Intrinsic limits of reflectance spectroscopy in identifying pigments in paint layers

L Pronti¹, A Pelagotti², F Uccheddu³, L Massini Rosati¹, A C Felici¹
¹Department of Basic and Applied Sciences for Engineering, LANDA-Laboratory of Non Destructive Analysis and Archaeometry, University of Rome Sapienza, via A. Scarpa 16, 00161, Rome, Italy
²National Institute of Optics, (INO) CNR, L.go E. Fermi 6, 50125 Firenze
³Department of Industrial Engineering, University of Florence, via Santa Marta 3 50123 Firenze

Corresponding author: lucilla.pronti@uniroma1.it.

Abstract. The study of pigments is of fundamental importance for authentication and restoration purposes of painted artworks. To this aim reflectance spectroscopy has been widely studied on samples and in a number of real cases. A number of valuable efforts have been dedicated to this quest; however, the identification of a pigment on a painting surface by means of reflectance spectroscopy appears to be possible only in very few cases also due to the fact that artist materials are often mixed. In this paper we review a number of relevant works and present results on a new set of test samples especially produced for exploring the possibilities of reflectance spectroscopy on pigment mixtures. We also include a case study of a real painting.

1. Introduction
The chemical composition of materials used to create an artwork is crucial information. Materials for art production changed over time or between a production place and another, an artist and its competitors. Assessing them is thus vital for e.g. uncovering forgeries. Historically, chemical analysis of paint layers has been among the first scientific tests performed on artworks. This is still an invasive technique and the results are representative only of a limited area. For quite some time scientists have been trying to replace these analyses with non-destructive methodologies. Reflectance spectroscopy has been often proposed. The underlying assumption is that each material displays a specific spectral signature in the ultraviolet (UV), visible (Vis) and infrared (IR) regions, which carries more information compared to what the eye is able to discriminate. However, while it proved to be very useful for monitoring the presence of alteration products and for the analysis of colour changes on paintings (see eg. [1], [2]), we argue that it can be severely misleading when used for the identification of pigments. In fact, although some pigments present a specific spectral behaviour, in practical applications pictorial layers are hardly ever composed by a single pigment (or colorant). Paint mixtures or paint overlaying are very common practices, but a model for how the different components contribute to the final reflectance spectrum has not been conclusively defined yet, thus unmixing the signals is not trivial. In order to characterize spectral signatures, mostly peaks and inflection points (or flexes, i.e. points of the curve where the curvature
changes its sign and the second derivative equals zero) are described, giving the max or min values and making approximation with e.g. Gaussian forms (see e.g. [3], [4]). In this work we analyse some of the critical issues regarding the use of the reflectance spectroscopy for the identification of pigments or dyes, making reference to existing literature, providing evidence using samples realized ad hoc, and presenting an exemplificative case study.

2. Reflectance spectroscopy in identifying pigments in paint layers. A brief review

Reflectance spectroscopy from its debut in 1938 [5] has been extensively used [6], [7]. Soon, it became apparent that if the technique was to be used for pigment identification, a database of spectra of artist's materials was needed for comparison. A number of such databases have been developed in the years for several pigments, binders and paint methods (see e.g. [8], [9], [10]) although it is probably intrinsically not conceivable to cover the full spectrum of paints and paint mixtures used by artists over several centuries, including the most recent years. For this reason, a method to recognize single pigment in mixtures would be needed [11], [12].

Several methods were researched in order to characterise the spectral signature of each given material, i.e. its typical variation of reflectance or emittance. Some methods have been proposed for spectra classification [13], [14]. They however show how reflectance spectroscopy on its own does not generally permit pigment identification even for a single material [4]. The implications are very relevant. For example the spectra of Naples Yellow and of Cadmium Yellow are very alike but the use of the first is compatible with an Old Master painting while latter is a modern compound.

In the analysis of real paintings the possibility of identification of pigments by reflectance spectroscopy is moreover complicated by the presence of several additional elements like the geometry of painting surfaces [11], the fact that pigments are generally present in mixtures [13] and/or as overlapping layers [15] of varying thickness [16]. Moreover also aging plays a role, with the intense yellowing of the binder or of the overlapping varnish, due to oxidation processes occurring with natural ageing [17] and/or other environmental agents like light, humidity, and temperature [12] that can alter some pigments. Moreover other intrinsic factors like the nature and grain size of pigments [19], the differences of provenance [20], [21], [22] and of manufacturing processes, also play a significant role, generally making pigment identification with reflectance spectroscopy not conclusive.

Moreover, when extending reflectance spectroscopy to the near IR region, the transparency of most thin layers layer of pigments to the IR radiation complicates the matter. In the red and/or NIR region the depth of the penetration of the radiation into painted layers can reach the preparation layer, and this will affect the acquired spectrum depending of the reflectance properties of the preparation layer.

3. Materials and methods

3.1. Samples

In order to specifically investigate the spectral response of complex paint structures, a number of samples were produced and investigated. The set covers 31 pictorial layers consisting of two or three pigments mixed with linseed oil or egg yolk, 32 oil colour tubes, 30 home-made oil based paints and 15 red-glazes spread on two different pictorial layers.

- **31 pictorial layers composed by two or three pigments mixed with linseed oil or egg yolk:**
  - MIX SL: 10 samples mixtures of Lead White and Raw Sienna Earth at different volume percent, 5 of which diluted with linseed oil and the other with egg yolk;
  - MIX SLG: 6 samples are mixtures of Lead White, raw Sienna Earth and Green Earth with linseed oil. 3 of them are mixtures of Lead White and raw Sienna Earth at 50:50 volume percent with an increase of the quantity of Green Earth (0.10g, 0.20g and 0.30 g) at each sample and the others are mixtures of Lead White and raw Sienna Earth at 10:90 volume percent with the same increase of the quantity of Green Earth (0.10g, 0.20g and 0.30 g);
  - MIX LZn: 6 samples are mixtures of Lead White and Zinc White at different volume
percent, 3 of which diluted with linseed oil and the other with egg yolk.

- Zn_H: 1 sample of a mixture of Zinc White and Hematite with linseed oil;
- Pb_H: 1 sample of a mixture of Lead White and Hematite with linseed oil;
- Zn_Pb_H: 1 sample of a mixture of Lead White and Zinc White at 50:50 volume percent with linseed oil; 1
- MIX LZH: 6 samples are mixtures of Lead White and Zinc White at 50:50 volume percent with an increase of the quantity of Hematite (0.05g, 0.10g, 0.15g), 3 of which diluted with linseed oil and the other with egg yolk

- **32 oil colour tubes and 30 hand-made oil colours:**
  - Oil colour tubes from several manufacturers: Maimeri, Ferrario, Van Dick, Pēbēo, Williamsburg
  - Home-made oil colours with pigments from several manufactures: Maimeri, Zecchi, Poggi. The pigments are diluted with linseed oil (Lefranc & Bourgeois). all the oil colour were spread on a microscope slides.

- **15 red-glazes spread on two sets of pictorial layers.** Red-glazes produced by mixing commercial alizarin based-pigments with linseed oil (Lefranc & Bourgeois) were spread on microscope slides and on two different “tempera” pictorial layers (Red Ochre mixed with egg yolk and Cinnabar mixed with egg yolk). Moreover two different thicknesses were produced: one more covering than the other. Both the two “tempera” blends were spread on a commercial-prepared wood panel. The commercial alizarin-based lakes were purchased by Kremer Pigmente and Zecchi.

3.2. **Reflectance spectroscopy equipment**

Measurements were performed by means of an Avantes AvaSpec spectrophotometer equipped with a halogen lamp (HL-2000 FHSA, Avantes and a diffraction grating of 300 lines/mm, blazed at 500 nm, with (300 - 1100 nm spectral range), and a CCD linear sensor (2048 pixels). The spectral resolution is 0.8 nm. We illuminated the samples at 45° with a bifurcated fiber (diameter of 600 μm. The reflected light was collected with a 200 μm diameter fiber at 90° respect to the surface. When using microscope slides, we had a white background.

4. **Reflectance spectroscopy applied on case studies**

Given the limited space, we present here only very few of the spectra we acquired, although similar conclusions could be drawn from many others.

The reflectance spectrum of a mixture of two or more pigments is a combination of their spectra. The way the spectra combine is however not clarified. But, even adding white pigments, (having reflectance practically constant over the visible range), to a mixture, it generally modifies at least the flexes position, generally without retaining any information about the pigment added. Which white pigment has been used in a painting is however of crucial importance. Lead or Zinc White could completely change the dating of a painting, being the first an ancient pigment and the latter a modern one. Unfortunately, when Lead White is mixed with other pigments it is impossible to recognize it, as shown in **Figure 1**. In the case of Zinc White, although it has a very specific behaviour in the UV region, when in combination with other pigments, the peak at 390 nm is hardly visible. See e.g. the spectrum Pb_H and the mix LZE: the two spectra in the range 400-900 nm are practically not easily distinguished, especially considering that in real cases the peaks and the absorption bands will be less pronounced [4]. The situation is not dramatically better even when the pigments have distinctive spectral signatures e.g. for blue pigments. For example Smalt is characterized by an intense absorption in the 550-650 nm range, with three sub bands at 540 nm, 590 nm and 640 nm [23]. However it is extremely transparent and the spectral behaviour is strongly influenced by the underlayer [14]. Reflectance spectra in **Figure 2A** exhibits different ratios between the reflectance maximum in the blue range and the red-NIR range. Minima values disappear when the layer thickness is high and when smalt is spread on a black layer.
Figure 1: A) Reflectance spectra of the samples of Hematite mixed with: Lead White (Pb_H), Zinc White (Zn_H) and a mixture of Zinc White and Lead White 50:50 (Zn_Pb_H) in linseed oil. B) Reflectance spectra of a mixture of Lead White and Zinc White 50:50 with increasing quantities of Hematite in linseed oil (solid lines) or egg yolk (dash lines).

Figure 2: A) Reflectance spectra of Smalt in linseed oil. The terms “m.s. white” refers to microscope slide laid on a white support, “m.s. black” on a black support. The addition of “THIN_” refers to the thickness of the thin pictorial layer. B) Reflectance spectra of modern oil tube of Cobalt Blue (black line) and a powder of Cobalt Blue dispersed in linseed oil (gray line). C) Reflectance spectra of two modern oil tubes of Ceruleo: PÉBÉO (black line) and Maimeri (gray line). D) Reflectance spectra of green oil colours.

Cobalt blue dispersed in linseed oil (home-made oil based paint) presents two absorption bands at about 480 nm and 495 nm, as shown in Figure 2B, however this spectral features are linked to the specific manufacturer recipe. Ferrario Cobalt blue shows e.g. two minima at about 417 and 430 nm. The same we can say for many Blue pigments (like Cerulean), Figure 2C, and green pigments, Figure 2D.
Yellow pigments, except Cadmium Yellow, that contain Zinc sulphide as lithopone [9], are generally identified by the position of flexes and shoulders. However, the inflection points could shift when the pigment is mixed with others and the position of the shoulders could be modified due to the increase of transparency at longer wavelengths. Although some yellow pigments present a characteristic reflectance curve, mixing them with a white pigment, such as Lead White and a green pigment, such as Green Earth (MIX SLG sample), we obtain different spectral features, as shown in Figure 3A. The two blends 50:50 and 90:10 volume percent of Raw Sienna Earth and Lead White, mixed with green earth and linseed oil as a binder, show different inflection points at about 525 nm and 550 nm, respectively. The reflectance spectra of the samples with the highest quantity of Raw Sienna Earth, and lower of Lead White, are weaker at long wavelengths and show a second well-pronounced band at 750 nm. Despite the low quantity of Green Earth, all the reflectance spectra show weak bands between 650 nm and 800 nm of the Green Earth pigment, Figure 3B.

Figure 3: A) Reflectance spectra of the samples of raw Sienna Earth, Lead White and Green Earth in linseed oil or egg yolk. Samples 1 to 3 are mixtures of raw Sienna Earth and Lead White 50:50 and increasing quantities of Green Earth mixed with linseed oil, while 4 to 6 are mixtures of raw Sienna Earth and Lead White 90:10 and increasing quantities of Green Earth mixed with egg yolk. B) Reflectance spectra of the samples of Green Earth with linseed oil (solid line) or egg yolk (dash line).

Figure 4: A) Reflectance spectra of madder lake with linseed oil spread on Red Ochre bonded with egg yolk (O) and on Cinnabar in egg yolk (C). The number 1 and 2 is referred to the thickness of the layer: thin (1) and thicker (2). B) Reflectance spectrum of madder lake in powder. C) Reflectance spectra of red ochre mixed with yolk egg (gray line) and Cinnabar with yolk egg (black line).
Also the identification of red inorganic pigments are mainly associated to the position of inflection points and shoulders, except for the iron-based pigments that show a characteristic shape [9], [24]. The reflectance spectroscopy is used also to recognize red dyes e.g. [20], [25], [26], however this approach can be misleading when the lakes are spread above another layer, for example Vermillion, as it generally occurs in real paintings. In this case, the spectral features of the tempera layer of red dyes could be recognized if it is spread as dilute mixture or as thin layer, but the positions of the absorption bands could be shifted [20]. To study the lakes, we prepared 15 red-glazes spread over two different pictorial layers. The reflectance spectra of one lake (37202_Kremer) can be considered representative of the entire set of samples depicted in Figure 4. The absorption bands of this Alizarin-base lake (Madder Lake), at about 505 nm and 550 nm, is completely indistinguishable in linseed oil, Figure 4B. When the red lakes are spread above Red Ochre or Cinnabar layers, the spectral features of the red lakes are completely modified, as shown in Figure 4A, as far as, the presence of a superficial lake layer modifies the spectral behaviours of the Red Ochre and the Cinnabar pigments, Figure 4C. In the case of real paintings, the interpretation of the reflectance spectra could be extremely difficult and could lead to a wrong identification of the artist’s palette. To this aim we report a case study of “Virgin and Child and Saint Catherine of Alexandria” painting by Matteo di Giovanni (or an imitator), in storage at the Accademia di San Luca (Rome), Figure 5A.

The reflectance spectrum of the Virgin’s mantle shows a flat trend, as shown in Figure 5B suggesting the use of a black pigment, however XRF1 analysis revealed the presence of copper, as reported in Table 1, probably to be attributed to a copper-based pigment, generally appearing green or blue. These results could suggest a multilayer system or a blackening of the surface that could be caused by a high pigment/binder ratio or to an alteration [27]. The reflectance curves relative to vest, flowers and cuff show approximately the same inflection point at 590 nm. This could suggest the presence of Cinnabar or Vermillion (these two pigments are anyway difficult to discriminate with non-invasive techniques). However XRF analysis, a very sensitive technique, reveals this pigment only in the Saint’s dress through the detection of mercury (Hg). For the others areas we can suppose the presence of Red Ochre and pigments at low atomic number. The Y1 curve relative to the Y1 area (Saint’s hair) shows two minima at about 430 nm and 630 nm (weak), an inflection point at about 540 nm, a shoulder at about 580nm, and a weak band at 670 nm. The absence of the typical S-shape could indicate the absence of Iron-based pigments, although we detect a moderate count of Iron by means of XRF. Naples Yellow presents a shoulder at about 580 nm [9] but XRF did not detect Antimony, also

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1 X-Ray Fluorescence Spectroscopy performed with an X-ray tube (EIS srl) with an anode target of palladium and a beryllium window of 150 µm of thickness, powered with an accelerating potential difference of 40 kV and an electronic current of 0.4 mA. The detector is a Peltier cooled silicon drift with amplifier and integrated multi-channel analyser (Amptek 123-SDD) which provides for every X photon revealed a current pulse of amplitude proportional to the photon energy. The detector has a surface of 25 mm² and a thickness of 500 µm, a beryllium window of 12.5 µm and its energy resolution is 140 eV full width half maximum of the manganese Kα line at 5.9 keV.
Cobalt yellow presents a shoulder at about 580 nm and a second one at about 670 nm, similar to those of the Y1 curve [9], but XRF did not find Cobalt. We may suppose the use of a mixture of more pigments and/or dyes, however we cannot identify which ones could possibly have been employed.

| S   | Cl | K  | Ca | Ti | Cr | Mn | Fe | Cu | Zn | As | Sr | Hg | Pb  |
|-----|----|----|----|----|----|----|----|----|----|----|----|----|-----|
| B1  | 112| 71 | 395| 5892| 56 | 232| 2536| 287157| 3822| 2045| 378 | -  | 17128|
| R1  | 372| -  | 271| 1875| -  | 332| 1417| 597 | 627 | -  | 792 | 175 | 102271|
| R2  | 417| -  | 327| 2295| 49 | 149| 1126| 352 | 501 | -  | 259 | 147 | 115636|
| R3  | 1063| 58 | 1560| 51 | 90 | 85 | 756 | 543 | 300 | -  | 56767| 58387|
| Y1  | 560| 48 | 53 | 597 | -  | 53 | 3616| 394 | 271 | -  | 642 | 115 | 53317|

Table 1. X-Ray Fluorescence counts.

5. Conclusions
In this paper we discussed the inherent limitations of reflectance spectroscopy for the purpose of material identification on a painting. We reviewed the existing literature and presented results on a set of test samples especially produced for exploring results on pigment mixtures, with an increased degree of complexity compared to the single pigment swatches that are often used. We also discussed the application of this technique to a real case. Results show how this technique is often not conclusive for several reasons. The databases used for comparison cannot be exhaustive, as many pigments come in different formulas, showing different spectra, also depending on the manufacturer. The fact that in most cases pigments are not used pure but mixed with others, in the absence of a way of modelling interactions, leads often to the impossibility to find the components of the mixture. Moreover aging and other factors change the reflectance of pigments in a not always known or predictable way. We can therefore conclude that currently this technique should not be proposed for the purpose of non-invasive pigments identification. A correct analytical approach should at least involve the integration of complementary techniques for the analysis of chemical and physical features of the materials employed.

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