Historic period of fine art painting detection with multispectral data and color coordinates library

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Abstract
A characterization of the history of materials are studied to compare and sort spectral imaging of fine art painting. The comparison between the various palettes contains significant information regarding the evolution of shades and colors throughout this history. Results allow a non destructive methods to detect retouching of the paintings or sort them out according to their color range. A pigment database is used to convert frequency information into colorimetric coordinates representing historic periods and color subgroups. The amount of points are multiplied by simulating or measuring the pigment’s change (mixture, varnish, light or surface conditions).

Introduction
The multispectral acquisition technique enables us to obtain new data to study fine art paintings. We recreate the spectral curves of every single pixel of a picture based on the system’s various physical or algorithmic parameters. These curves enable us to recognize the signature of certain colored materials which make up the work’s paint layer. Artists’ palettes have varied throughout the various periods of art history – limited to a mere handful of pigments in prehistory, they have now become overabundant. The reflectance curves of the pigments used during a specific period may be converted into colorimetric coordinates in order to create a set of points to represent the range of shades available to painters. The joint studies of the various data stemming from the multispectral acquisition of a painting and a pigment database may enable us to date the work back to a specific period based on the use of the materials.

Historic
Back in the Paleolithic period, palettes only comprised black, red and sometimes yellow. Black was of organic (charcoal or bone char) or mineral origin (manganese oxide), and red and yellow were derived from iron oxides. There is plenty of yellow iron oxide in the ground and red – which is less common – may be produced by heating an iron hydroxide over 250°C. This return to original pictorial expressions takes us back to the beginning of the use of pigments. Now, let’s briefly study the specific enhancement of the range of paint dedicated to art – commonly called a palette. At the beginning, palettes comprised natural pigments of mineral, vegetable or animal origin. Earth, ocher, minerals, cochineals and plants illustrate the variety of materials which made it possible to achieve colored substances. Among others, crimson stems from sea mollusks, carmine from cochineals and sepia from cuttlefish. Plants enabled the creation of dyer’s weed and Turkey red lacquer and indigo. There is a great deal of natural materials available, but in fact few hues given the range of colors offered by nature. Some colors are more present than others – e.g. there is no blue in cave art, given that nature offers few blue
dyes or pigments and that the lighting conditions (torches) did not make it possible to enhance this color. The same remark can apply to green, which was also not very common. Egypt was dynamic in producing pigments. In 2500 BC, synthetic pigments were created through complex recipes. Egyptian blue was used until the 9th century. In the Middle Ages, painters used mineral pigments and lacquered pigments achieved with coloring dyes. The palette range was extended with the synthesis of new colors such as vermilion, which is made of mercury and sulfur. Maritime explorations and trade routes enhanced the palette and made it possible to exchange materials and know-how. The textile industry and fire were the driving force behind research of new substances. Until the 18th century, the amount of pigments did not change much. From the 17th and 18th century onwards, science and new technologies significantly improved the palette. Chromium and cobalt were discovered, and alchemy was replaced by chemistry. Chemists such as Michel Eugène Chevreul started searching for new dyes and the first quarter of the 19th century was marked by the synthesis of both old and new mineral pigments such as chromium yellow. With his synthetic ultramarine, Guimet developed the chemical industry in France in the region around Lyon. The real turning point as regards the outburst of dyes was the birth of chemical synthesis. In 1857, the first synthetic dye factory was built and produced mauveine – a derivative of aniline, discovered by a young chemist called William Henry Perkin. Robiquet and Colin discovered alizarin – the main dye used to create Turkey red –, which was then synthesized by C. Graebe and C. Liebermann in 1869. The birth of organic chemistry and the understanding of carbonaceous chains made it possible to create new substances. New types of reactions were discovered, such as diazotization in 1858 by Peter Griss. The synthesis of coloring dyes put an end to the culture of plants used to manufacture dyeing extracts and to the production of cochineals. Entire regions underwent major changes. Fine art paintings rapidly took advantage of the discoveries made in the textile sector. During the 20th century, toxic pigments were forbidden and replaced by new substances. From 1870 onwards, painters used new bright colors, which turned out to be rather transient. The famous bright pink geranium lacquer used by Van Gogh turned into a shade of pale blue. In order to offset its imperfections, the chemical industry came up with much more stable products, such as azoic colors (shades of yellow – end of the 19th century), phthalo cyanine colors (shades of blue and green – around 1930), quinacridone colors (shades of red and magenta – around 1950), and more recently DPP (shades of red and orange). Before the 18th century, painters only had about forty pigments and hardly used half of them. We were still in the ‘all natural’ era and gradually moved to the synthetic era from the 19th century onwards. At that time, people showed keen interest for industrially-produced paint.

Method

We have at our disposal a pigment database which comes from the Perego collection, containing 250 pure pigments. Each pigment is then sorted into various dilutions on a black and white background and also mixed with titanium white.

Figure 1: Measure the of Perego collection with spectroradiometer.
The database comprises a reflectance curve for each element (380-780nm), the origin of the pigment, relevant color index, composition, name, date of use or production and practical information concerning measurement (instrument and geometry). We have put each pigment in chronological order and sorted them out according to the periods which represent palette enhancement: ancient times, from Middle Ages to the 17th century, 18th century to the 19th century and 20th century. A second classification based on the color index gathers the pigments in color groups: white, orange, blue, brown, purple, yellow, red, green, black and earth. Some pigments are redundant in the spectral library, we have classified 152 irredundant pigments (CVP or various origins). In ascending amount of pigments, we have yellow, red and blue – which are called primary colors because they can’t be obtained by mixing other colors –, followed by secondary colors – orange, green and purple, which are obtained by mixing two primary colors.

**Color coordinates library results**

We previously described the development of the painter’s palette, the evolution of which is featured in our spectral library, the turning point of which is the 18th century. The two last centuries are dynamic and account for 56% of the total material available from ancient times to the 18th century. Even better, with groups of colors such as shades of purple or orange, which respectively combine 87.5% and 83.3% (see Figure 2). The discovery of new materials in several cases (white, green and yellow) is more regularly spread out over the various periods. First of all, we shall compare the pigments of a specific color group throughout the various periods and highlight the different colorimetric features. Based on the representation of pure pigments in two color spaces, we shall suggest criteria such as saturation in order to characterize a specific period. We shall consider extending possible hues based on the Kubelka-Munk turbid-media theory, by simulating a mixture with a shade of white and that of several pigments among each other.

With the spectral library, it is possible to convert frequency information into colorimetric coordinates representing historic periods and color subgroups. Secondly, the amount of points can be multiplied by simulating or measuring the pigment mixture or overlay, dilution, presence of varnish, exposure to light or different surface states. The data becomes sufficient enough to create a group and define a limit between the various palettes. We can thus compare and observe the spaces which are used or unused by fine art materials throughout the various periods. Firstly, we have represented in a CIELAB 1976 a*b* projection (see Figure 3) the total pure pigments of the Perego collection and distinguished the various
relevant periods. We can note that there is a different
distribution with hue and saturation limitations for the
most ancient periods. There are many red-shaded
pigments, which feature major saturation
characteristics throughout all the different periods.
The period representing ancient times features a
scatter of points crossing the diagram from cyan blue
to oranguy yellow, including desaturated points. The
following period features higher color saturation,
spread out over a larger amount of hues. Then,
saturation increases in ratio to the chronology of the
history of pigments. The more recent the materials are,
the more significant saturation is (see Table 1). The
18th century period did not bring about new colors,
but thanks to chemistry old pigments were replaced
and their relevant manufacturing and production were
facilitated. The last two periods illustrate the outburst
of pigments with high levels of saturation, e.g. green
with phthalocyanines. Pure purple, which had not
been represented much so far, was correctly defined.

<table>
<thead>
<tr>
<th>Chroma (mean)</th>
<th>Chroma (max)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ancient Times</td>
<td>38.77 95.11</td>
</tr>
<tr>
<td>Middles ages - 17th</td>
<td>45.13 107.7</td>
</tr>
<tr>
<td>18th</td>
<td>46.55 109.52</td>
</tr>
<tr>
<td>19th</td>
<td>66.49 119.38</td>
</tr>
<tr>
<td>20th</td>
<td>66.13 112.13</td>
</tr>
</tbody>
</table>

Table 1: Chroma variations throughout the various periods.

<table>
<thead>
<tr>
<th>Surface (%)</th>
<th>Volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ancient Times</td>
<td>11.66 4.81</td>
</tr>
<tr>
<td>Middles ages - 17th</td>
<td>20.66 7.06</td>
</tr>
<tr>
<td>18th</td>
<td>17   6.9</td>
</tr>
<tr>
<td>19th</td>
<td>25.22 10.7</td>
</tr>
<tr>
<td>20th</td>
<td>32.16 10.68</td>
</tr>
</tbody>
</table>

Table 2: Surface and volume variations throughout the various
periods. Percentage of asimplified rectangular parallelepipded
volume of CIELAB 1976.

In order to achieve a better understanding of available
hues and the evolution of saturations, we have also
used the CIELCh colorimetric coordinates. Ancient
times were full of yellow pigments, the hue angle of
which was between 90° and 60° (orpiment, Naples
yellow, massicot yellow), orange (litharge or orange
lead) and red saturated with an angle of approximately
30° (red bole, cinnabar/vermilion, minium/red lead);
on the other hand, blue, green and cyan pigments are
not very saturated – except for Egyptian blue made by
a manufacturer of fine arts materials, which features
totally different characteristics to the coordinates of
the same pigment recreated by the restorer François
Perego. Shades of blue appeared between the Middle
Ages and the 17th century – smalt, lapis lazuli – with
a high level of saturation. New green hues between
150° and 210° also appeared (cobalt green, copper resinate) along with the verdigris pigment featuring a higher level of saturation than the pigments of the same hue. Yellow hues inherited reinforced saturation with Indian yellow, lead-tin yellow and gamboge. From the 18th century onwards, yellowy green pigments filled in the 150°-90° hue angle, which had so far few pure pigments. Numerous orangey yellow and magenta pigments appeared during the 19th century, respectively in the 80°-30° and 330°-270° angles. The latter, which link up the pure purple, are classified along with red (ultramarine pink), purple (cobalt violet) or blue pigments (Cerulean blue). The last period is similar to the latter, with enhanced access to materials for red hues (quinacridone colors and DPP), deep blue hues around the 270° angle (manganese blue, phthalocyanine blue) and green hues with phthalocyanine green, thus enabling an unprecedented level of saturation. Based on this comparison, the hues and levels of saturation vary according to the different periods. As regards hues, it is essential to chiefly study primary colors, which can’t be obtained by mixing colors. We shall take this fact into account later on. The saturation value makes it possible to characterize a period, given that its highest value is achieved in the presence of a pure pigment. We can thus compare primary color hues and the entire saturations based on the data gathered further to measurements or the multispectral acquisition of a work of art. Overall, the periods up to the 18th century and the two last periods may be distinguished by specific criteria. Then, blue and green hues shall be the next ones studied in order to identify the most ancient periods.

**Multispectral Results**

The last stage consists in checking the results obtained using the color coordinates library on the data of multispectral imagery. We have used a 13-channel high definition multispectral camera belonging to the Lumière Technology 2 Company (see Figure 4). After validation of modeling of the estimated spectra conversion, we display the palette of the digitized work in the form of a volume in a CIELAB 1976 space or a diagram in a CIEYxy 1931 space.

We have analysed ten paintings from ancient times to 20th century. Among then we have selected two most significative results in terms color properties (see figure 5). The intersection (logic operator AND) between painting gamut and period palette allows to select the most close volume. For each case, we have a very good agreement between the calculation and real datation of the painting (see Table 3).

This is a first approach. The artist painters could access to a specific palette of their time. However, all of them, did not use the complete palette. The method is more robust to detect retouching and is potentially usable for forgery detection. With knowledge of characteristics of the photographic dyes, we put in evidence a realistic painting reproduction constituted with photos covered with a hand varnish layer. The near infrared technic available in the same system allows an additional check.
Figure 5: Comparison of clouds, painting 2: 20\textsuperscript{th} century (points) and different periods (conex hull method). Last line, simplified rectangular parallelepiped volume of CIELAB 1976.

<table>
<thead>
<tr>
<th>Period</th>
<th>Painting 1</th>
<th>Painting 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ancient Times</td>
<td>86.84</td>
<td>66.96</td>
</tr>
<tr>
<td>Middles ages - 17th</td>
<td>81.58</td>
<td>71.37</td>
</tr>
<tr>
<td>18th</td>
<td>76.32</td>
<td>68.28</td>
</tr>
<tr>
<td>19th</td>
<td>71.05</td>
<td>79.74</td>
</tr>
<tr>
<td>20th</td>
<td>71.05</td>
<td>85.9</td>
</tr>
</tbody>
</table>

Table 3: Intersection between painting gamuts (1: 15\textsuperscript{th} and 2: 20\textsuperscript{th}) and various periods. Results are a percentage of intersection with a simplified rectangular parallelepiped volume of CIELAB 1976.

Conclusion

The comparison between the various palettes contains significant information regarding the evolution of shades and colors throughout the history of materials, but comparing them with the color coordinates data of works enables other investigation channels. We shall begin with non-destructive methods to detect retouching of the paintings or sort them out according to their color range. We shall study in next publication the most typical spectral signatures of each of them by comparing each reflectance curve with the entire subgroup studied and – if need be – a second similar subgroup in borderline cases where the reflectance curve is halfway between two colour groups. The white hues are one of the most convincing examples as regards identification of a period. Lead white, zinc white, zinc sulfide, lithopone, chalk and titanium white are the main shades of white used. Each period features a characteristic signature of its white pigment. We shall extend the results to the near infrared by adding information regarding the sample’s capacity to reflect or absorb this type of wavelength. Research in near infrared with solely binary data (presence or lack of absorption) has enabled us to make out other features or to separate pigments with curves which may be similar in that which is visible, e.g.: Prussian blue (absorbent) versus phthalocyanine blue (reflective). Using them requires additional experience (visual inspection, spectroscopy, chemical analysis, etc.) as well as the knowledge of a restorer to obtain objective evidence, given that paint layers are extremely complex (layer stratigraphy, various techniques, discolorations, etc.).

Acknowledgements

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References

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