chromophore mineral is goethite, α-FeO·OH. The maximum peak in the first derivative spectrum is in the 535–555 nm range and therefore distinguishable from semiconductors; two absorption bands, absent in semiconductors, may be present, centred around 640 nm and 900 nm. A further absorption band is present between 400 and 500 nm. These features can be easily identified in the different
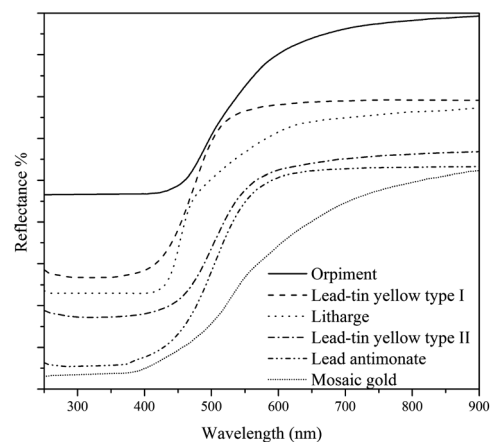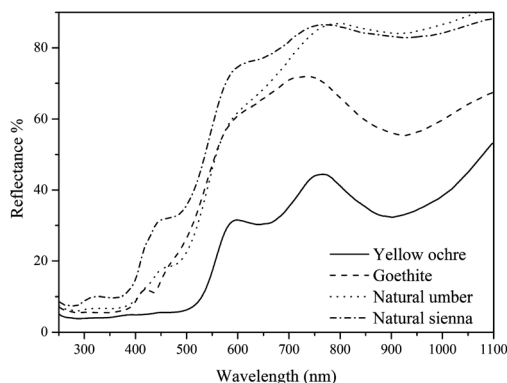

Fig. 4 Spectra in log(1/*R*) coordinates of red dyes.

Fig. 5 Spectra of yellow pigments.

Fig. 6   Spectra of yellow iron oxide pigments.

Fig. 7   Spectra in log(1/*R*) coordinates of yellow dyes.

yellow iron-based pigments (Fig. 6), such as yellow ochre, goethite, natural sienna and natural umber earths; the latter usually contains both iron and manganese oxides, resulting in a brownish hue. Again, it is not possible to discriminate among the different yellow iron-based pigments mentioned on the basis of their FORS spectra alone.

Yellow dyes

The same observations described for red dyes are valid for yellow dyes, with concern to the mechanism of light absorption and to the diagnostic problems bound to mordanting practices. One should also keep in mind that, in the case of paints with low hiding power, a significant contribution could derive from the underlying parchment, the spectrum of which is similar to those of yellow colourants. Yellow dyes were certainly used in miniature paintings as they are frequently cited in ancient treatises, but since their identification is difficult in non-invasive ways, there are still very few diagnostic confirmations to literary information. Possible candidates are saffron from *Crocus sativus*; weld from *Reseda luteola*; yellow safflower, *i.e.* the yellow component of the juice obtained from *Carthamus tinctorius*; unripe berries of the *Rhamnus* species – the so-called *stils-de-grain* or *graines d'Avignon*; turmeric from *Curcuma longa* which is typical of Islamic illumination.

The identification of yellow dyes with FORS is difficult. Their main spectral feature in the UV-Vis range is the inflection point. This can vary greatly as a consequence of dilution with a white pigment[33] and of preparation methods as recently shown by a study on historical textiles;[43] the spectral features cited below should therefore be regarded as indicative only. Another relevant spectral feature is an absorption band in the 400–450 nm range, which occurs in similar position among the different dyes (Fig. 7).

Weld shows an absorption band centred at *ca.* 410 nm and an inflection point at *ca.* 460 nm, similar to the one of yellow safflower whose absorption band is located at *ca.* 400 nm. Saffron can be distinguished in that its main absorption band occurs around 435 nm, with a shoulder around 480 nm that is typical of carotenoids.[44] The yellow juice from unripe *Rhamnus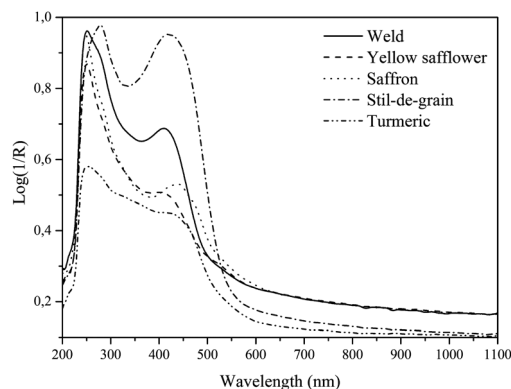* berries shows an absorption band at *ca.* 420 nm and an inflection point at *ca.* 485 nm. These spectral features are very similar to those of turmeric.

Green colourants

The range of greens in miniature painting was mostly limited to the pigments malachite, green earth, and verdigris, to which two dyes, sap green from ripe berries of the *Rhamnus* species and iris green from *Iris germanica*, can be added. Another green colourant frequently used on easel paintings is copper resinate; its use for manuscript illumination has been suggested as possible[45,46] but there is no diagnostic evidence supporting this hypothesis.

Absorption of light is due to electronic d–d transitions of the ligand field type for inorganic pigments and for copper resinate, whereas it is due to transitions in delocalised molecular orbital for the dyes. The reflectance spectrum for greens is generally characterised by a maximum of reflectance in the blue-green region and two main absorption bands in the UV-violet and red-infrared regions (Fig. 8).

Since the reflectance maximum can be notably shifted in some instances, for example in mixtures, identification can be based more reliably on the position of the apparent absorption band and on the shape of the spectra. Verdigris shows an
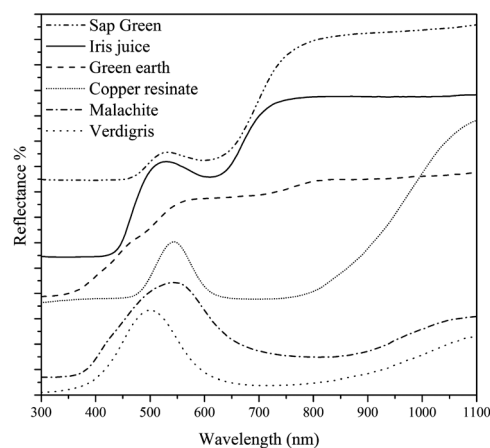

Fig. 8   Spectra of green colourants.

absorption band centred at 720 nm, while that of malachite occurs at *ca.* 800 nm and that of copper resinate at *ca.* 695 nm. The spectrum of green earth has an absorption band centred at 760 but it is less pronounced than in the other pigments; the reflection band is also less symmetrical. Other less common sulphate and chloride copper pigments, such as posnjakite, brochantite, and atacamite, show absorption bands similar to verdigris and cannot be easily distinguished from it. Green dyes, in contrast, show absorption bands centred at much lower wavelengths, between 595 and 615 nm.

A common alternative to the use of pure green colourants was a mixture made of a blue and a yellow colourant. Medieval painters, especially in the early Middle Ages, used the so-called *vergaut*, a mixture of indigo with a yellow colourant (usually orpiment or a yellow dye). The presence of an indigo mixture can be easily identified and discriminated from a pure green colourant since the absorbance spectral features of the blue component are usually apparent. The yellow component, however, can only be identified by using additional analytical techniques, such as XRF or Raman spectroscopy.

Blue colourants

As is the case for red colourants, miniature painters used blue materials in a hierarchical way in relation to their monetary value. Natural ultramarine blue (also called *lapis lazuli*) was the most precious, being produced from the semiprecious *lapis lazuli* stone; then followed azurite and finally blue organic pigments obtained from indigo or woad. Absorption of light occurs with different mechanisms: in ultramarine blue, absorption of light is due to charge transfer, whereas ligand field transitions determine the blue colour in azurite; finally, delocalised molecular orbitals determine the absorption mechanisms for indigo and woad. The reflectance spectrum for blue colourants is characterised by a maximum reflectance peak in the blue region (Fig. 9). Indigo and woad can be easily identified (though not distinguished from one another) by an asymmetrical peak close to the violet region and by an overall low reflectance, with a typical steep rise in the far red region; the absorption maximum is around 660 nm. Azurite and

ultramarine blue show similar visible maxima but can be differentiated with respect to the absorption maximum which is around 600 nm for ultramarine blue and around 640 nm for azurite; moreover, ultramarine blue has a typical rise in reflectance in the red and NIR region, where azurite shows lower reflectance.

Another blue pigment used in miniature paintings starting from the Renaissance is the cobalt-based smalt, which shows a very typical and intense absorption band in the 550–650 nm range, due to ligand field transitions; this band is structured in three sub-bands.[47] Smalt can be revealed by FORS even in low concentration, because the very intense absorption bands of Co(II) ions are easily detected.

For the sake of completeness, Egyptian blue, identified in early Middle Ages manuscripts,[48] must also be cited. This pigment shows an absorption band around 629 nm, due to a ligand field transition, and characteristic spectral features in the region 800–1100 nm.

Violet and purple dyes

To reproduce violet, purple and sometimes blue hues, medieval miniature painters used mostly dyes, or else they had to mix red and blue colourants, since no inorganic pigments of these colours were available. In addition to the already mentioned cochineal, kermes, madder, and brazilwood that can be turned to violet with a suitable mordant or pH, painters would add to their palette the highly valuable Tyrian purple from *Murex* or *Purpura* molluscs and its less valuable substitutes: folium, the extract at neutral pH from *Chrozophora tinctoria* plant also known as turnsole; orchil, the alkaline extract from lichens such as *Roccella tinctoria*; elderberry from *Sambucus nigra*. Purple hues could also be obtained by mixing red and blue dyes, *e.g.* madder with indigo, or by superimposing a blue/red dye on a red/blue underlying layer, a practice known as *top-dyeing* and cited since Roman times for textiles;[49] from the diagnostic point of view, however, it is hard to demonstrate that this practice was actually applied to manuscript illumination. It is well known that purple dyes were used to dye the parchment of the highly valuable *purple codices*.[50]

The reflectance spectra of these colourants, which absorb the UV-Vis radiation in a way similar to all other dyes, show an inflection point at wavelengths higher than 600 nm, a typical reflectance maximum in the violet-blue region and a typical absorption band, the latter being the most reliable spectral feature for diagnostic purposes. Fig. 10 shows the FORS spectra obtained on these dyes dissolved in water and gum arabic. Tyrian purple shows a pronounced absorption maximum at *ca.* 530 nm, with a shoulder at 660 nm due to a chromophore system analogous to indigo. Folium shows two absorption maxima, located at *ca.* 545 and 580 nm. The spectrum of orchil is similar to that of folium, presenting two absorption maxima at *ca.* 545 and 595 nm; this is not surprising since these two dyes, though being of different origin (plant *vs.* lichen), appear to contain similar molecules.[51,52] Terminology for folium and orchil has actually been rather confusing in the past, since similar terms were frequently used to indicate these two
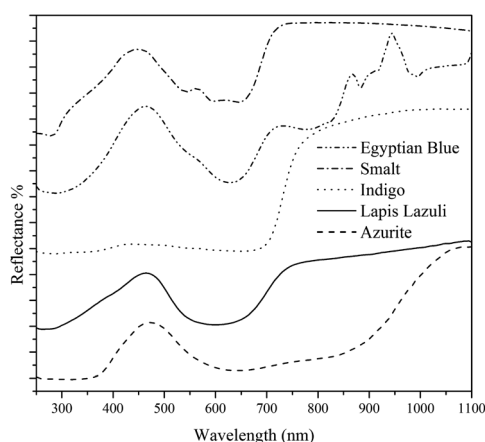

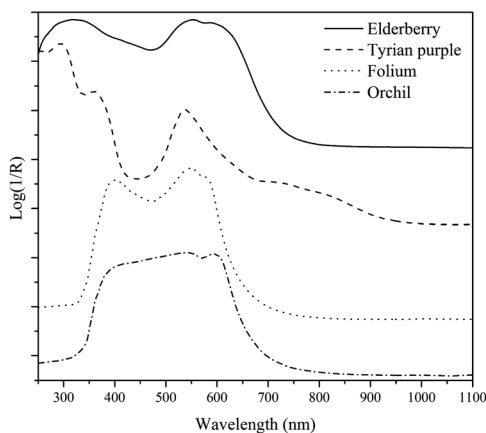Fig. 9 Spectra of blue colourants.

Fig. 10 Spectra in log($1/R$) coordinates of purple and violet dyes.

Fig. 11 Spectra of metallic pigments.

materials in technical treatises. Elderberry also shows two absorption maxima located at *ca.* 555 and 590 nm, but its hue is blue rather than violet.

As already noted for red and yellow dyes, the spectral features of these violet colourants are not completely diagnostic as they can change according to the preparation conditions.

Metallic pigments

The use of metallic pigments for illumination must be regarded as a way to embellish the manuscript and to improve its symbolic value. Metallic pigments were used either in leaf or in powder form, the latter being called *shell* metal (*i.e.* shell gold, shell silver) according to the habit of preparing paints from powdered metal inside shells; shell metals were also used for writing, *i.e.* in chrysography (with gold), argyrography (with silver), *etc.* The most precious and most widely used metal was obviously gold. Due to its high price, sometimes painters substituted it with cheaper colourants such as the already mentioned *mosaic gold* (stannic sulphide) or various copper alloys. A copper/zinc alloy with zinc ranging between 10 and 18% shows a golden yellow colour, and the same is true for a copper/tin alloy very rich in copper. Another widely used precious metal is silver. Though FORS is not the ideal technique to identify metals, some indications can be nevertheless obtained, in those cases where metallic pigments have not suffered from extensive oxidation. Reflectance spectra of these pigments (Fig. 11) show the typical behaviour of metals (apart from mosaic gold that is a semiconductor), with a generally low reflectance.

The spectrum of gold, irrespective of its form, *i.e.* both in leaf and in powdered form, is characterised by a rise around 490 nm, with a fairly defined inflection point at 510 nm; such rise is not as steep as in semiconductors, but more typically "rounded". Mosaic gold shows a spectrum with a similar shape where rise and inflection point occur at 500 nm and 525–535 nm, respectively, so that it can be distinguished from pure gold. Inflection points differ for metallic copper and its alloys: they occur around 580 nm for pure copper, around 570 nm for a 94/6% Cu/Sn alloy and around 535 nm for an 88/12% Cu/Zn
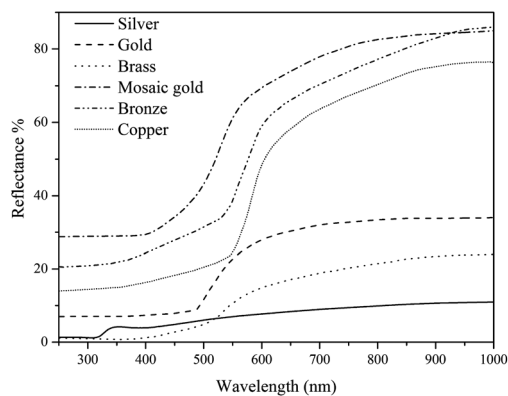
alloy. These spectral features are well defined on pure samples but usually cannot be recognised on real artworks. In fact, copper and its alloys hardly ever retain their original golden hue in manuscripts; they tend to alter to green-brown hues as a consequence of copper degradation.[53] A similar behaviour is shown by silver: it can be recognised through a typical inflection point at 330 nm in the reflectance spectrum, but in most cases, painted or leaf silver is converted to black silver sulphide, so that the inflection point is hardly apparent.

White, grey and black pigments

The lack of colour makes these materials difficult or impossible to identify using UV-Vis FORS. White corresponds to almost total reflection of Vis radiation, so reflectance spectra of lead white, bone white and gypsum, three among the mostly popular pigments in manuscript illumination, are very similar in the near UV and visible range, showing a relatively flat line at high reflectance values. Black, in contrast, corresponds to total absorption. All carbon-based pigments used in miniature painting, *i.e.* lampblack, vine black, and bone black, show absolutely identical reflectance spectra with nearly 0% reflectance. Iron-gall ink, sometimes used as a black pigment, can be discriminated from carbon-based pigments due to a typical slow rise in the red region, as previously discussed.

Mixtures of colourants

Miniature painters, like all other painters, obtained their preferred hues by mixing two or more colourants in suitable proportions. Unfortunately, this practice lowers the diagnostic capabilities of FORS in the identification of colouring materials. In most cases a mixture of two or more colourants generates a rather confusing spectrum, in which the reflectance features of the individual materials are barely recognisable and may be completely hidden. As already mentioned, even the simple dilution of a colourant with a white pigment, in order to adjust its saturation and brightness, may induce a shift in its reflection maximum or inflection point.[33] An even more pronounced shift can be induced by mixture with another *coloured* material: for example, the maximum reflectance peak of a blue or green

compound can be strongly red-shifted by addition of a yellow colourant.

One may compare the spectra measured on real objects with spectra of those colourants whose presence is suspected, and try to interpret differences in terms of possible mixtures. As already mentioned, one must look for absorption bands rather than for reflectance peaks. There are some cases, in fact, in which a careful examination of the spectrum reveals information useful for the characterisation of the mixture. The following four cases are well representative:

(1) As already mentioned, *vergaut* was a green mixture of indigo and a yellow colourant. The FORS spectrum of vergaut (Fig. 12), while showing the reflectance features of a green colourant, still displays the absorption maximum of indigo near 660 nm, whatever the yellow component. In contrast, the spectral features of the yellow component, usually consisting of an inflection point, cannot be identified because they are completely levelled off by the strong light absorption of indigo in the region between 200 and 600 nm. The presence of the yellow component causes also a slight shift of the inflection point of indigo from 720 nm to about 715 nm. This is a typical example explaining why absorption features are more reliable than reflectance features: it would not be possible to identify either of the components of the mixture based on the reflection features alone.

(2) A more favourable situation is a mixture of two colourants, both showing one or more absorption maxima. In the case shown in Fig. 13, a mixture of indigo and red safflower was used on a Persian manuscript to dye paper in a particular purple hue.

The FORS spectrum of the mixture shows the absorption maxima of red safflower around 530 nm and of indigo around 660 nm. Again, the typical inflection point of indigo at 720 nm has a hypsochromic shift at 710 nm caused by the presence of the red component.

(3) As mentioned, when used in combination with other analytical techniques, FORS can reveal interesting features of the colourants involved in a mixture. In this example (Fig. 14), a light green colourant, used by the illuminator to paint grass, contains malachite as suggested by Raman analysis. The maximum reflectance peak in this spectrum, however, shows a red shift with respect to a reference spectrum of malachite.
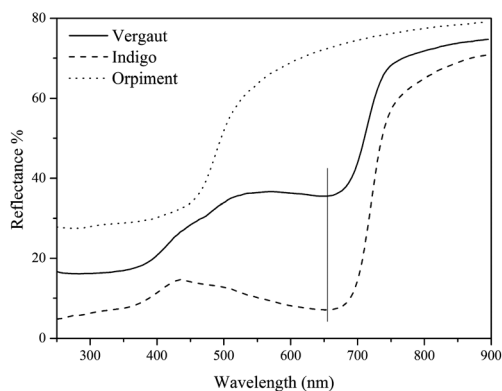

Fig. 12 Spectra of vergaut, a mixture of indigo and a yellow colourant.
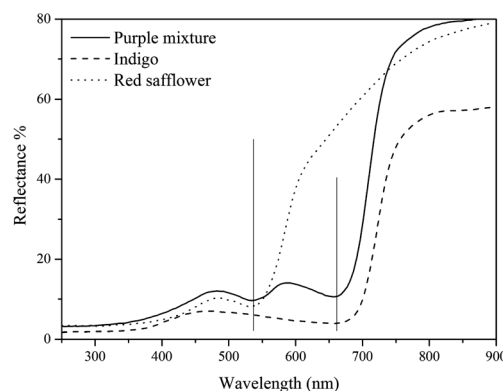

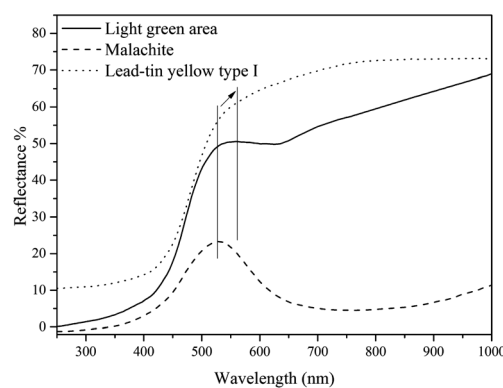Fig. 13 Spectra of a purple mixture containing indigo and red safflower.

Fig. 14 Spectra of malachite, lead–tin yellow type I and of a light green area.

Analysis by both Raman and XRF showed the simultaneous presence in this area of lead–tin yellow type I, which is the cause for this shift. Interestingly, analysis of similar areas in the same manuscript allowed identification of a good correlation between the Sn concentration and the shift of the maximum peak towards the yellow region in the reflectance spectrum, revealing that the painter made his malachite "yellower" by mixing it with varying amounts of lead–tin yellow type I, according to his needs.

(4) Finally, an interesting task is the quantification of the components in a mixture based on the reflectance spectrum, as already proposed by other authors.[54,55] A mixture sometimes occurring in miniature painting was cinnabar/minium, either as an intentional mixture or following the adulteration of the more precious cinnabar with the cheaper lead compound. When these two pigments are mixed, a sigmoid-shaped curve with two inflection points is to be expected (Fig. 15), which are more evident as two maxima in the first derivative spectrum; they can be fully resolved as they differ by at least 20 nm.

Calibration with mixtures at known concentration of the components and application of deconvolution software tools could in some cases be used to quantify the components in unknown samples. Quantification must be based on relative measurements such as ratios, since the absolute reflectance can
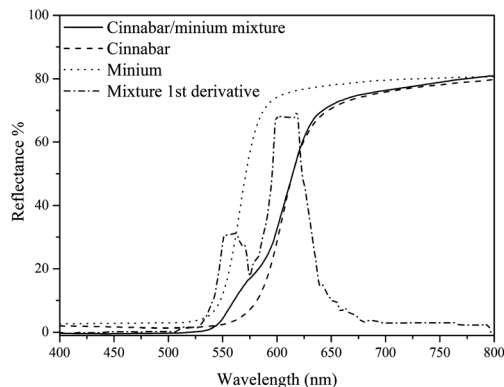
Fig. 15 Spectra of cinnabar, minium and cinnabar/minium 1 : 1 mixture with the 1st derivative curve.

change dramatically, *e.g.* with respect to surface roughness, as well explained by Simonot and Elias.[56]

Extended range of analysis

As already mentioned, the features of reflectance spectra in the Vis-NIR range are due to several mechanisms of electronic transition. The shortwave infrared (SWIR: 1100–2500 nm) range is instead characterised by the presence of vibrational band overtones and combinations.

Several minerals used as pigments contain functional groups such as hydroxyls, sulphates and carbonates, which do indeed show absorption bands in the SWIR. For these materials, extending the range of FORS analysis into the SWIR proves to be a great advantage, as the *fingerprinting* ability of the spectra increases.

A notable example is the blue copper carbonate azurite (Fig. 16), whose reflectance spectra show characteristic absorption bands at about 1495, 2285 and 2350 nm due to the presence of hydroxyl and carbonate groups. These make it possible, for example, to identify azurite and distinguish it from malachite, even when used in a mixture with a yellow colourant to produce a green paint.

Another very interesting consequence of acquiring FORS spectra in an extended spectral range is the possibility to
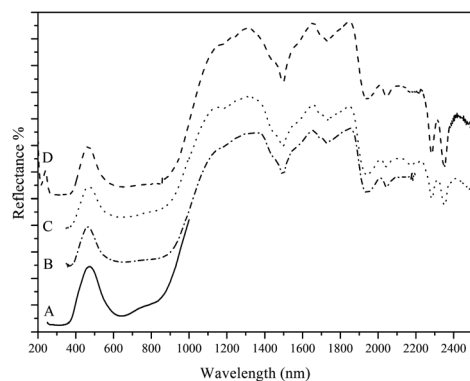
distinguish among the three white pigments previously mentioned. Lead white usually shows an absorption band around 1445 nm,[23] while gypsum displays a very characteristic triplet at 1448, 1492 and 1523 nm, as well as additional bands at 1942, 2212 and 2268 nm.[57,58] In the absence of any characteristic absorption in the SWIR, the presence of bone white can be hypothesized.

Finally, recent research has shown the possibility to use FORS analysis in the SWIR range to identify the presence of fat-containing paint binders, such as drying oils and egg yolk, distinguishing them from binders based on polysaccharides and proteins such as gums and egg white.[14]

Case studies

FORS was applied to the analysis of artists' materials used in making the *Graduale of San Domenico* (Inv. 1918 n. 558) by Beato Angelico, at the San Marco Museum in Florence (Fig. 17). Guido di Pietro, better known as Beato Angelico or Fra Giovanni da Fiesole (*ca.* 1400–1455), was one of the most important artists of the 15th century, excelling at wall-painting, panel painting and at manuscript illumination. FORS spectra were acquired on numerous sites of the *Graduale*, showing that the blue areas were painted with ultramarine blue (*lapis lazuli*). Ultramarine blue was also used in mixture with a red lake at different concentrations to depict violet-purple details, while azurite was used only for the watermarked letters. Yellow areas were painted with orpiment, unambiguously identified by the presence of arsenic in the XRF spectra. As previously discussed, the FORS spectrum of orpiment, as well as the reflectance spectra of most yellow pigments, could be easily modified in mixtures with white, green, or red pigments. Red lake was mainly used in the *Graduale* to paint purple-violet glazes and to produce hues from pink to purple, rather than being used to depict red areas. Green hues and shadows were obtained using a copper-based pigment and a green earth, rather than mixtures of blue and yellow
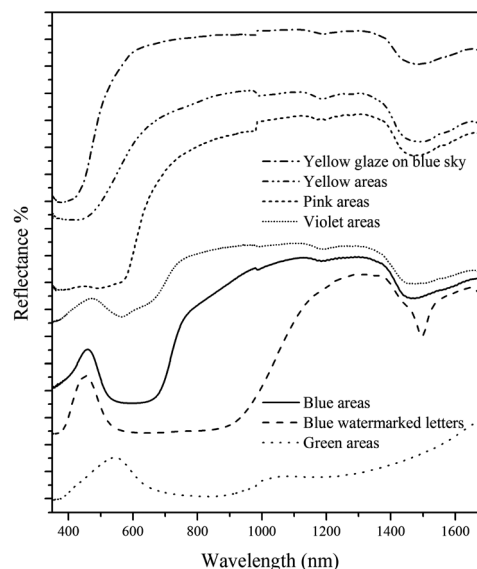

Fig. 16 Spectra of the azurite reference sample, acquired at UPO (A), IFAC-CNR (B and D) and NGA (C).

Fig. 17 Spectra from Graduale 558 in the UV-Visible-NIR range.

colourants. In one case however, in one case only, the use of a yellow pigment (probably lead–tin yellow type I) painted as a glaze on the blue sky made with *lapis lazuli* was identified.

Conclusions

The availability of an extensive spectral database of historic colourants facilitates the use of FORS for the identification of pigments and dyes in ancient manuscript illumination. The usefulness of this analytical method is confirmed, despite undoubted difficulty in the identification of some colourants, and although a multi-technique approach is generally required when performing non-invasive analyses. Due also to its portability, FORS is certainly well suited to serve as a preliminary step in analysis, before the application of more selective techniques such as Raman or FT-IR spectroscopy. Moreover, FORS can yield information on mixtures of colourants when proper calibrations are performed. The extension of the spectral range analysed into the shortwave infrared range (to 2500 nm) greatly facilitates the identification of some mineral pigments as well as opening the way for the non-invasive identification of paint binders. It seems that future work should focus on the exploitation of such an extended range and on the production of additional reconstructions in order to fully evaluate how raw materials and preparation methods affect the spectral characteristics of historic colourants.

Acknowledgements

Notes and references

1 R. J. H. Clark, *Chem. Soc. Rev.*, 1995, **24**, 187–196.

2 R. J. H. Clark, *J. Mol. Struct.*, 2007, **834–836**, 74–80.

3 M. Aceto, A. Agostino, E. Boccaleri, F. Crivello and C. Garlanda, *J. Raman Spectrosc.*, 2006, **37**, 1160–1170.

4 D. Bersani, P. P. Lottici, F. Vignali and G. Zanichelli, *J. Raman Spectrosc.*, 2006, **37**, 1012–1018.

5 P. Vandenabeele, B. Wehling, L. Moens, B. Dekeyzer, B. Cardon, A. von Bohlen and R. Klockenkämper, *Analyst*, 1999, **124**, 169–172.

6 S. Bruni, S. Caglio, V. Guglielmi and G. Poldi, *Appl. Phys. A: Mater. Sci. Process.*, 2008, **92**, 103–108.

7 L. Bussotti, L. Giuntini, M. P. Carboncini, P. A. Mandò and E. Castellucci, *Stud. Conserv.*, 1997, **42**, 83–92.

8 T. A. Cahill, B. H. Kusko, R. A. Eldred and R. N. Schwab, *Archaeometry*, 1984, **26**, 3–14.

9 M. Budnar, M. Uršič, J. Simčič, P. Pelicon, J. Kolar, V. S. Šelih and M. Strlic, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 2006, **243**, 407–416.

10 N. Grassi, L. Giuntini, P. A. Mandò and M. Massia, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 2007, **256**, 712–718.

11 S. Bruni, F. Cariati, F. Casadio and L. Toniolo, *Spectrochim. Acta, Part A*, 1999, **55**, 1371–1377.

12 A. Duran, J. L. Perez-Rodriguez, T. Espejo, M. L. Franquelo, J. Castaing and P. Walter, *Anal. Bioanal. Chem.*, 2009, **395**, 1997–2004.

13 F. Rosi, A. Daveri, C. Miliani, G. Verri, P. Benedetti, F. Piquè, B. G. Brunetti and A. Sgamellotti, *Anal. Bioanal. Chem.*, 2009, **395**, 2097–2106.

14 P. Ricciardi, J. K. Delaney, M. Facini, J. G. Zeibel, M. Picollo, S. Lomax and M. Loew, *Angew. Chem., Int. Ed.*, 2012, **51**, 5607–5610.

15 M. Aceto, A. Agostino, G. Fenoglio, M. Gulmini, V. Bianco and E. Pellizzi, *Spectrochim. Acta, Part A*, 2012, **91**, 352–359.

16 C. Miliani, F. Rosi, B. G. Brunetti and A. Sgamellotti, *Acc. Chem. Res.*, 2010, **43**, 728–738.

17 B. F. Barnes, *Tech. Stud. Field Fine Arts*, 1939, 7, 120–138.

18 W. W. Wendlandt and H. G. Hecht, *Reflectance Spectroscopy*, Interscience Publishers, New York, 1966.

19 M. Bacci, F. Baldini, R. Carlà, R. Linari, M. Picollo and B. Radicati, *Appl. Spectrosc.*, 1993, **47**, 399–402.

20 M. Bacci, *Sens. Actuators, B*, 1995, **29**, 190–196.

21 M. Leona and J. Winter, *Stud. Conserv.*, 2001, **46**, 153–162.

22 M. Bacci, A. Casini, C. Cucci, M. Picollo, B. Radicati and M. Vervat, *J. Cult. Herit.*, 2003, **4**, 329–336.

23 M. Bacci, M. Picollo, G. Trumpy, M. Tsukada and D. Kunzelman, *J. Am. Inst. Conserv.*, 2007, **46**, 27–37.

24 F. Déroche, A. Berthier, M. G. Guesdon, B. Guineau, F. Richard, A. Vernay-Nouri, J. Vezin and M. Isa Waley, Les matériaux de la couleur dans les manuscrits maghrébins (XII°s-XV°s). Éléments d'identification et de comparaison, in *Manuel de codicologie des manuscrits en écriture arabe*, ed. F. Déroche, Bibliothèque Nationale de France, Paris, 2000, pp. 145–167.

25 S. P. Best, R. J. H. Clark, M. A. M. Daniels, C. A. Porter and R. Withnall, *Stud. Conserv.*, 1995, **40**, 31–40.

26 M. Picollo, A. Aldrovandi, A. Migliori, S. Giacomelli and M. Scudieri, *Revista de Historia da Arte*, 2011, **1**, 219–227.

27 J. Delaney, P. Ricciardi, L. Glinsman, M. Facini, M. Thoury, M. Palmer and E. R. de la Rie, *Stud. Conserv.*, 2013, DOI: 10.1179/2047058412y.0000000078.

28 P. Ricciardi, J. Delaney, M. Facini and L. Glinsman, *J. Am. Inst. Conserv.*, 2013, **52**, 13–29.

29 F. Brunello, *De arte illuminandi*, Neri Pozza, Vicenza, 1971.

30 D. V. Thompson, *The materials and techniques of medieval paintings*, Dover Publications, New York, 1956.

31 A. Caffaro, *Scrivere in oro*, Palladio, Salerno, 2000.

32 F. Brunello, *Il libro dell'arte*, Neri Pozza, Vicenza, 1971.

33 M. Gargano, N. Ludwig, M. Milazzo, A. Moneta and G. Poldi, Variazioni dello spettro di riflettanza di pigmenti in miscele di pigmenti antichi, in *Proceedings of the IV Congresso Nazionale di Archeometria*, ed. C. Arias and M. P. Colombini, ETS, Pisa, 2006.

34 G. Kortüm, *Reflectance spectroscopy: principles, methods, applications*, Springer-Verlag, Berlin, 1969.

35 M. Bacci, UV-Vis-NIR, FT-IR, and FORS Spectroscopies, in *Modern Analytical Methods in Art and Archaeology*, ed. E. Ciliberto and G. Spoto, J. Wiley & Sons, New York, 2000, pp. 321–360.

36 K. Nassau, *The Physics and Chemistry of Color*, J. Wiley & Sons, New York, 2nd edn, 2001.

37 C. Montagner, M. Bacci, S. Bracci, R. Freeman and M. Picollo, *Spectrochim. Acta, Part A*, 2011, **79**, 1669–1680.

38 M. Elias, C. Charter, G. Prevot, H. Garay and C. Vignaud, *Mater. Sci. Eng., B*, 2006, **127**, 70–80.

39 L. Burgio, R. J. H. Clark and R. R. Hark, *Proc. Natl. Acad. Sci. U. S. A.*, 2010, **107**, 5726–5731.

40 M. Bacci, A. Orlando, M. Picollo, B. Radicati and G. Lanterna, Colour analysis of historical red lakes using non-destructive reflectance spectroscopy, in *Compatible Materials for the Protection of Cultural Heritage, PACT series 58*, ed. A. Moropoulou, G. Biscontin, J. Delgado Rodrigues, M. Erdik, I. Siotis and S. Zoppi, Technical Chamber of Greece, Athens, 2000, pp. 21–35.

41 C. Bisulca, M. Picollo, M. Bacci and D. Kunzelman, UV-Vis-NIR reflectance spectroscopy of red lakes in paintings, in *Proceedings of Art2008, 9th International Conference on non-destructive investigations and microanalysis for the diagnostics and conservation of cultural and environmental heritage*, ed. A. Notea and Y. Shoef, ISAS International Seminars, Jerusalem, 2008.

42 C. Clementi, B. Doherty, P. L. Gentili, C. Miliani, A. Romani, B. G. Brunetti and A. Sgamellotti, *Appl. Phys. A: Mater. Sci. Process.*, 2008, **92**, 25–33.

43 M. Gulmini, A. Idone, E. Diana, D. Gastaldi, D. Vaudan and M. Aceto, *Dyes Pigm.*, 2013, **98**, 136–145.

44 O. Orfanou and M. Tsimidou, *Food Chem.*, 1996, **57**, 463–469.

45 D. M. Grim and J. Allison, *Archaeometry*, 2004, **46**, 283–299.

46 D. A. Scott, *Copper and Bronze in Art: Corrosion, Colorants, Conservation*, Getty Publications, Los Angeles, 2002.

47 M. Bacci and M. Picollo, *Stud. Conserv.*, 1996, **41**, 136–144.

48 J. Vezin and P. Roger, *Comptes-rendus des séances de l'Académie des Inscriptions et Belles-Lettres*, 2007, **151**, 67–87.

49 Pliny the Elder, *Natural History, Book 9*, Harvard University Press, The Loeb Classical Library, Cambridge (Massachussets), 1952.

50 S. Baroni, Pergamene purpuree e scritture metalliche nella tradizione tecnico artistica. Un quadro introduttivo, in *Oro, argento e porpora*, ed. S. Baroni, Tangram Edizioni Scientifiche, Trento, 2012, pp. 11–37.

51 B. Guineau, *Revue d'archéologie médiévale*, 1996, **26**, 23–44.

52 D. Cardon, *Natural dyes*, Archetype Publications, London, 2007.

53 M. Aceto, A. Agostino, E. Boccaleri, F. Crivello and A. Cerutti Garlanda, *J. Raman Spectrosc.*, 2010, **41**, 1434–1440.

54 G. Dupuis and M. Menu, *Appl. Phys. A: Mater. Sci. Process.*, 2006, **83**, 469–474.

55 J. M. Fernandez Rodrıguez and J. A. Fernandez Fernandez, *Color Res. Appl.*, 2005, **30**, 448–456.

56 L. Simonot and M. Elias, *Color Res. Appl.*, 2003, **28**, 45–49.

57 G. R. Hunt and J. W. Salisbury, *Mod. Geol.*, 1971, **2**, 23–30.

58 R. N. Clark, Spectroscopy of rocks and minerals and principles of spectroscopy, in *Manual of remote sensing, remote sensing for the earth sciences*, ed. A. N. Rencz, J. Wiley & Sons, New York, 1999, vol. 3, pp. 3–58.