Available online at www.sciencedirect.com
SciVerse ScienceDirect
Procedia Chemistry 8 (2013) 45 – 54
Procedia Chemistry

Youth in Conservation of Cultural Heritage, YOCOCU 2012

Pigments and mixtures identification by Visible Reflectance Spectroscopy

Tiziana Cavaleri[a]*, Annamaria Giovagnoli[a], Marco Nervo[a]

[a]*Centro Conservazione e Restauro "La Venaria Reale", via XX Settembre 18, 10078, Venaria Reale (TO), Italy*

Abstract

Non-invasive techniques, as well assessed, are commonly used as preliminary investigations on the superficial constitutive materials of works of art.

In particular, when the sampling on the artwork is not permitted, non-invasive techniques, such as Visible Reflectance Spectroscopy, can face successfully the problem of pigments' identification and characterization.

Nevertheless, the application of this diagnostic tool could be more difficult when pigments' mixtures are present in the painting layer. Moreover, the various ratio possibilities among different pigments and the eventual yellowing due to the binder's decay could modify the spectral reflectance behaviour.

In this study, about a hundred of standards of different pigments and mixtures have been realized using linseed stand-oil as binder, in order to simulate simple and complex pictorial layers. All the standards were analysed by Visible Reflectance Spectrometry, building up a specific database of reference spectrophotometric curves. Besides, every standard was analysed by XRF analysis and multispectral techniques to implement the database itself.

In this paper an extract from the database and some case-studies, among the most interesting and complex ones, will be presented, highlighting the importance of an integrated use of different non-invasive techniques for the identification of pigments and mixtures.

Selection and peer-review under responsibility of the IA-CS (Italian Association of Conservation Scientists) and University of Antwerp

Keywords: pigments; mixtures; visible reflectance spectroscopy.

* Corresponding author. Tel.: +39 340 5417394; fax: +39 011 4993099.
E-mail address: tiziana.cavaleri@centrorestaurovenaria.it

Selection and peer-review under responsibility of the IA-CS (Italian Association of Conservation Scientists) and University of Antwerp
doi:10.1016/j.proche.2013.03.007

1. Introduction

Thanks to the identification of pictorial materials used in works of art, some restorers' chooses concerning cleaning and conservation interventions can become more conscious and specific. In particular cases, when the artwork shows a very altered aspect - not due only to the yellowing of the varnish-, the challenge is to understand of which colour it originally was and, more specifically, which pigments the artist had used to create it. Even when original chromatic aspect is not retrievable - because of not reversible alteration processes-, information about original pigments and hues can be anyway exploited by operators, e.g. for virtual restoration.

Non-invasive techniques, as well assessed, are commonly used as preliminary investigations on the superficial constitutive materials of works of art. In some cases, in order to preserve the integrity of our cultural objects - since every item is a unique piece -, the sampling on the artwork is not permitted: in these situations the application of non-invasive analyses is the only diagnostic tool for reaching requested information.

In this way, this paper aims at highlighting how the potentiality of visible reflectance spectroscopy could be implemented by means of a particular database, which is directly *inspired* by works of art.

Visible reflectance spectroscopy is based on the principle of selective light absorption: the spectral behaviour of a painted surface to a source emitting the visible wavelength range can give information about its composition. The results of this analysis are reflectance spectra in which both *reflected* and *scattered* light is recorded: while absorption of light is a relatively straightforward phenomenon, scattering of light - that also is encountered with pigments-, is more complex. For instance, it depends on the difference in the refractive index of the pigment and the suspending medium, and on particle size relative to the wavelength of the incident light [1].

Scientific literature shows that this technique is an helpful tool for pigments identification, even if, in general, *superficial inhomogeneity* and *compositional complexity* of the pictorial material make the discrimination more difficult [2, 3, 4]. This is the reason why databases of reference spectrophotometric curves are commonly built up using well-known pigments and binders: some databases are also available on line [5].

For qualitative and quantitative analyses on pigment mixtures some efforts were already done but, in real cases, the technique shows to be limited because of different variables [6]. For instance, the various ratio among different pigments, the eventual yellowing due to the binder's decay as well as the alteration of some pigments could modify the spectral reflectance behaviour.

For this reason, the aim of our research was to try to overcome some limits of the spectrophotometric technique, by reproducing pigment mixtures really detected in works of art and by analysing their spectral behaviours; the comparison between real and experimental paints could allow to better understand the phenomena occurred in reality.

2. Experimental

Starting from scientific data that we collected on artworks by means of typical diagnostic techniques (such as multispectral imaging, X-ray fluorescence and scanning electron microscopy), some pigment mixtures were created in order to simulate real pictorial cases. Their visible reflectance spectra were collected and inserted in a database. Pigments that we used were also analysed as they are and then as simple oil paints by means of visible reflectance spectroscopy, X-ray fluorescence and multispectral techniques, to complete the database itself.

The final aim was to evaluate the effectiveness of the visible reflectance spectroscopy in the process of pigment mixtures' identification, using a simple portable instrument and exploiting the visible wavelength range only.

The comparison between real and experimental paints will provide an improvement in our diagnostic protocol.

2.1. Experimental samples

A set of 130 reference paints were prepared using stand linseed-oil as binder and blue, red, yellow and green pure pigments powders produced by Kremer Pigmente GmbH &Co.KG company. In particular, we used: Smalt (Cobalt glass), Azurite, Egyptian blue, Lapis lazuli, Indigo, artificial Ultramarine, Prussian blue; Cinnabar, Cadmium red, red lake, red ochre, Minium; Lead-Tin yellow, Orpiment, Cadmium yellow, Indian yellow, Curcuma, yellow ochre, Sienna, Massicot, Naples yellow; Malachite, Copper resinate, green earth, Cobalt green, Chrome green, Viridian (Guignet's green), Verdigris.

As mentioned, pigment powders were firstly analysed as they are. Afterwards, reference paints were created as follows:

- oil paints of pure pigment,
- oil paints of one pigment mixed in different weight percentages[1] of Lead White,
- oil paints of mixtures made of two or three pigments simulating some areas of paints really detected in works of art.

For their rich chromatic assortment, two particular artworks were chosen for the last series of paints: a 15th century fresco found in an ex-church in Piedmont and a 16th century Venetian oil painting.

Samples are 4 cm x 4 cm dimensioned and roughly 100 µm thick. Thickness was controlled as much as possible, spreading and levelling oil painting by means of a spatula, inside a tracing paper mask fixed upon a Melinex polyester film: this kind of film allows to detach the reference paint from the support whenever necessary. Figure 1 illustrates some examples.

Fig. 1 Examples of oil paints prepared for the experimental research.

[1] Percentages are referred to the total weight of the mixed powder pigments.

2.2. Experimental set-up

A spectrophotometer CM-700d Konica Minolta was used to record reflectance spectra. The instrument employs the di:8°/de:8° geometry (diffused illumination, 8-degree viewing angle) and it offers measurement with automatic SCI (specular component included) and SCE (specular component excluded) switching. Spectra are collected along a 400 to 700 nm wavelength range every 10 nm.

Inside the instrument, a xenon lamp diffuses light on the inner surface of an integrating sphere and it illuminates the sample uniformly. The light reflected from the sample surface, at an angle of 8° to the normal of the surface, is received by the measuring optical system.

The light diffused in the integrating sphere is received by the illumination-monitoring optical system and guided to the sensor. The light reflected from the sample surface and the diffused light are divided into each wavelength component by the measuring optical system and illumination-monitoring optical sensor respectively, and the signals proportional to the light intensity of each component are output to the analogue processing circuit.

Two measurements areas are enabled, SAV (small area view, ∅ 3 mm) and MAV (medium area view, ∅ 8 mm), according to the specimen and applications. We used MAV, as we selected areas of paints wide and homogeneous enough.

Data were analysed using a software that we developed on National Instruments LabVIEW platform (fig. 2). This software allows to analyse the spectral data of each pigment, evaluating typical parameters as maximum, minimum and flexes, and it can also compare an unknown spectrum with the spectra collected on the database recorded with different spectrophotometers. A colour-based filter simplifies the search of reference spectra.

Within a project in collaboration with INRIM (Istituto Nazionale di Ricerca Metrologica) reflectance factor measurements were carried out on some samples by means of a spectrometer Perkin Elmer Lambda 900.

These spectra - acquired along a 250 nm to 2500 nm wavelength range at 1 nm spectral resolution - were compared with the spectral data set collected by CM-700d Konica Minolta along the 400 to 700 nm wavelength range. For each sample, a good correlation was found between the two spectral data sets.

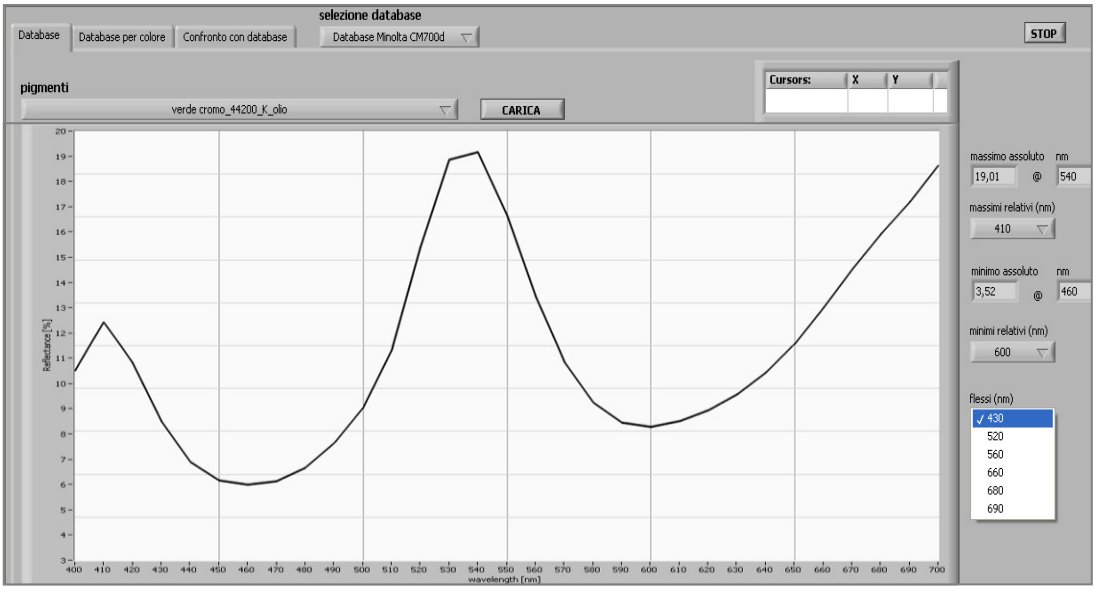


Fig. 2. The software created on National Instruments LabVIEW platform.

3. Data analyses

In the first step of the research work we compared visible reflectance spectra of pigment powders to the ones of their respective oil paints. The aim was to evaluate differences induced by the suspending medium in the pigment's visible light absorption. Some examples are reported in figure 3. To make sure that differences were really representative, 10 reflectance spectra were collected on each oil paint moving within the 4 cm x 4 cm area; the calculated standard deviation always showed very low values, proving a good *homogeneity* of the surfaces.

The collected spectra would also represent the *zero time* for monitoring, in the future, the effects of oil's yellowing and decay as expected as time goes by.

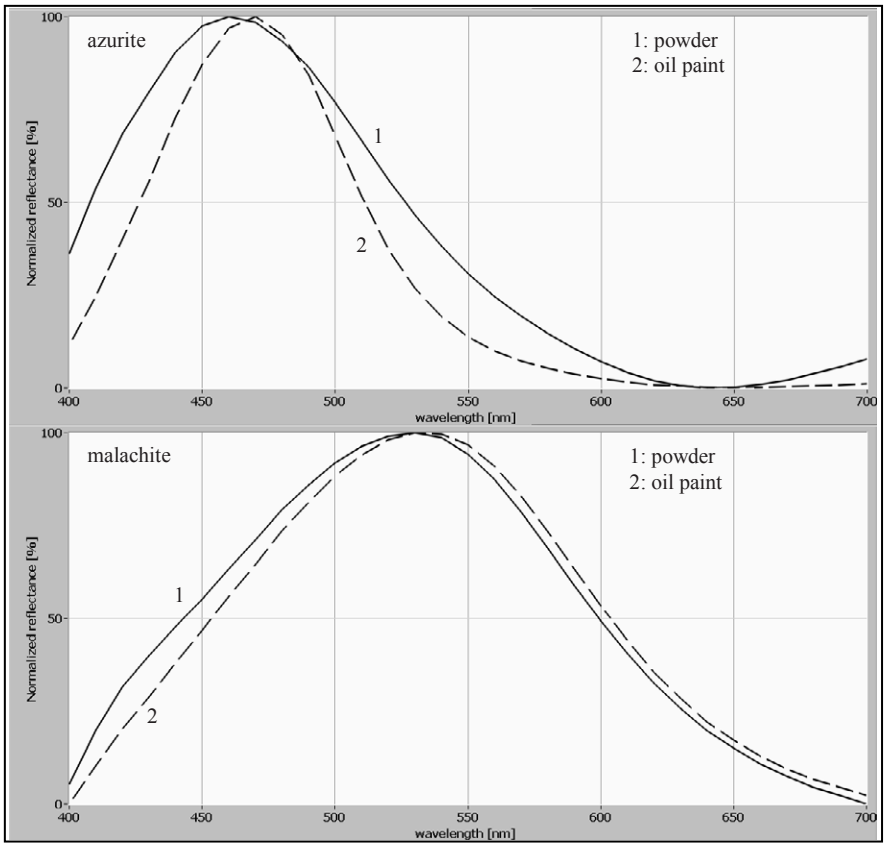


Fig. 3. Normalized reflectance spectra of pure pigment powders (curves 1) and respective oil paints (curves 2).

As you can see in figures 3 and 4, all curves are normalized both to the maximum and minimum values. This simple transformation allows to solve the low reflection region, making the discrimination of the coloured pigment easier: in fact, it is not the nature of the spectral reflection but the character of the *absorption* that is definitive for analytical identification [1]. In such a way, the normalization process emphasizes the contrast between absorption and reflection of paints as if they had the highest saturation[2]. Therefore, normalization is particularly useful when measuring and comparing very dark or neutral surfaces.

[2] When the different percentages of a white pigment in a coloured paint have to be evaluated, normalization is not useful.

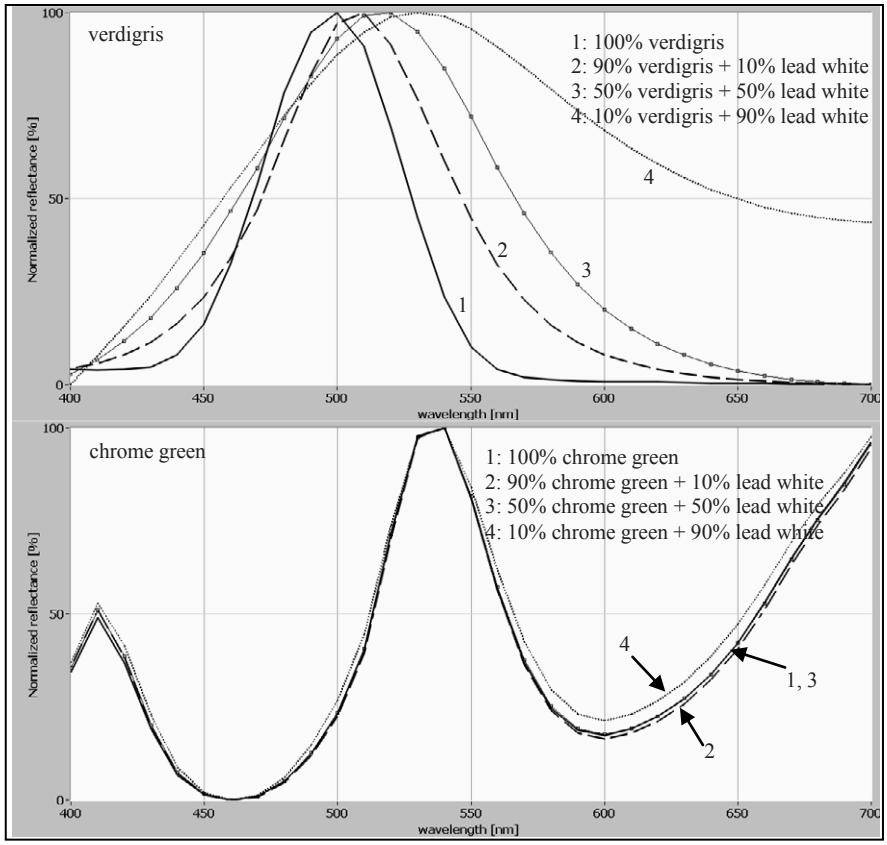


Fig. 4. Reflectance spectra of oil paints and respective pigment mixtures in different percentages of Lead White.

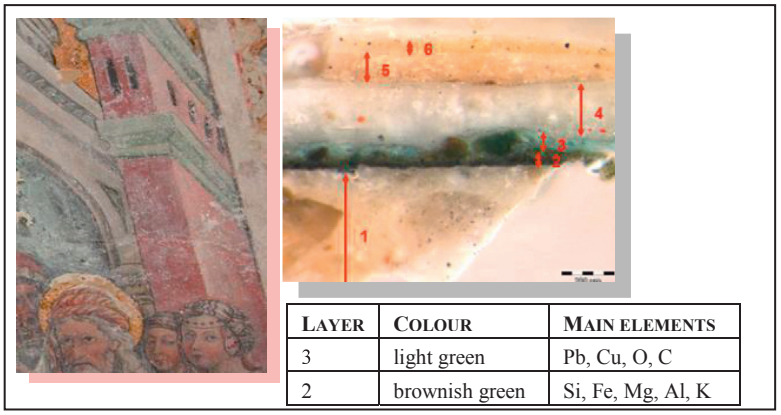
For the same reason, to see the characteristic absorption of pigments, you can dilute them with white pigment or apply them as incomplete hiding over a reflecting substrate [1]. Mixture with white pigment is even a common practise of painters. These remarks interested and addressed the second step of our research work: for each pigment we prepared paints with different percentages of Lead White and then we acquired their spectral reflectance curves. Among whites, Lead White was chosen because it has been by far the most important of the white pigments used in Europe from the Roman period onwards [7]. Our aim was to evaluate how much the white pigment influences the paint's spectral behaviour, as it usually occurs in real cases. Figure 4 shows two examples of these different effects.

In the end, as already mentioned, two particular artworks *inspired* the last series of reference paints. The first artwork is a 15th century fresco found in an ex-church in Piedmont: in 2009, significant whitewash coverings were removed from walls and, thanks to the restoration intervention, beautiful frescos were brought to light. After that, non-invasive and invasive analyses were carried out during three diagnostic measurement campaigns and original pictorial materials were identified. The second one is a 16th century Venetian oil painting on canvas. When the painting arrives in our Restoration Laboratories, it showed a very altered aspect, in particular from a chromatic point of view: in fact, not only the varnish was definitely yellowed, but some areas of paints also seemed to be very altered and darkened. On this painting also, non-invasive and invasive analyses were carried out in order to identify the artist's palette. All mixtures noticed both in the fresco and in the painting were recreated in our laboratory, approximating the ratio among different pigments and using - for simplicity - linseed stand oil as binder in any case. Our final aim was to verify the correspondence between real paint surfaces and reference paints in terms of visible reflectance spectra.

4. Results

4.1 The case of 15th century fresco in an ex-church in Piedmont

Here the case of one green area of the fresco is reported. The polished cross section of a sample was observed under an optical microscope and analysed by a Scanning Electron Microscope equipped with an Energy Dispersive X-ray probe (SEM-EDX). Under three layers of whitewash coverings, two superimposed green layers were detected (figure 5): the upper one was composed by a green Copper-based pigment and Lead White; in the lower one, Potassium, Magnesium and Iron Aluminium Silicates were detected.



LAYER	COLOUR	MAIN ELEMENTS
3	light green	Pb, Cu, O, C
2	brownish green	Si, Fe, Mg, Al, K

Fig. 5. Detail of the fresco in an ex-church in Piedmont (left). Polished cross section and SEM-EDX results (right).

After removing the whitewash coverings, spectrophotometric analyses were performed. Involving this research project, the aim was to verify the possibility of identifying the kind of Copper-based pigment (used on the surface) despite the presence of other pigments in mixture – Lead White in this case-, by its reflectance spectrum. The green pigment was identified as Malachite: in Malachite-based references (fig. 6), Lead White influences the spectral behaviour, not modifying the Malachite curve's shape but only bringing reflectance values up. Comparing spectra, it's also possible to note that *green fresco* lies between references 3 (*50% malachite + 50% lead white)* and 4 (*10% malachite + 90% lead white)*. This can suggest a possible range of pigment dilution.

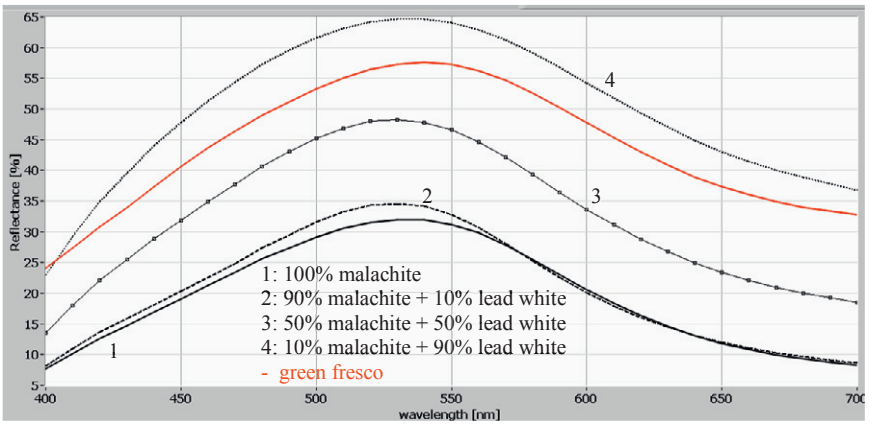


Fig. 6 Visible reflectance spectra of the Green fresco (red curve) and of Malachite-based references (black curves).

4.2 The case of a 16th century Venetian oil painting on canvas

Concerning the case of the 16th century oil painting, the diagnostic investigation on the colours of the sky is presented.

In the blue and light blue areas of the sky, infrared false colour (IR-FC) imaging technique suggested the presence of two different blue pigments: as you can see in figure 7, some areas show a dark blue false-colour, other ones has a red false-colour.

X-ray fluorescence analyses were carried out selecting two distinct areas: Cobalt was recorded as main signal in correspondence of the red false-colour areas *(b)*, while in the blue ones *(a)* the Copper signal was detected.

Spectrophotometric analyses were performed after the aged varnish was removed: red false-colour areas were identified as Smalt (Cobalt glass) and blue ones were attributed to Azurite, confirming XRF outcomes.

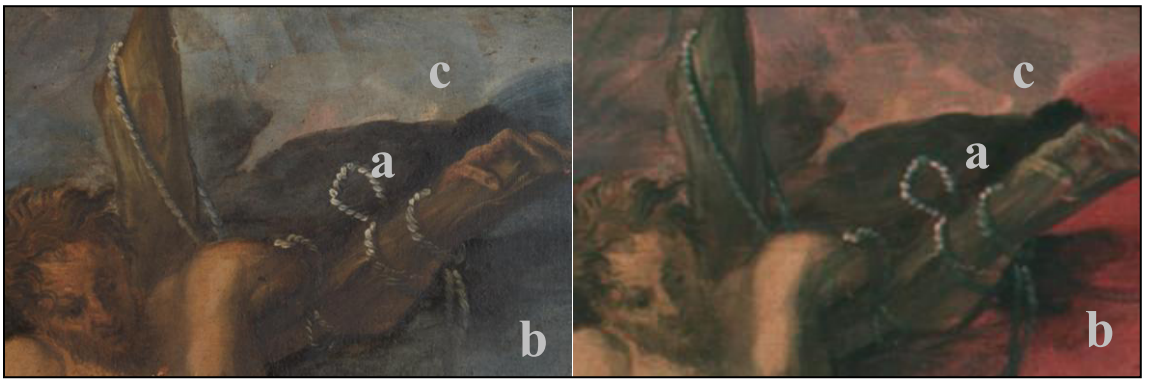


Fig. 7 Detail of a 16th century Venetian oil painting. Comparison between visible light photograph (left) and IR-FC image (right).

Since then, we focused our interest on those areas characterised by a combination of red and blue false-colours (area *c* in figure 7): in those areas, X-ray fluorescence analyses recorded Copper, Cobalt and Lead as main signals. Starting from the elemental analyses outcomes, that suggested the presence of both two pigments, reference oil paints were created mixing Smalt, Azurite and Lead White in oil.

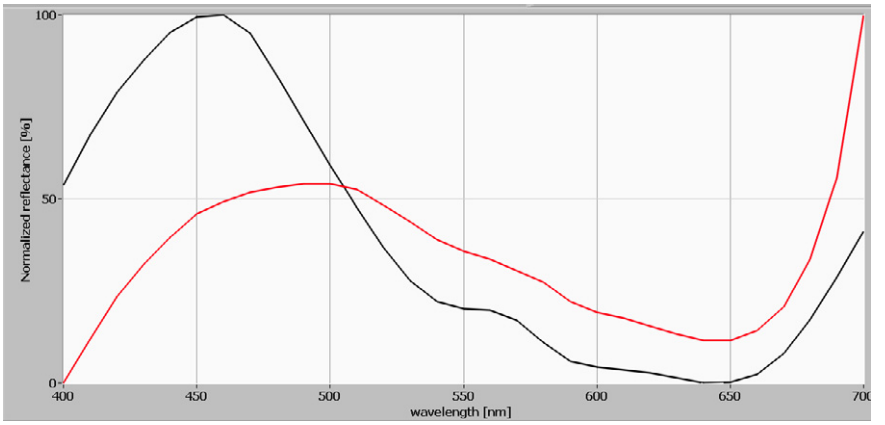


Fig. 8 Reflectance spectra of area *c* of the sky (red curve) and mixture paint reference of *20% Smalt +20% Azurite+ 60% Lead White* (black curve).

As known, in XRF analysis and FC-IR technique, the recorded information does not come from the very upper layer only. Visible reflectance spectroscopy, that is a superficial technique instead, was carried out in the area *c* of the sky, aiming at understanding if Smalt and Azurite could be really present as a pigment mixture, or rather if they could be present as two different superimposed layers.

Red curve in figure 8 is relative to the area *c* of the sky: for the analytical identification it was compared to all Smalt and/or Azurite based references of the database. As you can see, it shows a good correspondence with the reference *20% Smalt+ 20% Azurite+ 60% Lead White* (black curve): the characteristic absorption of both Smalt and Azurite are recognizable in the spectrum, improving the diagnostic investigation.

5. Conclusion

Non-invasive techniques, as well assessed, are commonly used as preliminary investigations on works of art. When the sampling on the artwork is not permitted, the application of these analyses is the only diagnostic tool for reaching requested information. Non-invasive technique of visible reflectance spectroscopy, based on the principle of selective light absorption, can give information about the superficial pictorial material composition.

In general, *superficial inhomogeneity* and *compositional complexity* of the pictorial material make the analytical identification more difficult. For this reason, up to now, reference databases of reflectance spectra had been built up using well-known pigments and binders. In real cases, however, the technique is limited because of the presence of very different variables: first of all, the execution technique of the artist, the various ratio among different pigments, the nature and grain size of pigments themselves, the eventual yellowing due to the binder's decay, as well as the alteration of some pigments can modify the spectral reflectance behaviour.

The potentiality of visible reflectance spectroscopy can be implemented by means of a particular database, which is directly *inspired* by works of art: by reproducing some pigment mixtures really detected in works of art, it was possible to demonstrate that pigments' characteristic absorptions are detectable in real cases as in reference paints. This means that pigments could be identified by analysing their spectral behaviours even when they are present in mixture.

Spectrophotometric results were shown to be very clear when the areas of paint are composed by a coloured pigment added with white. In these cases, spectra normalization process is useful for the coloured pigment identification but - as expected - not for evaluating the presence of white. For this purpose spectra have to be compared as they are. The database does not pretend to be a tool for pigment mixtures' *quantitative* analyses: anyway, the comparison between unknown spectrum and references allows not only to identify the coloured pigment but also to hypothesise the percentage of white. Aiming at simulating typical pigment mixtures, we decided to start from scientific data already collected on some works of art to prepare the references. In this way, a multi-technical approach in diagnostic investigation has always to be preferred.

Concerning *more complex* mixtures (e.g. Lead White + two coloured pigments), spectrophotometric outcomes seem to be very interesting. In the experimental phase, the comparison between mixtures and relative pure pigments allowed to better understand the light reflection and scattering phenomena that occur when two coloured pigments are contemporary present in a paint. The spectral behaviour interpretation is not so simple because the resulting curve's shape changes, depending on those absorptions. However, in the reported example of a real painting, the mixture of Smalt and Azurite was found to be easily detectable by its reflectance spectrum: the simulating sample and the real case show very similar reflectance spectral behaviours. For pigment mixture identification a complete database is even more important. The final aim is to understand which combinations of pigments could be detected by means of visible reflectance spectroscopy, in order to improve the non-invasive protocol in the diagnostic investigation process.

Our future purpose is to carry on the research about pigment mixtures focusing our attention on the effects of ageing – such as yellowing due to the binder's decay and darkening due to the alteration of some pigments – on the spectral reflectance behaviour.

Acknowledgements

The authors would like to express their gratitude to Gabriele Piccablotto for the measurements carried out in INRIM.

References

[1] Ruth Johnston-Feller. *Color science in the examination of museum objects, Nondestructive procedures*, Getty Conservation Institute; 2001.
[2] Bisulca C, Picollo M, Bacci M, Kunzelman D. UV-Vis-NIR reflectance spectroscopy of red lakes in paintings. In: *9th International Conference on NDT of Art, Jerusalem Israel, 25-30 May*; 2008.
[3] Bacci M, Casini A, Cucci C, Picollo M, Radicati B, Vervat M. Non-invasive spectroscopic measurements on the Il ritratto della figliastra by Giovanni Fattori: identification of pigments and colourimetric analysis. *Journal of Cultural Heritage 4*; 2003, p. 329-336.
[4] Miliani C, Rosi F, Brunetti BG, Sgamellotti A. In situ nonivasive study of artworks: the MOLAB multitechnique approach. *Accounts of chemical research* 2010; **43**; p. 728-738.
[5] *Fiber optics reflectance spectra (FORS) of pictorial materials in the 270-1700 nm range* (fors.ifac.cnr.it).
[6] Depuis G, Menu M. Quantitative characterisation of pigment mixtures used in art by fiber-optics diffuse-reflectance spectroscopy. *Applied physics A* 83; 2006, p. 469-474.
[7] Eastaugh N, Walsh V, Chaplin T, Siddal R. *Pigment compendium, A dictionary and optical microscopy of historical pigments*. Oxford, Butterworth-Heinemann; 2008; p. 239-241.