

Near infrared investigations of works of art

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Introduction

The uniqueness of works of art means that analytical techniques that cause the least possible damage to the work itself must be used. Indeed, by now, micro-analytical techniques have been developed which provide reliable data from even the smallest samples. However, these techniques may be unsatisfactory at times, particularly since no alteration to the object is desired. Moreover, it is natural that micro-analytical techniques suffer from limited sampling. The results obtained cannot, therefore, be representative of the whole object. Thus, the use of completely non-destructive and non-invasive techniques, that make it possible to carry out investigations throughout the whole object and, if possible, time after time without any sampling, is highly recommended. Near infrared (NIR) spectroscopy is particularly suitable for use in a non-invasive manner. In fact, recent advances in fibre optics and remote sensing systems (video cameras) have made the entire NIR range available to fibre optics reflectance spectroscopy (FORS) and image spectroscopy (IS), respectively. For many years in our laboratory, FORS and IS have been developed in both the visible and NIR ranges and applied to actual works of art.¹⁻⁶ Here, we review some recent results from our laboratory with the aim of illustrating the potential of both FORS and IS for the study and further knowledge of art objects. Since the non-destructiveness of the method permits the recording of a large number of NIR spectra, particular attention is paid to applying multivariate techniques⁷⁻⁸ in order to extract as much information as possible from the spectral data obtained.

Experimental

FORS measurements were performed in the range 1200–2200 nm using a Guided Wave 260 spectroanalyzer equipped with optical fibres and a probe-heads which had been purposely modified in our laboratory.³ A Perkin-Elmer spectrophotometer, Lambda 19, was utilised for laboratory tests and methodological studies, owing to its better signal-to-noise ratio. IS measurements were performed in the 800–1550 nm range using home-made apparatus and by acquiring images with interference filters (10 nm bandwidth) every 50 or 100 nm (the central wavelengths of the available filters are: 800 nm, 850 nm, 900 nm, 950 nm, 1000 nm, 1050 nm, 1100 nm, 1150 nm, 1200 nm, 1300 nm, 1400 nm, 1450 nm and 1550 nm). Further details concerning the instrumentation and the measurement conditions, with particular regard to the problems of repositioning and refocusing, can be found elsewhere.^{3,5,6}

Results and discussion

Quite surprisingly, very few NIR spectra of pigments or dyes are reported in the literature. In fact, to the best of our knowledge, only some data concerning pigments, which are important from a mineralogical and remote sensing point of view (e.g. azurite, malachite, cinnabar, various ochres, etc.), have

been published.^{9–11} Therefore, it appeared particularly interesting to investigate the NIR spectral features of materials constituting works of art, for identification purposes. In Figures 1(a) and (1b), the NIR reflectance spectra of some blue pigments (smalt, azurite, indigo, lapis lazuli and Prussian blue) are displayed as examples. Apart from smalt, the above pigments are often not easily distinguishable in the visible region, while they present characteristic features in the NIR region, making a sure identification possible. A strong electronic d–d absorption band dominates the NIR spectrum of smalt. This band is centred at about 1520 nm and is structured into three sub-bands originating from the Jahn–Teller split transition ${}^4A_2 \rightarrow {}^4T_1$ (F), due to the cobalt (II) ion in a tetrahedral co-ordination.⁴ Azurite, a basic copper (II) carbonate, $2CuCO_3 \cdot Cu(OH)_2$, shows a sharp band at 1498 nm, which is due to the first overtone of the O–H stretching. Further bands are observed in the same pigment at 2044 nm, 2286 nm and 2350 nm. These are due to combination and overtone transitions of the carbonate ion.⁹ The spectrum of the Prussian blue, $Fe_4[Fe(CN)_6]_3 \cdot xH_2O$ is much more complex: in fact, the spectrum is characterised by a strong band at 2370 nm and a shoulder at 2404 nm. These are probably due to the combination of the IR active C–N stretching of T_{1u} symmetry with the Raman active C–N stretching of A_{1g} and E_g symmetry, which are found at 2155 cm^{-1} and 2095 cm^{-1} , respectively. Four other bands of medium intensity are present around 2000 nm, in which a contribution from bound water cannot be excluded. Also indigo is marked by a typical and very structured spectrum. The first overtone of the N–H stretching appears as a medium band in the NIR region at 1547 nm, while three very intense bands occur at 2058 nm, 2154 nm and 2273 nm, where a contribution from the C=O and C=C stretching modes is likely. A sharp and medium intensity band at 1674 nm could tentatively be attributed to the first overtone of aromatic C–H stretching. Lastly, lapis lazuli shows no distinctive absorption bands in the entire range investigated (800–2500 nm).

Likewise, in the past years, little attention has been paid to the NIR spectra of other materials having a potential interest for works of art. For example, although the spectrum of gypsum or calcium sulphate, $CaSO_4 \cdot 2H_2O$, has been widely reported owing to its mineralogical and industrial importance,¹¹ our laboratory has only recently¹² published data concerning calcium sulphite, $CaSO_3 \cdot 1/2H_2O$. Indeed, the latter has been suggested^{13,14} as an important intermediate product in the sulphating process of calcareous stones and its early detection on statues or monuments could make a timely protective intervention possible. The NIR spectra of gypsum and calcium sulphite are displayed in Figure 2 together with that of calcium carbonate. In the case of gypsum, three characteristic absorption bands are observed at 1446 nm, 1490 nm and 1538 nm. These contain contributions from the first overtone of

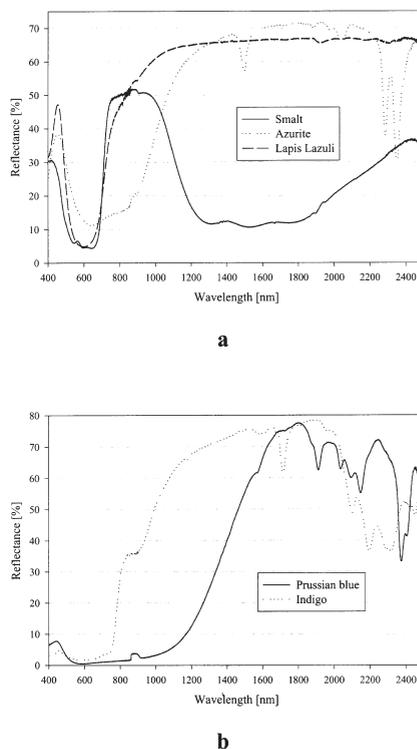


Figure 1. Near infrared reflectance spectra of. (a) smalt, azurite, lapis lazuli; (b) indigo, prussian blue.

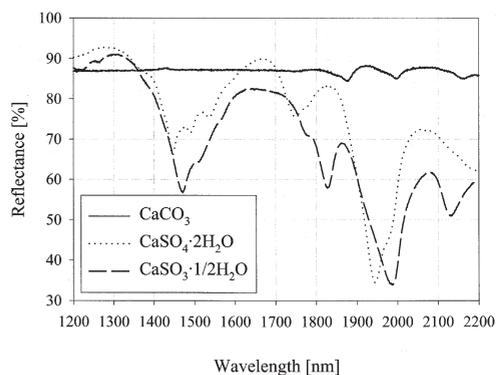


Figure 2. Near infrared reflectance spectra of gypsum (dotted line), calcium sulphite (dashed line) and calcium carbonate (continuous line).

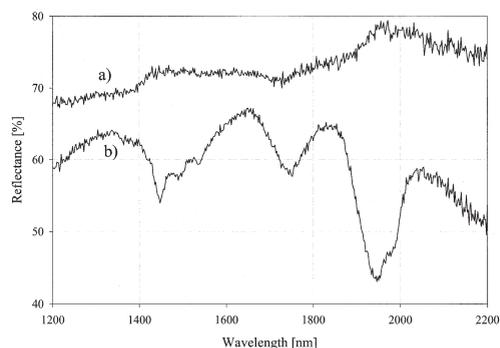


Figure 3. Near infrared reflectance spectra acquired on the “Holy Trinity Predella” by Luca Signorelli: (a) spectrum of a cinnabar painted area; (b) spectrum of an ochre painted area.

the O–H stretch and from the combination of the O–H stretching and bending modes. Two further bands, still due to the water molecules, are observed at 1760 nm and at 1900 nm.¹¹ As in the previous case, the bands in the NIR spectrum of calcium sulphite can be assigned to overtone (1471 nm) and combination (1508 nm, 1827 nm and 1987 nm) bands of the water molecule.¹² In spite of this apparent similarity, the two spectra are quite separate from each other, and quite different from that of calcium carbonate, which does not show any band till 1875 nm.^{9,12} Accordingly, NIR spectroscopy can be used as an effective and powerful method for non-destructive monitoring of the conservation state of calcareous works of art.

As is well known, NIR radiation can penetrate through the paint layer to an extent that varies, depending on the binding medium and pigments.¹⁵ In fact, in Figure 3, the NIR spectra of two different areas of the same painting are displayed. This painting is known as “Holy Trinity Predella”, and is now on display at the Uffizi Gallery. It is an oil-painted panel, realised by Luca Signorelli in the early years of the sixteenth century. Spectrum (a), displayed in Figure 3, corresponds to an area painted with cinnabar (HgS) and does not show any characteristic features, as might be expected, because cinnabar has a good hiding power and no absorption band in the range considered. Instead, spectrum (b), in Figure 3, which, according to its visible reflectance spectrum, was acquired from an ochre painted area, is superimposed on that of gypsum. In fact, the latter material was used in combination with animal glue to spread the preparatory layer of the painting, in accordance with traditional Italian recipes.

Pigment (or other material) identification can be attempted on the basis of the best correlation between the spectrum of the examined area and the spectra of probable materials taken as reference. Here, as an example, a study concerning the distribution of the areas, in which the preparatory layer of gypsum can be detected, is reported. Several hundreds of spectra were recorded throughout the entire panel by using FORS, in addition to a sequence of 13 multispectral images acquired by means of IS in the 800–1550 nm range. A principal component analysis (PCA) was performed separately on both FORS and IS data, in order to investigate the structure, in terms of variability, of the reflectance spectra obtained and of the pixels constituting the image, respectively. In Figure 4(a), the PC1 v. PC2 score plot (96.5% of total variance) relative to the FORS spectra is reported. In an effort to enhance the identification of structures in the data, a Kernel Density Estimation (KDE) method was applied to the first two Principal Components (PCs).^{16,17} Figure 4(b) reports the estimated density values, which suggests

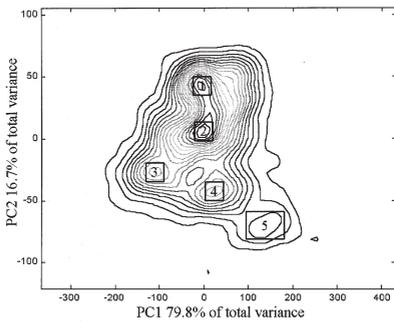
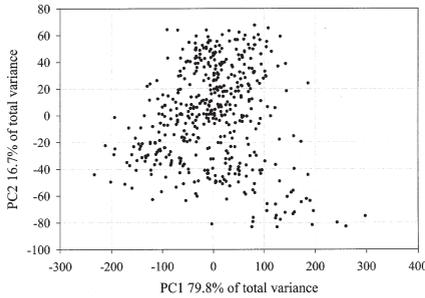


Figure 4. PC1 vs. PC2 score plot from PCA on FORS spectra acquired on the “Holy Trinity Predella” by Luca Signorelli: (a) raw data; (b) density isopleth curves obtained by means of the KDE technique.

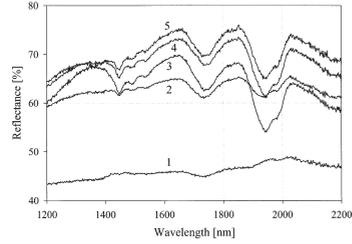


Figure 5 Average reflectance spectra of the clusters marked in Figure 4(b).

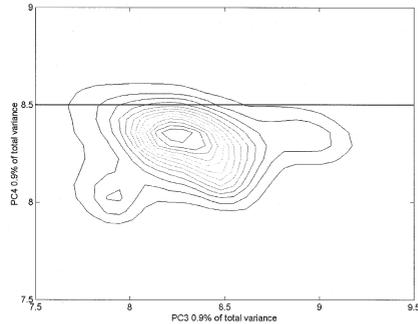


Figure 6. PC3 v. PC4 score plot from PCA on near infrared images of the “Holy Trinity Predella” by Luca Signorelli. Pixels above the horizontal line are characterised by gypsum spectral features.

the presence of five groups. The average reflectance spectra of the above groups are shown in Figure 5, where it is evident that three spectra (3-4-5) reveal the characteristic features of the gypsum spectrum. Accordingly, it can be affirmed that the three clusters, 3, 4 and 5, correspond to the areas in which gypsum can be detected. Likewise, in Figure 6, the PC3 v. PC4 score plot relative to the IS data is reported. The analysis of the PC eigenvectors had indicated the fourth PC as the most meaningful for revealing gypsum, since the PC4 eigenvector received a higher contribution from the band at 1450 nm, compared with the other bands, in the 800–1550 nm spectral region. Unfortunately, in this case, a clear clustering by means of PC4 does not occur, due to the low spectral resolution of IS data. However, the pixels belonging to the areas where gypsum is detectable can be effectively evidenced by evaluating the ratio of the 1450 nm image to the 1300 nm image, as shown in Figure 7. In fact, at 1300 nm no absorption occurs and the



Figure 7. Ratio of the 1450 nm image to the 1300 nm image. The areas that reveal gypsum below the painted layer appear as darker zones.

reflectance is always higher than at 1450 nm. By doing so, the areas that reveal gypsum below the painted layer appear as darker zones in the ratio image. Furthermore, it can be checked that the above areas correspond to pixels whose representative points lie above the horizontal line drawn in Figure 6 for $PC4 = 8.5$.

Conclusions

The few examples of non-destructive FORS and IS here reported are limited to the NIR range only. In spite of this, they can supply useful information to the conservator and the restorer. It is quite evident that the extension of the methodology to the visible and mid-infrared range can further increase the obtainable information about the composition and structure of the paint layer. Nevertheless, at the present stage, the methodology cannot be considered self-exhaustive, but it can constitute a powerful tool, together with a minimal micro sampling, for an extensive knowledge of works of art.

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