Non destructive identification of the colouring substances on the monuments studied by colorimetry

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Abstract

This work was carried out in the framework of a complete effort of maintenance and restoration of the colours of the monument of Philippe Dagobert (1222-1232) exhibited in the cathedral of Saint Denis in Paris and aimed at the identification of the colouring substances through colorimetry - spectrophotometry (visible spectrum).

Based on the bibliographic information about the pigments used in Middle Age and their preparation and application on the working surfaces we have reproduced reference coloured samples in the laboratory, for these pigments. Our study was based on the comparative analysis of IR reflectance spectra with relation to the measurements made in situ and at the laboratory.

The observation of the different plots allowed a primary identification of the chromatic identity as follows: It is suggested that the blue stimuli come from a mixture of equal concentrations of azurite and malachite, the green ones are due to a mixture of malachite and green earth (equal concentrations too) and the red and yellow ones, are probably related to a red and yellow ochre presenting signs of aging. Some conclusions about the parameters that seem to affect the reflectance spectra and which by naked eye may not be perceived have been drawn as well.

1. Introduction

The colour in general is a basic element of human perception and could be defined as the impression formed in the eye because of different luminous irradiations. For instance, a coloured surface is the result of the interference of the electromagnetic radiation with matter in the visible spectra (380-780nm). Every colour corresponds to a precise wavelength and its image takes birth only in our brain after the meaning given by the cortex of the eye to each optical sign received. Consequently, every chromatic expressure is directly related to the human psychism [3].

For the scientists, the concept of the colour is relevant to the characterisation of a spectral property resulting from the diversion of luminous radiation when it interacts with matter. The most important one, which could also be defined as the fingerprint of each colour, is the coefficient of spectral reflectance R(λ) representing the percentage of the reflected irradiation for a given wavelength. The coefficient of spectral reflectance contains information about the dominant wavelength and chromaticity of a pigment [1,3].

All the pigments used in this work were in the form of powder. Some were very difficult to find and could be very expensive and others were very easy to obtain. The pigments used by medieval craftsmen were composed mainly of mineral and vegetable substances. Old texts dealing with techniques used in the preparation and fabrication of colours also enable us to confirm their compositions. However, many of these texts were unfortunately destroyed by time and history. Modern technology for physical and chemical analysis of samples has enabled us to define the type of the products used and their origin as well as to know with certainty their compositions [5].

For instance, for the determination of the chromatic identity of the monument we studied, we used the colorimetry, a method visualising the result of the interference of the light with a coloured surface and capable to reproduce correctly the three primary stimuli R (red), G (green), B (blue) responsible for the erection of human optical cells. For a given incidence angle and luminous source, the spectrum of the intensity of the reflected radiation gives access to the characteristics of the coloured surface. This spectrum is nothing more than a record of the energy propagated by the surface for every wave length of the light transmitted (ultraviolet, visible or infra-red). Each spectrum is a function of the wavelength of the radiation, allowing the identification of the colours through respective spectral comparison. Practically thirty two measures, one for every 10nm, are sufficient to give the visible spectrum of a luminous irradiation [1,2,3,4].

2. Experimental Part
Materials and Methods

Through the ages the most part of the colours disappeared and the following colours were left coloured on the dresses and other parts of the statue. The colours that were left are the following:

- Yellow on Philippe's hair and lion's mane, the angels' wings, as well as some golden shades.
- Blue on the angels and Philippe's dress.
- Red on the upper pillow of Philippe's elbow, the inside of Philippe's dress and on lion's body.
- Green on the lower pillow

We made two series of measurements one in the Cathedral of Saint-Denis (in situ) (Figs. 1a and 1b) and one in the laboratory, where we produced coloured samples to provide reference measurements, to mach those in the Cathedral.

Figure 1a: In situ measurement in the Cathedral of Saint-Denis

Figure 1b: In situ measurement in the Cathedral of Saint-Denis

More precisely, according to bibliography, the monument was made of limestone originally from Saint Maximin quarry, a region northern of Paris, where we procured plates of that quality and pigments used in Middle Age as prescribed.

We prepared 10 plates 10x15cm (Fig.2) that we enumerated and filed per colour in order to simplify further treatment of the results. Pigments used were mostly ochre, minerals and lead products and as connective we used a natural resin – Dammar – coming from a kind of an Indonesian pine.

Figure 2: Several Reference Samples

For practical reasons, each plate was divided to eight different colouring areas. A first layer of white lead (powder of white lead dissolved in water, 1:2) was applied in order to fill the pores of the plate and let to drain for a week before moving on polishing the surface to obtain a uniform working surface.

Colour preparation consists of mixing the pigment with the adhesive in precise ratios relative to pigments' nature – for the majority of the mineral ones the ratio was 1:1 whereas for the ochre and the black was 1:3 – and they were left to rest and form with time colloidal systems.

Colour coating, usually took place some days after colour preparation and thus sometimes we needed to dissolve them with spirits of turpentine (naphtha). For multiple application of the colour, it was necessary to wait until complete drying of each layer and the use of an intermediate varnish that would isolate each one.

We considered important to study the influence on the reflectance spectrum of various parameters such as the presence of the initial white lead support and that of the intermediate varnish, so we prepared three testifier plates. These plates were consisting of samples of all colours studied, but differed in the consistence of the initial layer. Colours were directly applied on plate N°14, whereas plate N°15 had an initial layer of white lead and plate N°2 had an initial white layer and an intermediate varnish one.

Once our specimens were prepared and after ensuring the same measuring conditions, reference plots were obtained.

Measures in situ were taken in almost absolute darkness in order to increase the accuracy of our results by eliminating the influence of ambient light. At this point we should mention that we could not ensure identical measuring conditions (mostly as far as the incidence angle is concerned) as the monument surface presents great particularities (deep cavities, irregular curves…).

Given the sensibility of the measurements, we managed to minimise the error of measuring because of the instability of human hand by using an improvised disposition allowing a more precise and stable focus.

The plots given from the software after the measurement treatment were normalised in order to represent the reflectance for comparison.

3. Results and Discussion

To be able to come up to conclusions, we compared diagrams from both measurement series for each colour as well as those corresponding to testifier plates.

As far as the influence of the initial layer is concerned, diagrams corresponding to the three testifier plates were used. To illustrate the situation, we took as example the case of malachite (Fig.3). We noticed that for all the pigments except dark ones, the presence of a white lead substrate intensifies the colouring impression. Reflectance in that case, takes greater values as the white bed eliminates the colour's ingress in the limestone and at the same time provides a kind of composite faded pigment. Diagrams related to the testifier plate N°2, where there is an intermediate varnish layer, show a tendency of reducing the reflectance and thus making the colour look darker.

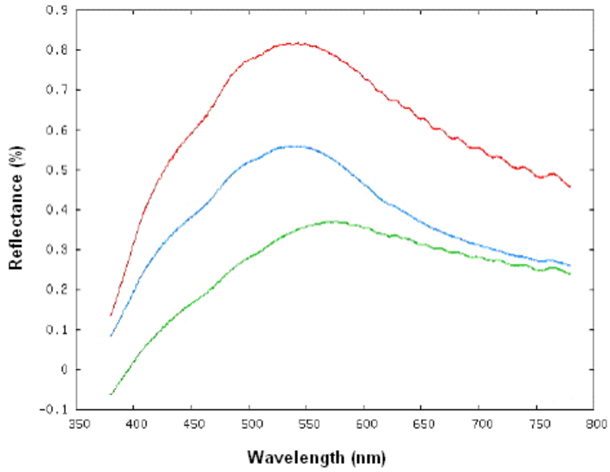


Figure 3: Spectral Reflectance of malachite on white lead substrate (red line), with an intermediate varnish layer (blue line) and without substrate (green line).

In fact, the intermediate varnish stratum works as a stabilizer of the under layer and as an insulator for the second one eliminating any chance of mixing of the paint with the white bed. Finally, a slight transposition of the pick is seen in the case of complete absence of underlay. This may be attributed to the light yellow colour of the limestone, probably interfering in the measurement.

For dark pigments such as haematite or black ones (Fig. 4), which naturally have low reflectance, the presence of a sub layer has a different impact. More precisely, we still remark an increase of reflectance levels becoming less intense when a varnish layer exists as for the rest of the pigments, but when initial layer is missing, reflectance values remain relatively high. Actually, dark pigments usually consist of bigger grains and are much denser than other pigments, stiffening colour diffusion in the pores of limestone.

Studying blue expression: Principal blue pigments used in Middle Age as prescribed by bibliography, are azurite and lapis lazuli. Relevant spectral reflectance, however, gives significantly different plots, as can be clearly seen below (Fig. 5).

For azurite, dominant pick is situated at a wavelength of approximately 480nm whereas for ultramarine blue, we have two picks, a maximum at 490nm and a minimum at 610nm.

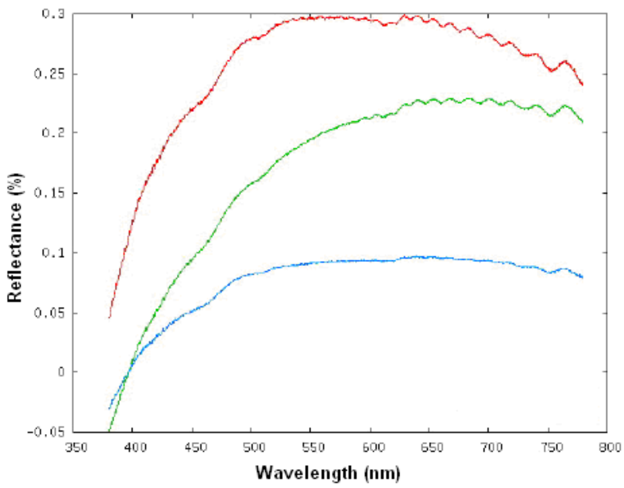


Figure 4: Spectral Reflectance of black pigment on white lead substrate (red line), with an intermediate varnish layer (blue line) and without substrate (green line).

Plotting at the same diagram the results of in situ and laboratory measures, we realised that ultramarine's spectrum is by far different from those corresponding to in situ values and thus we exclude its presence (Fig. 6).

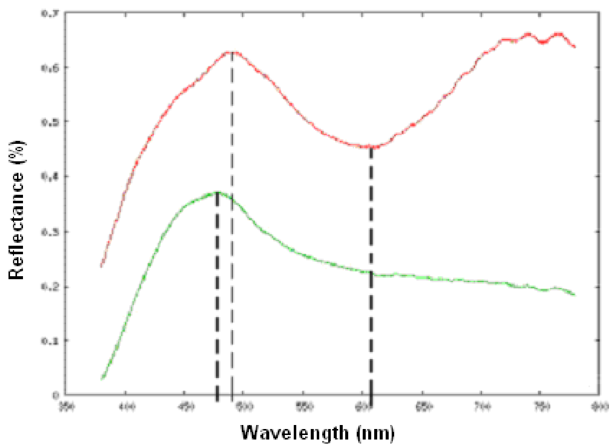


Figure 5: Spectral Reflectance of azurite (green line) and lapis lazuli (red line).

In situ measures spectrum presents a peak at 540nm, wavelength value corresponding to green colour and almost coinciding with the malachite's spectrum one. At this point we should mention that azurite used to turn into green with time and given the chemical affinity of azurite with malachite, often in azurite we could find malachite.

We assume at this point that probably the blue colour of the monument was obtained by mixing azurite with malachite. Our assumption concerning the presence of azurite is confirmed by a second measurement taken in situ from a less exposed area and for which relevant plot's peak almost coincides with the one corresponding to azurite and general form looks like malachite's, excluding once again the possibility of ultramarine's presence (Fig. 7).

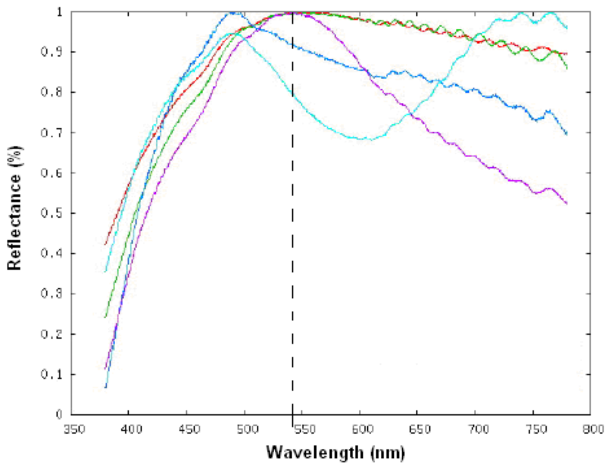


Figure 6: Spectral Reflectance of blue stimuli in situ (lines green and red), for azurite (blue line), for malachite (mauve line) and ultramarine (turquoise line).

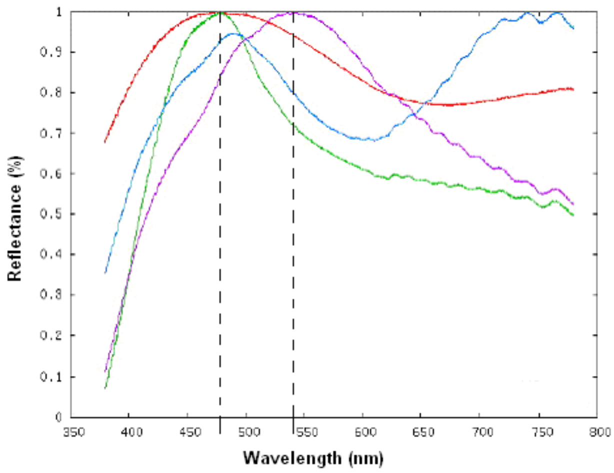


Figure 7: Spectral reflectance of blue stimuli in situ (red line), azurite (green line) and malachite (mauve line).

Concerning green stimuli, pigment identification did not present any difficulties as relevant reflectance spectrum for green earth and malachite, are quite different not only in terms of general appearance but also concerning peak location. In the common diagram of spectral reflectance of the pigments, a 1:1 mix of them and in situ measurements, we notice that equal quantities mix of the two pigments, give a reflected intensity of the same type as the one given from monument measures (Fig. 8).

Yellow stimuli identification origin was slightly more complicated as in situ measurements plot did not present any characteristic peak but its general appearance for high wavelength values approaches the one corresponding to lead oxide and yellow ochre JFLES blend (1:1) and for low values that of yellow ochre JFLES (Fig. 9).

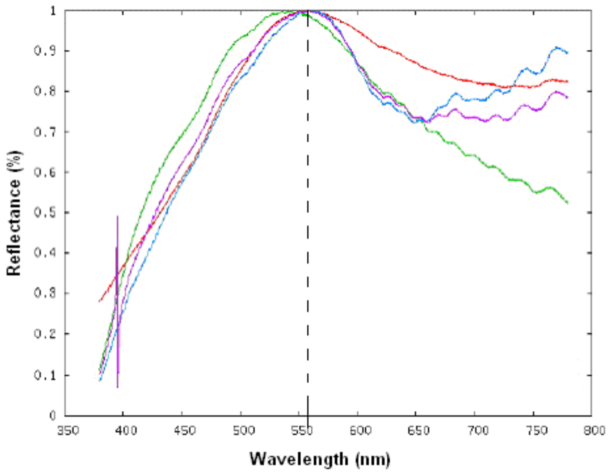


Figure 8: Spectral Reflectance for Green Stimuli in situ (red line), for malachite (green line), green earth (blue line) and a 1:1 mix of the two pigments (mauve line).

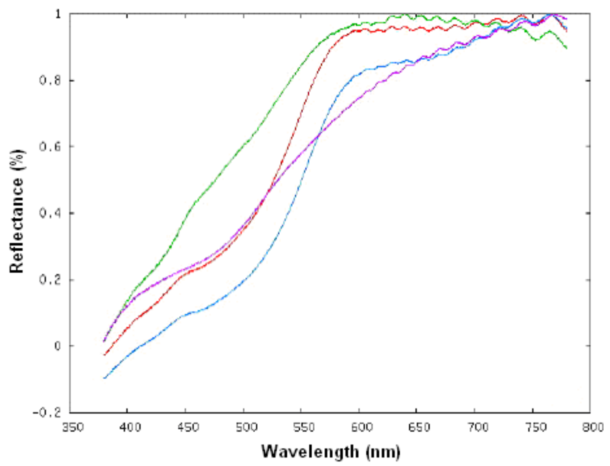


Figure 9: Spectral Reflectance of yellow stimuli in situ (mauve line), blend of lead oxide and yellow ochre JFLES (green line), yellow ochre JFLES (red line) and blend of hematite and yellow ochre JFLES (blue line).

The idea of mixing the ochre with a red pigment was coming from the way ochre gets on with time. Thus we tried the same comparison with a blend of red and yellow ochre, but the results still remained insufficient. Thus, we decided to consider that yellow stimuli were the result of yellow ochre that has turned to almost brown because of time.

Finally, red stimuli both in situ and in laboratory correspond to very characteristic plots that however do not have any peaks as seen at the diagram of Fig. 10. We notice that spectral reflectance of red ochre is alike to the one of the in situ measurements that is slightly transposed. This shift is in accordance to the aging of the colours resulting in lower reflectance values, as already seen for the yellow stimuli.

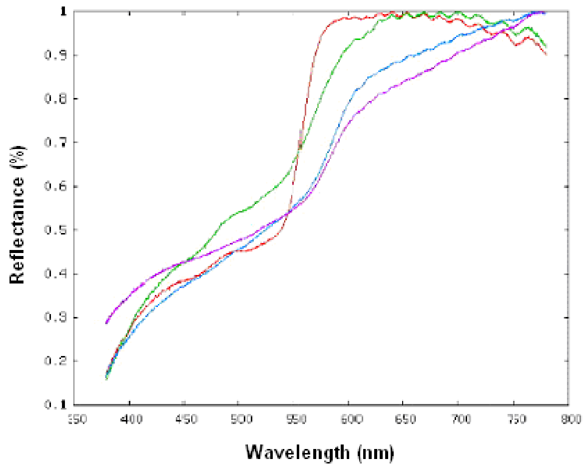


Figure 10: Spectral Reflectance of red stimuli in situ (blue and mauve lines), red ochre (green line) and minimum (red line).

4. Conclusions

The present study allowed to come up to the following conclusions about the parameters influencing spectral reflectance values with the use of spectrophotometry:

1. The adhesive surrounding pigment particles annihilating any possibility of bilateral mixing, it explains as well the action of the intermediate varnish layer between the substrate and the coloured coating. Thus reflectance spectrum stays characteristic to the pigment.

2. The presence of a white lead substrate averts the penetration of pigment particles in the working surface, whereas at the same time phenomena of white pigment's diffusion to the examined stimuli are noticed, resulting to an additional reaction of both spectra and higher values of reflectance. On the other hand, absence of a sub-layer reduces reflectance as a part of the pigment is absorbed from the pores of the working surface and thus the quantity of the colour measured is less important. Furthermore, characteristic peaks tend that way to eclipse and the spectra are transposed as we have the interference of the limestone's colour.

3. Dark pigments are by nature characterised by low reflectance values, intensified by the presence of a white lead substrate but rudely annihilated by the intermediate varnish layer. Moreover, unlike the rest of the pigments, when no sub lay does not exit reflectance takes intermediate values as chromaticity and grains' size stiffens pigment's absorption by limestone.

4. Aging of the pigments is reflected by the blunting of characteristic peaks and for ochre by a general transposition of the plot attributed to the loss of luminosity.

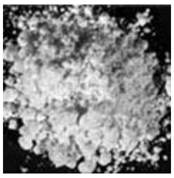
5. In general terms, "colorimetry" is judged appropriate for the initial investigation of the chromatic identity of monuments.

6. Comparative analysis of the reflectance corresponding to laboratory measurements with the in situ ones, confirm bibliographic data about pigments used in Middle Age.

5. References

[1] D. Dupont and D. Steen, *Theoretical elements of colorimetry*, Techniques de l'ingénieur, R 6 440 – 443 (in French)
[2] V. Orfanakos, *Chromatometry: basic principles*, Stamouli Editions, Athens, 2004 (in Greek)
[3] D. Malacara, *Color Vision and Colorimetry, Theory and Applications*, Spie Press Editions, USA, 2002
[4] M. Kartsonaki, *Colorimetry - Spectrophotometry*, project report, Ecole Centrale Paris, 2005 (in French)
[5] G. Loumyer, *Traditional techniques of medieval painting*, (réimpression of the 1920's Edition) 1996 (in French)

Table 1. Pigments figuring at craftsmen during Middle Ages

Pigment	Chemical Type	Discovered	Origin	Remarks
		WHITE		
White-lead	$2PbCO_3.Pb(OH)_2$ 	4th century B.C.	Europe	- Very toxic
		BLACK		
Black from smoke or grapes	Amorphous C 	Antiquity	Europe	
		BLUE		
Ultra marine Blue or Lazuli or Lapis Lazuli	$Si_6Al_6Na_{10}S_2O_{24}$ 	3500 B.C.	Afghanistan, Iran	- Semiprecious stone, principal use for jewellery - Very good covering and plating capacity - Very expensive
Copper Blue or Azurite	$2CuCO_3.Cu(OH)_2$ 	Antiquity	Russia, Africa, Hungary	- May be extracted from mines or produced artificially

		GREEN		
Green Earth	Fe_2SiO_3 		Roman Empire	- Found in argillaceous ground containing minerals such as Glauconite
Malachite	$CuCO_3.Cu(OH)_2$ 	Antiquity	Siberia, Central Europe, Russia, Africa	- Varicolor semiprecious stone - Non miscible
		RED		
Minium	Pb_3O_4 		Roman Empire	- very toxic - comes from the charring of white lead - gives an orange red colour
Red Ochre	Fe_2O_3 	Antiquity	France	- comes from clays rich in iron oxides or calcination of yellow ochre - according to the quantity of iron oxide, these clays provide all shades from red to brown
		YELLOW		
Ochre	$Fe_2O_3.3H_2O$ 	Prehistory	Northern France	- ideal chemical stability for mixing - very good covering capacity and simple application - not expensive
Lead oxide	PbO 	Antiquity		- mineral lead oxide - golden yellown shade - very toxic