

## Physics, colour and art: a fruitful marriage

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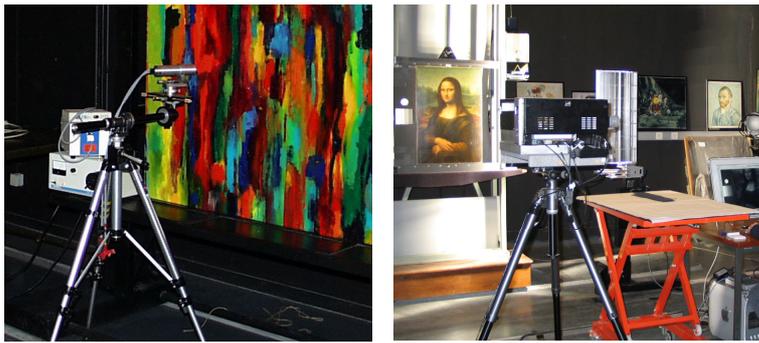
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This paper is a review of recent applications of colour for studying works of art. Three means to pursue the colour are suggested: a goniospectrometer in back-scattered configuration, a multi-spectral camera and modelling using radiative transfer. The procedures are non-destructive, contactless, implementable *in situ* and leading to quantitative results in real time. Colorimetric status reports are first developed as a tool for restorers, conservators and archivists. Examples of the follow-up of a restoration and of the assessment of an exposure in a museum are presented. Further analyses allow comparing the palette of different painters and discriminating different artistic techniques, such as glaze and pigment mixture, for art historians. Finally, the modification of the colour is studied due to a modification of the surface state or to the applying of a varnish.

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### Introduction

In art, the colour has been a long time aesthetically dangerous because its material nature, source of seduction and pleasure. The primacy of the colour on the drawing appears around the XVII<sup>th</sup> century with Roger de Piles in France, who defended Rubens against Poussin [1]. In science, one must wait until the XX<sup>th</sup> century to define quantified colour spaces. They can now be used as a fingerprint of masterpieces. It is a tool dedicated to curators for archiving their collections and for drawing up a status report before and after an exhibition, a loan or a restoration. It is tool for art historians for establishing the palette of an artist and further comparisons. Finally, it is a tool for Interpol to fight against forgery [2]. But colours are influenced by the modifications of the surface state or by a varnish and its ageing. These colour variations can be due to a restoration or to specific conditions of conservation or exhibitions and must be checked and analysed during the follow-up and the monitoring of conservation or restoration treatments. Measurements and modelling are now developed everywhere for answering these tasks. The implemented means in the INSP are summarised in Figure 1.



$$\begin{aligned} \frac{df(\bar{u})}{d\tau} &= -\frac{f(\bar{u})}{\mu} \\ &+ \frac{\omega}{4\pi} \frac{\mu}{|\mu|} \left( \sum_k \frac{F_k(\bar{u}_k)}{|\mu_k|} p(\bar{u}, \bar{u}_k) \right) \\ &+ \int \frac{f(\bar{u}_j)}{|\mu_j|} p(\bar{u}, \bar{u}_j) d\Omega_j \end{aligned}$$

Figure 1: Three means to pursue the colour of masterpieces in the INSP: goniospectrometer in back-scattered configuration (left) [3], multispectral camera of Lumière Technology (middle) [4], and radiative transfer equation RTE (right) [6,7].

Spectroscopic optics allows non-destructive, contactless measurements *in situ* leading to results in real time. According to needs, we use either a goniospectrocolorimeter in back-scattered configuration to record one diffuse reflectance spectrum [3] or a multispectral camera to record hundred millions of spectra [4]. The colorimetric coordinates are calculated from these spectra in the  $L^*a^*b^*$  or  $L^*C^*h^*$  space defined by the CIE in 1964 [5].

Modelling of the interaction light-matter and its comparison with measurements is also a fruitful tool for the discrimination of artistic techniques and for pigments identification. It calls upon the radiative transfer equation and its solving by the auxiliary function method [6-8]. We shall successively present some results issued from colorimetric status reports and studies of colour modifications. We shall conclude by the deficiencies of the colour for pigments and dyes identifications.

## Colorimetric status report

### *The palette of colours*



Figure 2: *The Pilgrims of Emmaüs* from Veronese, before restoration (left) and after restoration (right) – Musée du Louvre.

The colour recording of a masterpiece in known locations is useful for further comparisons. Besides archiving, it can be used for quantifying a restoration, for checking exhibition conditions or for comparing the palette of different painters. The measurements need to be implemented in the same locations and with the same instrument. The results, consisting of three coordinates for each colour point, are presented in a 3D  $L^*$ ,  $a^*$ ,  $b^*$  space, not easily readable, in the 2D  $a^*$ ,  $b^*$  plane neglecting  $L^*$  and finally by using the principal components analysis (PCA), the most satisfactory representation. We here present examples on a varnish removal and re-varnishing of a Véronèse's painting (Figures 2 and 3), on a test of exposure of Matisse's gouaches (Figures 4 and 5) and on the comparison of the palette of contemporary painters living in the XV<sup>th</sup> century and in North Europe (Figure 6).

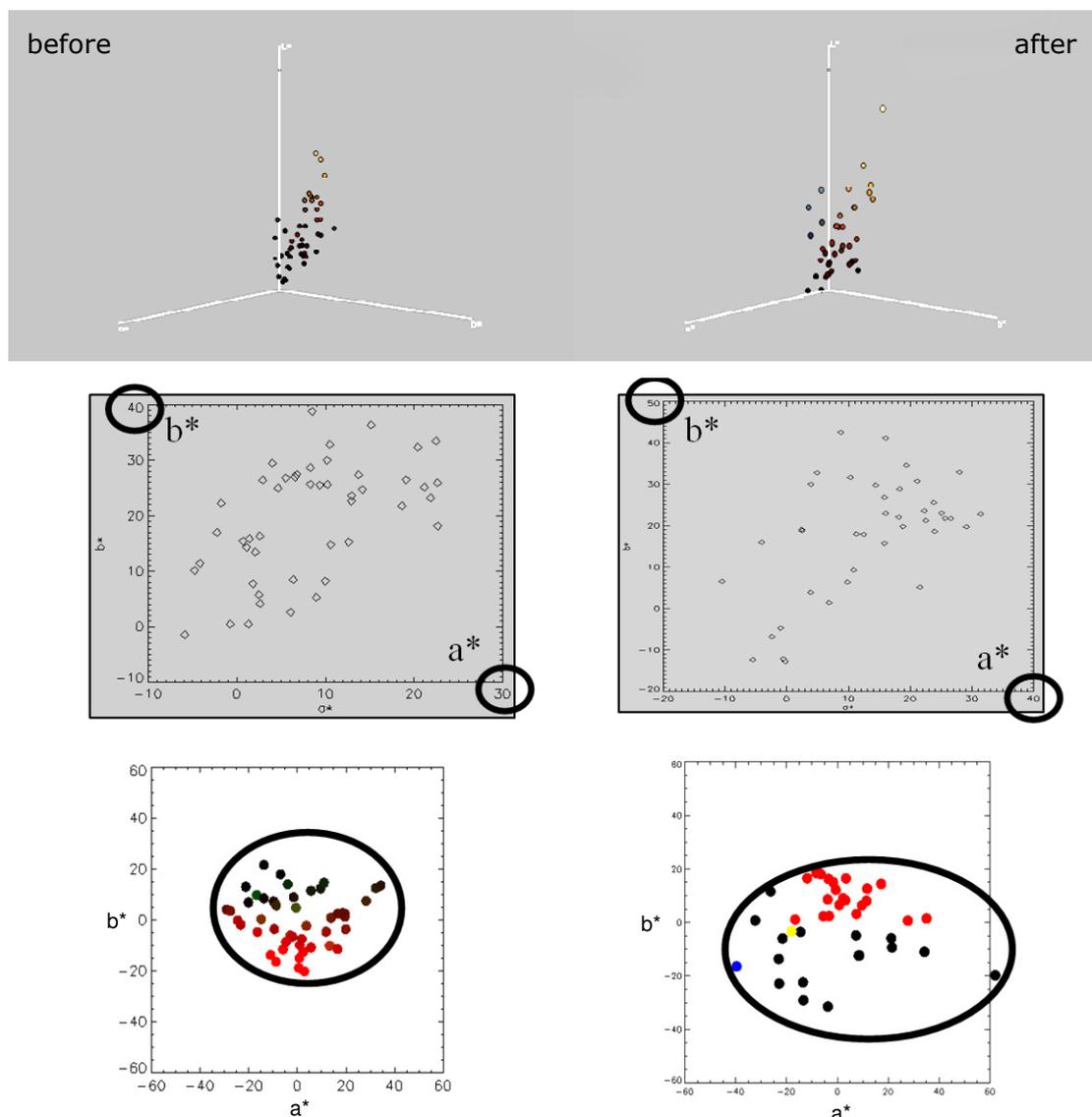


Figure 3: Colorimetric results in specific locations recorded in situ with our goniospectrometer (Figure 1). Colour calculations use the light source D65, the standard eye under 2° (CIE 1931). The 3D representation (top) shows an extension of the palette for each coordinate. The projection (middle) of these points on the  $a^*b^*$  plane quantifies this extension by an enlargement of both axis, but neglects the lightness evolution. The use of principal components analysis PCA (bottom), taking into account the three coordinates, clearly presents a larger overall surface after the removing of the ancient varnish.

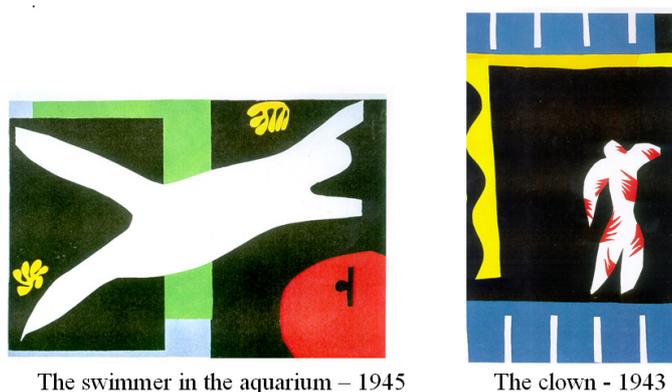


Figure 4: Two cut gouaches of the Jazz collection from Matisse. Musée d'art moderne - Centre Pompidou © RMN.

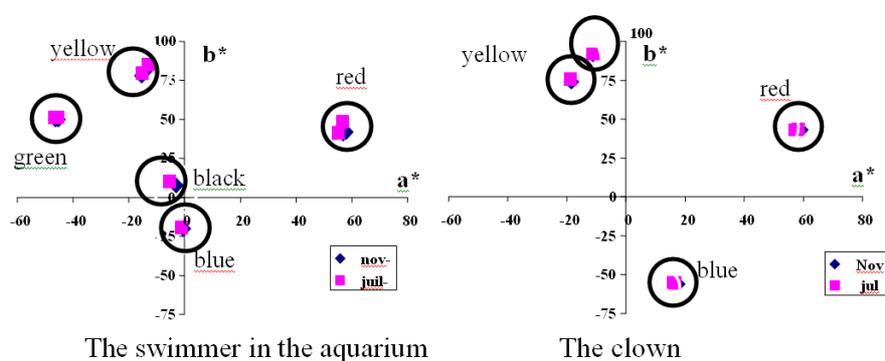


Figure 5: The colour evolution of both gouaches in the  $a^*b^*$  plane, after 6 months of exposure in the Museum. The measurements have been implemented with the previous spectrometer in the same locations. All the colour changes  $\Delta E$  are smaller than 2 and certify satisfying conditions of exposure.

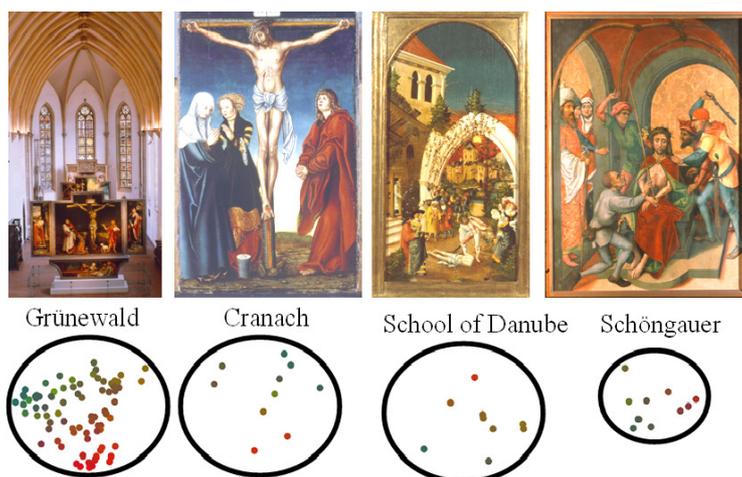


Figure 6: Issenheim's altarpiece from Matthias Grünewald (1475-1528) and other paintings from Lucas Cranach (1472-1553), from the school of Danube (1<sup>st</sup> half of the XV<sup>th</sup> century) and from Martin Shongauer (1450-1491). All these masterpieces are exhibited in the Unterlinden Museum of Colmar © Unterlinden museum. The PCA results are presented under each painting and the overall surfaces represent the painter's palette. Martin Shongauer used the most restricted palette.

### Discrimination between different artistic techniques

The colour recording of a homogeneous area also allows discriminating a glaze and a pigment mixture. The identification calls upon the colour representation in the lightness – chroma  $L^*C^*$  plane (Figure 7). The glaze technique is then characterised by an exceptional maximum of saturation (or chroma) that cannot appear with a pigment mixture [9].

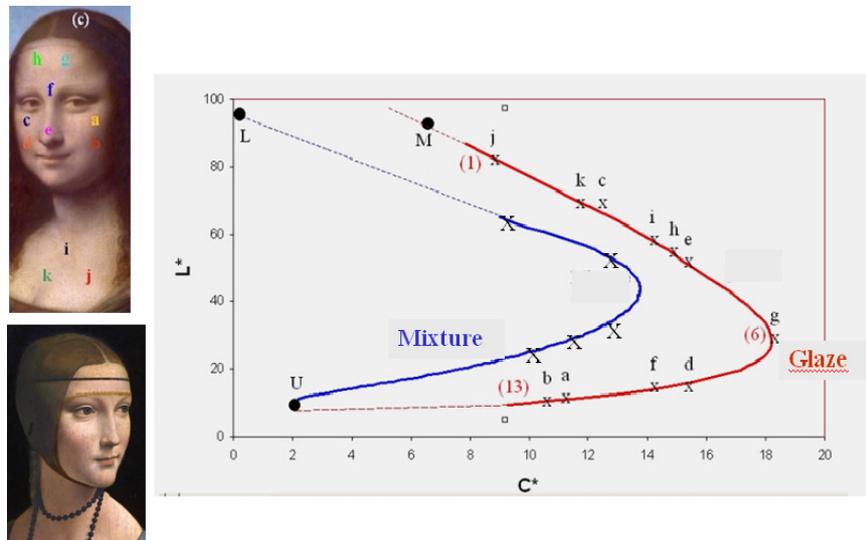


Figure 7: Colours of the faces of the *Joconda* and of the *Lady with Hermine*, painted by Leonardo da Vinci in 1503-1506 and in 1488-1490. The superficial layer of both paintings is made of a burnt umber. In the *Joconda*, the pigment is used in a glaze, characterised by a strong maximum of chroma, and Leonardo modulates the lightness by varying the number of the identical layers [10]. In the *Lady with Hermine*, the same pigment is mixed with lead white (L) with various concentrations and the chroma does not reach the previous maximum. The measurements (crosses) are in good accordance with the modelling (plain curves) using RTE when the upper layer is made of pure burnt umber (U) and the under layer is made of 1% vermilion and 99% lead white (M) for the *Joconda*. The complete composition of the *sfumato* is then determined [10].

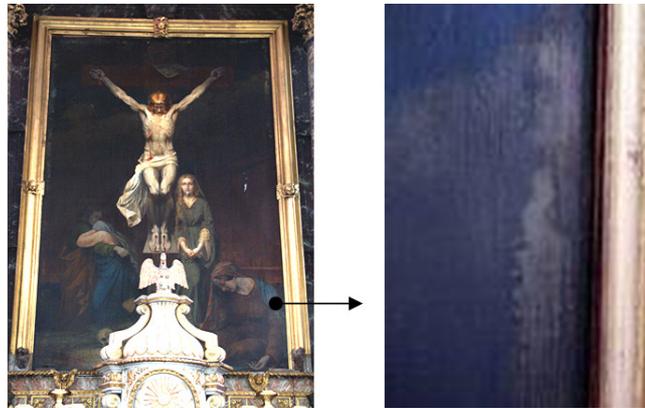
The visual appearance of both techniques is completely different and is explained by the interaction between light and matter. A pigment behaves as a filter. As long as the pigments remain the same and the light remains incoherent, more numerous are the pigments, better is the light filtering and larger is the purity of the scattered light. An important purity corresponds to a large chroma. In the case of a pigment mixture, the filtering is less important due to the addition of white (or black) pigments and the chroma is smaller. This explanation is validated by the modelling using radiative transfer equation and it is shown that multiple scattering is more important in a glaze while single scattering dominates in a pigment mixture [11].

### Modifications of the colour

On a given work of art, two main factors can modify the colour and it is important to measure and to model their influence. The colour change can be due to a modification of the upper surface state, or to a varnish applying and its eventual ageing.

### ***Influence of the surface state on the colour***

The roughness of such surfaces can be modified by external parameters, as UV-light, humidity, thermal variations, light restoration interventions as dust removing. Most of the time, they induce micro-cracking of the organic materials (varnish or binder) and produce a « chanci » (French word coming from the Italian word “crepare”). The effect on the colour is a bleaching, a colour desaturation and the pictorial layer becomes not easily visible (Figure 8).



*Figure 8: The altarpiece of Saint-Hilaire de Givet church painted by Antoine Rivoulon (1810-1864). The “chanci » near the frame is due to a too important ambient humidity.*

A modification of the surface state of the pictorial layer can also be a voluntary action of the artist to create a given visual appearance, used in modern art as the “ultra-back” paintings of Pierre Soulage (Figure 9) or Gerhard Richter.



*Figure 9: “Ultra-black” and “black-light” painted by Pierre Soulage with the same pigment but different roughness.*

Physically, a geometrical modification of the surface influences the reflected light, which is quasi-independent of the wavelength in the visible range. An increase of the roughness induces an upward translation  $A_0$  of the diffuse reflectance spectra (Figure 10).  $A_0$  increases with the roughness and can be analytically related to the geometrical characteristic of the surface, which is the ratio  $h/l$  between the root mean square (rms) roughness  $h$  and the correlation length  $l$  [12]. The ratio  $h/l$  quantifies the

rms slope of the micro-facets of the studied surface and increases with the roughness. In back-scattered configuration, with a back-scattered angle  $\theta$ ,  $A_o$  and  $h/l$  are linked together by Equation 1.

$$A(\theta) = \frac{I^2}{2h^2} \frac{1}{\cos^6 \theta} \left( \frac{n-1}{n+1} \right)^2 \exp\left(-\frac{I^2}{2h^2} \tan^2 \theta\right) \tag{1}$$

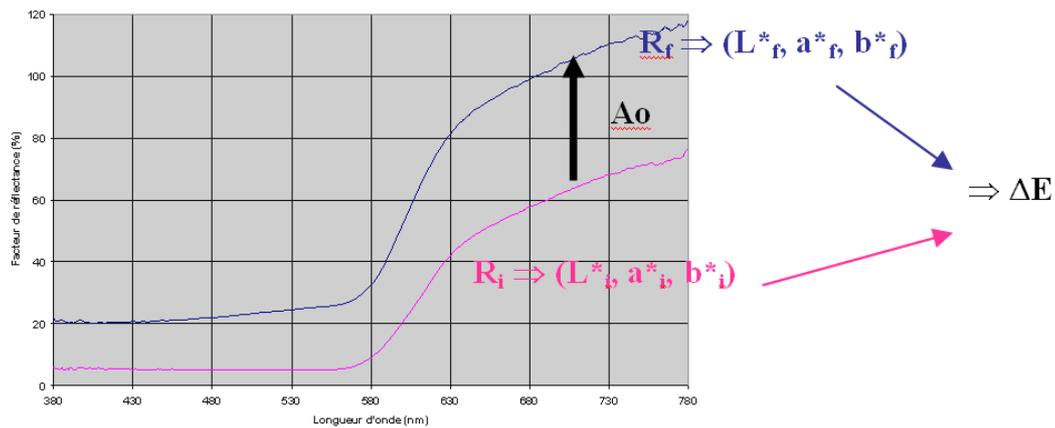


Figure 10: Modification of the reflectance spectrum of a red paint layer after an increase of the surface roughness.

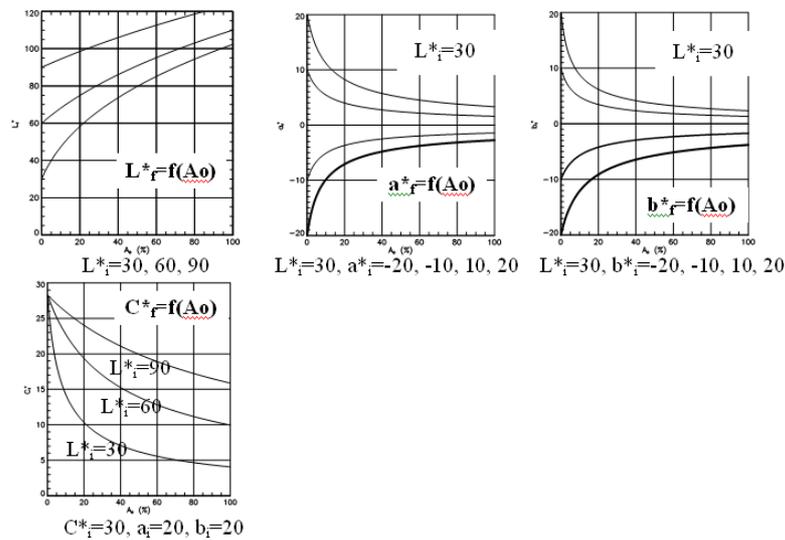


Figure 11: Colorimetric coordinates  $L_f$ ,  $a_f$ ,  $b_f$  and  $C_f$  as a function of the translation  $A_o$  of the diffuse reflectance spectrum, corresponding to an increase of the surface roughness, for different colorimetric coordinates  $L_i$ ,  $a_i$ ,  $b_i$  of the initial surface.

An increase of the surface roughness induces an increase of the lightness  $L$ , a decrease of the absolute values of the chromatic coordinates  $|a|$ ,  $|b|$  and  $|C|$  but does not modify the hue. These variations induce the following colour changes according to  $A_o$  or to the geometrical ratio  $h/l$  (Figure 12). The variations depend once more of the initial colour of the surface.

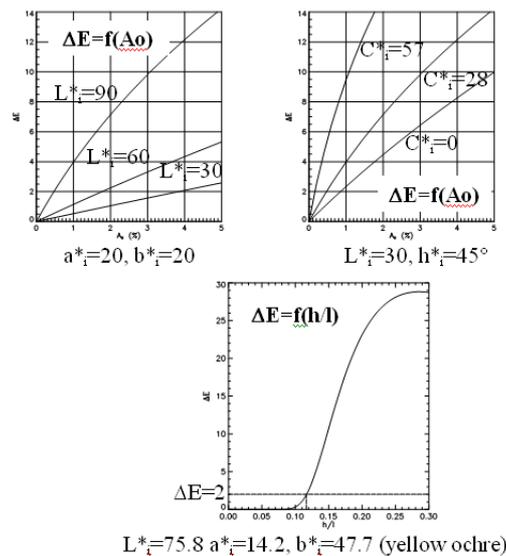


Figure 12: Colour changes according to the increase of the roughness, quantified by the translation of the spectra  $A_0$  or by the geometrical ratio  $h/l$ .

$\Delta E$  is all the more sensitive to the roughness variations as  $L_i$  and  $C_i$  are large. For  $\Delta E < 2$ , it is assumed that the eye does not discern any roughness variation, i.e. for a variation of the ratio  $h/l < 0.12$ , in the case of the yellow ochre paint presented in Figure 12.

### Influence of the varnish on the colour

The function of a varnish can be aesthetic or/and protective. In both cases, it induces a levelling of the pictorial layer (Figure 13). The first effect is an increase of the specular reflected light and of the gloss. The second effect is a decrease of the diffuse reflectance spectrum due to the absorption of the varnish layer. This decrease follows, at the first order, an homothetic transformation with a scale factor  $B < 1$ , such as  $R_{\text{varnish}}(\lambda) = BR_{\text{unvarnish}}(\lambda)$ . The more the varnish absorbs, the more  $B$  is small (Figure 13). The scale factor  $B$  can be analytically related to the thickness and to the absorption coefficient of the varnish [13-14].

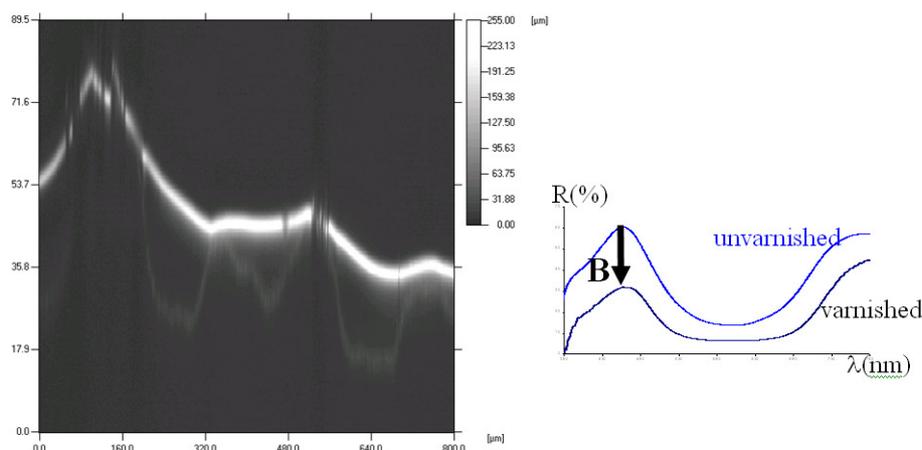


Figure 13: Cross section of a varnished pictorial layer recorded with a confocal microscope and corresponding diffuse reflectance spectra of the varnished and unvarnished surfaces.

Then the lightness, the chroma and the colour change obey to the following variations:

$$L^*_f = B^{1/3}(L^*_i + 16) - 16, \quad (2)$$

$$C^*_f = B^{1/3}C^*_i \quad (3)$$

and

$$\Delta E = (1-B)[(L^*_i + 16)^2 + C^*_i{}^2]^{1/2} \quad (4)$$

depending on the initial colour of the paint layer (Figure 14) [13].

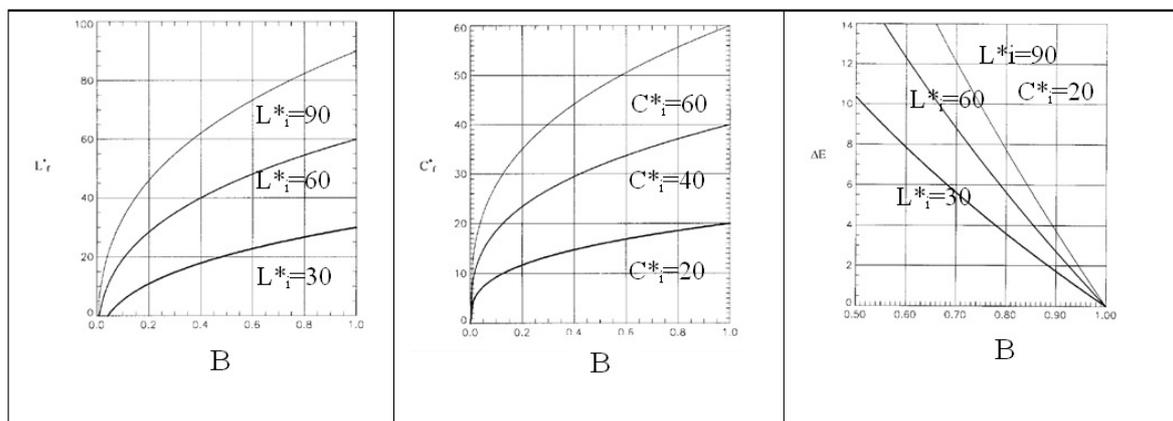


Figure 14: Lightness, chroma and colour change as a function of the scale factor  $B$ . Smaller this scale factor, stronger the absorption of the varnish.

For the same varnish thickness, the larger the initial values of  $L^*_i$ ,  $a^*_i$ ,  $b^*_i$  and  $C^*_i$ , the larger the decrease of  $L^*$ ,  $a^*$ ,  $b^*$ , and  $C^*$ , respectively. It means that the lighter and more saturated the initial paint, the greater the darkening and the desaturation of the final varnished surface. Here also, the hue does change. Moreover, the slopes of all these curves increase as  $B$  decreases. It indicates that the addition of a small quantity of varnish will induce a stronger effect on  $L^*$ ,  $a^*$ ,  $b^*$  and  $C^*$  if the initial surface has previously been covered by a thicker varnish layer.

More precisely, the absorption of a varnish with a thickness  $h$  follows a Beer – Lambert law on the light flux:  $F_{varnish} = F_{unvarnish} \exp(-\alpha h)$ . The study of numerous fresh and aged varnishes has led quantifying the variations of the absorption coefficient  $\alpha$  with the wavelength, according to  $Ln\alpha = A - B\lambda$  with  $A \approx 10$  and  $B \approx 0.02$ ,  $\mu\text{m}^{-1}$  for  $\lambda \leq \lambda_{max}$  with  $450 \text{ nm} < \lambda_{max} < 620 \text{ nm}$  [14]. In particular, this law expresses the yellowing of old natural varnishes. It has been applied to the numerous spectra recorded with a multispectral camera in order to provide a virtual removing of varnishes on old masterpieces. It is a non-destructive tool for finding again the original colours painted by the artist (Figure 15). Unfortunately, in the case of the Joconda, neither the thickness nor the nature of the old varnish had been identified, so different thickness have been tested for this virtual varnish removing [10].

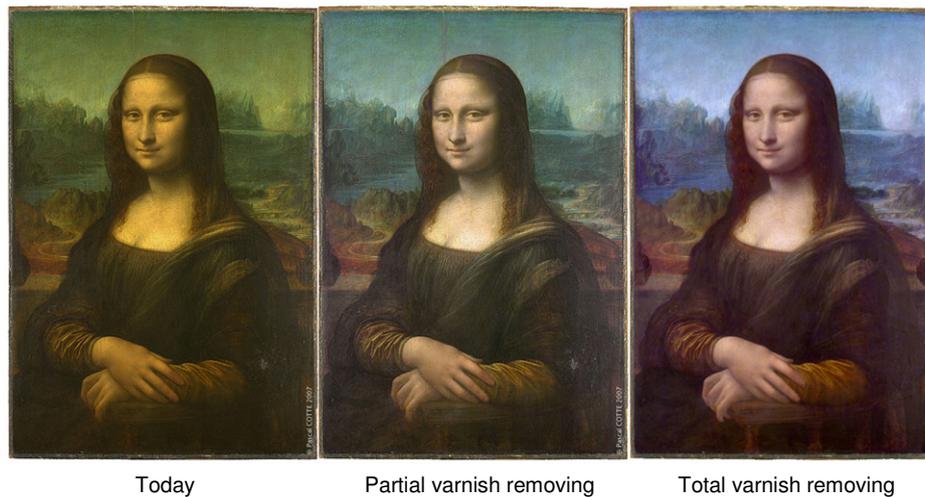


Figure 15: Virtual removing of the varnish of the Joconda by Leonardo da Vinci. Spectra are recorded with the multispectral camera of Lumière Technology. The Beer-Lambert law is then applied on each spectrum and the new trichromatic coordinates are calculated.

## Conclusions

We tried to convince that quantified colours produce a fingerprint of masterpieces that should belong to their status report, as UV-VIS-IR and X-ray photographs. The recent development of multispectral cameras allows recording spectra and calculating colours simultaneously for each pixel ( $\approx 1\mu\text{m}^2$ ) of the whole painting. Nevertheless, until now, the spectra must be recorded with the same instrument if further comparisons are needed for conservation and restoration applications. A digital transformation, based on the radiative transfer equation, has been recently developed to convert a given spectrum into any configuration. This improvement will soon allow remote sensing and comparisons whatever the used spectrophotometer.

The spectrophotometers must be largely prioritised, compared to simple colorimeters. In both cases, the measurements are non destructive recorded with portable instruments and the results are supplied in real time. But the analysis of the spectra is full of information and they can be analysed in real or delayed time. More than a colorimetric status report, the spectral analysis allows the identification of pigments and dyes [15] or pigment mixtures [16], that cannot be directly obtained from colours because metamerism. It also allows the analysis of the colour changes as a modification of the surface state or the presence of a varnish, when colour can only notice the effect. Finally, the association of colour measurements and imaging of stratified layers, developed recently with non invasive optical coherence tomography (OCT) [17] will be an important improvement in the knowledge and the follow-up of such unique and fragile objects.

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