Comparing spectrophotometry and photography with hyperspectral imaging for pigments' characterization on paintings

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Abstract

Pigments characterization on paintings is usually made with X-ray fluorescence, traditional false color photography and optical microscopy. The use of optical techniques based on reflectance spectra, like reflectance spectrophotometry or hyperspectral imaging, is limited today to some case studies. We would like to improve these optical techniques for pigment characterization, because they are non-invasive and can give a lot of information. After comparing the ways to calibrate to reflectance spectrophotometry and hyperspectral imaging, we develop the two techniques for the specific study of pigments. We develop a Matlab program to analyze (identify and quantify) reflectance spectra given by spectrophotometry, and a new methodology based on false color composites to use hyperspectral images in a simple way. The choice of the spectral bands to identify pigments takes its roots in the maximization of spectral differences, and leads to the generation of 3 false color composites - called variable composites FC1, FC2 and FC3 - to distinguish the pigments of the four categories (blue, red, yellow and green). The results of spectrophotometry and variable composites on a painting of the 17th century by French painter Eustache Le Sueur are encouraging and consistent with other techniques' results. Our results should promote the use of spectrophotometry and hyperspectral imaging for pigment characterization in the future.

Keywords: hyperspectral imaging, spectrophotometry, pigment, false-color composites, technical comparison

Introduction

The colors are the first things we see when we look at a painting. Describing these colors is a field by itself. Optical techniques like spectrophotometry and hyperspectral imaging are a way to objectively measure and characterize the colors spectra and their source, that is, pigments. Initially developed for military goals, the application of hyperspectral imaging to cultural heritage objects has been developing fast over the last ten years. As this technique takes its roots in optical spectrometry (or spectrophotometry), it is interesting to compare the spectra obtained by spectrophotometry and hyperspectral imaging. We will first compare the generation of reflectance spectra with both techniques and then compare the results on calibrated references. We then discuss the application of spectrophotometry and hyperspectral imaging to pigments characterization, as well as a new and simple way of processing hyperspectral imaging data. We will compare the results of the two techniques on a painting of the 17^{th} century, which has also been analyzed by other traditional techniques for pigments' characterization: X-ray fluorescence and optical microscopy.

The generation of reflectance spectra by spectrophotometry and hyperspectral imaging

Reflectance spectra are calculated as a quantity of light reflected by an object scaled with a white reference (calibrated to 100% reflectance) and a black reference (0% reflectance), as a function of wavelength. They depend on the chosen standard illuminant and standard observer. We usually choose illuminant D65 and the 2° standard observer of the CIE.

Spectrophotometry

The C2RMF is mainly using a spectrophotometer without contact that was developed for artworks in particular [1]. The geometry is not standard as the light is emitted with the same angle as the collecting sensor, 26°. This angle was selected in order to avoid the specular light and to be as close as possible from the standard configuration for color measurements of 45/0°. The spectrophotometer we developed is sold by the French company STIL and is called Ruby. The wavelength range is 380-780 nm, with a 1 nm precision. The measurement distance is 7.5 cm, which is a secure distance that avoids touching the artworks. The spectrophotometer is shown on figure 1.

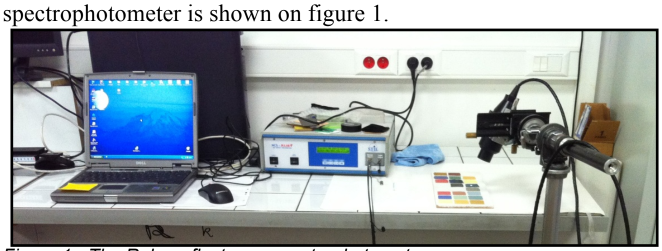


Figure 1 - The Ruby reflectance spectrophotometer

This machine works with a dedicated piece of software, Ruby Manager, which takes into account a measurement of a white Spectralon® and of a black reference, as well as illuminants and standard observers, to calculate the reflectance spectra of the studied objects. The spot size on the object can be modulated: 1, 3, 6, or 10 mm diameter. At each wavelength λ, the software uses the following equation to calculate the reflectance percentage:

Reflectance %= 100 ∗ (Sample spectrum − Dark reference spectrum) / (White reference spectrum − Dark reference spectrum)

Hyperspectral imaging

At C2RMF, we have a visible and near infrared Hyspex hyperspectral camera, ranging from 400 to 1000nm, in 80 to 160 spectral bands. The system is based on NEO's HySpex VNIR-1600 combined with a large (100cm*150cm) horizontal and vertical scanning stage, a fiber optic light source and a high resolution line scan camera yielding a scene pixel size of approximately 12µm at 30cm object distance.

Like in spectrophotometry, the raw images need to be calibrated to reflectance. We also need to suppress the light distribution influence. The latter step is called flat-fielding the image. The object is illuminated by white light, on a horizontal line of about 10 centimeters. The light comes from optical fibers coming through optical lenses that spread it on a horizontal line. As the object stays in place, the camera moves vertically to scan the whole surface of the object (figure 2 and 3). A grading spreads the light vertically on the visible and near infrared wavelengths, and the acquisition software re-builds the image in order to have, for each pixel, the corresponding spectrum (figure 4). Dark is automatically subtracted from the image. To flat-field the image as well as to calibrate it to reflectance, we use a Spectralon®, large enough to cover the whole horizontal size of the image. Then we take the mean of the lines of the white Spectralon®, and resize it to the size of our raw image. Finally, we divide the raw image cube, band after band, to the resized image of the white Spectralon®. As a result, we take into account illumination variability as well as calibrating the values between 0 and 1. The image cube is then ready for use, and a spectrum can be associated to each pixel.

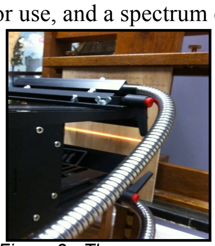


Figure 2 - The illlumination system

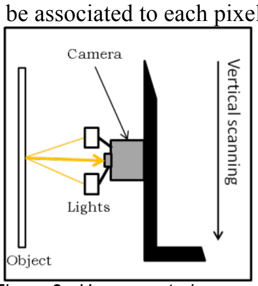


Figure 3 - Hyperspectral imaging scanning technology

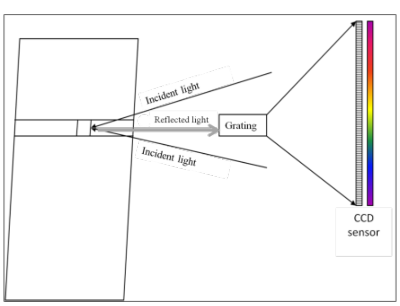


Figure 4 - Dispersion of the light for each pixel of the illuminated line of measurement

The comparison of the two techniques on calibrated references

We compared the results of hyperspectral imaging with traditional spectrophotometry by measuring reference targets (calibrated ceramics). The measurements were made by our Ruby spectrophotometer, with a spot size diameter of 6mm, and with our hyperspectral camera on low resolution (80 spectral bands). The spectra were acquired for different colors of ceramics, but we show here two representative types of ceramics: matte red and matte green (figures 5 and 6).

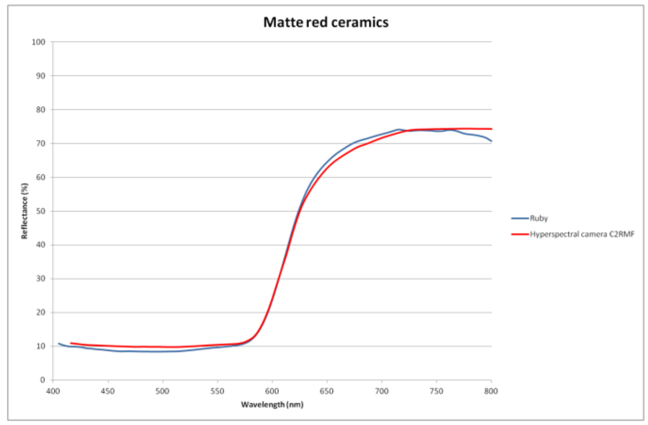


Figure 5 - Red ceramics spectra (red line is hyperspectral camera, blue spectrophotometer)

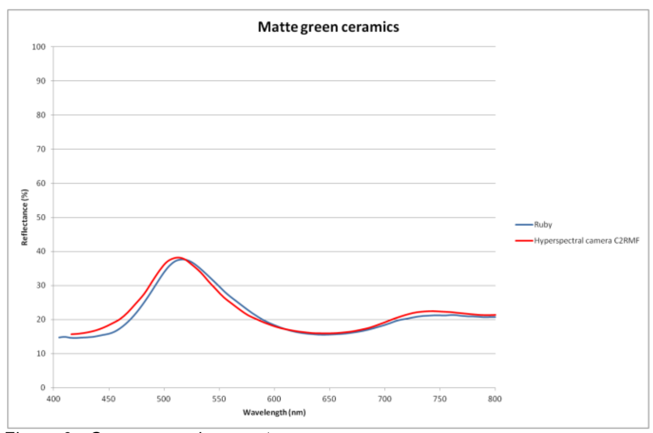


Figure 6 - Green ceramics spectra

The results are quite consistent. The curves do not differ more than from 3 or 4 percents reflectance. We can conclude that spectra calculated by hyperspectral imaging are as reliable as traditional spectrophotometry.

Characterizing pigments with spectrophotometry and hyperspectral imaging

Since the beginning of the 20th century, diverse theories have tried to establish a model to understand and quantify light behavior in a pictorial layer. One of the simplest theories is the Kubelka-Munk theory, developed in 1931 [2]. It is easy to apply, especially on opaque pigment layers, and for pigments mixtures (Kubelka-

Munk equations combined with Duncan equation), and is based on reflectance spectra. We can use this model with spectrophotometry to characterize pigments (pure or in a mixture) and we will explain it in a first step. As for hyperspectral imaging, it is typically used for pigment characterization by statistical tools, like principal components analysis or comparison to databases' spectra. We discuss the two techniques and their application first on pigment samples and then on paintings.

The pigment database

In order to have representative painting samples to test our optical pigment detection method, we made around a hundred pigment samples, pure or mixed, on wood planks prepared with two coats of a white acrylic paint. We chose in particular a system of a dozen different pigments of all colors (blues, yellows, greens, reds...) to test the two techniques. They correspond to the pre-18th century, when the pigments were limited and the mixtures quite simple (2 to 3 pigments). The chosen pigments are the following: azurie, smalt, indigo, lapis lazuli, lead-tin yellow, yellow ochre, Naples yellow, copper green, green earth, vermillion and red ochre as well as raw umber and lead white. We made pure pigment samples, pigment+white samples and pigment+pigment samples, as it was made in the 17th century. The pigments (in powder, with maximum particles size corresponding to art history) were first weighted, then mixed with oil and grinded with it on a glass plate. When the texture was correct, we applied it on wood planks in opaque layers. This way of making paint is similar to the one the painters of this period relied on.

Spectrophotometry

The Kubelka-Munk theory applied to opaque layers for pigment characterization has already proven to give good results for pigments identification [3,4] on paintings. We develop a Matlab program, which analyzes the reflectance spectra, and compares it to a pigment database. We built this database with the pigments samples, pure and mixed with white, to simulate the spectra of all the mixtures possible (2 pigments) with Kubelka-Munk and Duncan equations [5]. The equations we use are the following (for a mixture M of a pigment 1 mixed with pigment 2, in proportion x for pigment 1; for all the wavelength λ, R being the reflectance (between 0 and 1), K being the absorption coefficient and S the diffusion coefficient of the pigments) :

$$\left(\frac{K}{S}\right)_{1,2}(\lambda) = \frac{(1-R_{1,2})^2}{2R_{1,2}}(\lambda) \text{ (Kubelka Munk Equation for opaque layers)}$$

$$\left(\frac{K}{S}\right)_{M}(\lambda) = \frac{xK_1+(1-x)K_2}{xS_1+(1-x)S_2}(\lambda) = \frac{(1-R_M)^2}{2R_M}(\lambda) \quad \text{(Duncan Equation for mixtures)}$$

A Matlab program we made compares the measured reflectance curve to the database by maximizing the correlation coefficient of the reflectance curve itself with the database, and of the derivative of the reflectance curve with the derivative of the reflectance curves of the database. Then it proposes 3 choices for each method (reflectance or derivative) and the user can choose if the choice is correct by seeing the graphics were the curves are drawn, to detect if the shapes are the same or not. The results are quite good with our pigment samples. We tested the program on 37 pigment-pigment samples and 26 pigment-white samples, for identification and quantification. We consider that identification is correct if at least one of the three choices proposed by the program corresponds to reality, and for quantification, we authorize a 10 percent difference from the real percentage.

For pigment+white mixtures, the derivative correlation gives very good results (identification is correct in 92% of the cases, and quantification in 73% of the cases), and the spectra correlation is reliable as well (70% correct identification and only 46% correct quantification). As for pigment+pigment mixtures, the two ways of identification give approximately the same results, with the correct detection of the two pigments in 50% of the cases, and just one over two in the other 50% cases. Quantification can be trusted in 50% of the cases too. The errors appear in most cases when pigments spectra are very close, in chemical composition especially (azurite, which is a copper blue, can be confounded with copper green for example, or lead-tin yellow with lead white).

The critical interpretation of the results is also very important: seeing a peak missing or a very different shape of the curve on the graphics can be of good help to identify the potential errors of the program, as well as knowledge about the particular artist, the period... which can eliminate at first sight some pigments of the database. For example, if we know a painting dates from the 16th century specifically, the user of the program can eliminate from the propositions of the program all the pigments, which appeared after the 17th century. And if, graphically, the spectra of the pigments are too different from the measured one, the user can decide that the choice of the program is not right. The program can be modified and improved in the future by enlarging the database to additional pigments and by linking some types of pigments (or some mixtures) to the period of time or the geographical place where the painting was made. Spectrophotometry, coupled with the Matlab interface, can be a precious source of information to characterize pigments non-invasively.

Hyperspectral imaging

Spectral imaging techniques have made significant progress in recent years and are now able to characterize the pigments on paintings [6-9]. Traditionally, complex statistical tools are used: Principal Components Analysis (PCA) or Minimum Noise Fraction (MNF) are usually carried out, to separate the different categories of materials on the paintings. These tools can be used by the dedicated software ENVI, specialized in the processing of big data cubes. ENVI also allows the use of a tool named Spectral Angle Mapper (SAM), which compares the spectrum of each pixel to a known spectra database in order to find, with a specific tolerance, the closest matches. If we have an image in N dimensions (N being the number of spectral bands of our camera), SAM measures the distance between each pixel spectrum (which can be represented by a point in an N-dimension space) and the points of the spectra of the database. The points which are inside a cone (in N dimensions) of a chosen solid angle (tolerance) are considered close to the database pigments, the others are excluded; this leads to the formation of a category of pixels linked to each pigment of the database. The results in general are quite good, but the choice of tolerance angles for different pigments can be tricky.The use of PCA or MNF depends a lot on the materials we need to distinguish.

A new way to process hyperspectral data to characterize pigments: variable false color composites

The need of a specific piece of software like ENVI (which can be expensive) and also of powerful computers to process the big amounts of data can be challenging when using this powerful imaging tool for pigment characterization. As a result, we decided to develop a new methodology to process hyperspectral imaging data for pigment characterization in a simple way. We base our work on the comparison with a pigment database and the generation of variable false color composites with the numerous bands proposed by spectral imaging. Our approach is based on traditional false color photography, which allows to separate materials easily and to visually make a cartography of the pigments on the painting. False color photography is powerful but, as the wavelength range of absorption of each color channel R, G, B, IR in photography is quite large, this method lacks of precision and does not allow to identify all the pigments.

Infrared false color (IRFC) photography

False color photography is commonly used in conservation labs and at C2RMF to characterize and map pigments on paintings [10-13]. We first take a photography of the reflected light in the near infrared range (800-1000nm). This black and white image is very difficult to interpret so we developed the false color representation. Figure 7 describes the principles of IRFC photography well. These lie in suppressing the blue channel and shifting the green and red channel of a color image, and then adding an IR channel. It is very useful to map the materials (because if some zones of the painting show the same color, they might be made with the same pigment), as well as to distinguish between some pigments of a same category (red, green, blue or yellow). It allows us for example to distinguish between azurite and the three other blues of our database (smalt, indigo, and lapis) but cannot separate the aforementioned (all of them appearing the same pink color, whereas azurite appears purple). Some greens can be separated, but the method does not give much information on reds and yellows.

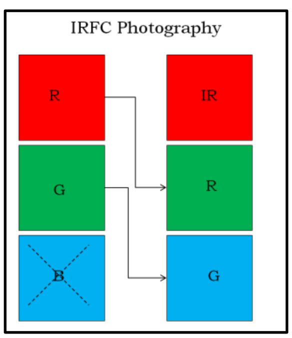


Figure 7 - Principle of IRFC photography

Our new use of hyperspectral images, which relies on the creation of variable false color composites, takes its roots in IRFC photography. As spectral imaging generates (with our camera) at least 80 spectral images of the painting, we can combine them together to generate more than 500,000 different false color composites, with narrow spectral information.

The spectra analysis

We have our pure pigments samples at our disposal. The goal here is to analyze the spectral shapes of each pigment of a category (blue pigments, yellows, greens, reds) to find the most adapted spectral band in order to differentiate the pigments. We are especially looking at wavelengths where the spectra of the pigments we want to distinguish are well separated in reflectance intensity, and we also look for the changes of order in the values of the curves to maximize the false color differences.

For example, to distinguish two blue pigments of our database, which are azurite and lapis, we can choose the following bands (figure 8): around 460nm, around 530nm and around 815nm. We choose theses bands because the spectra cross over twice in the 400-1000nm range, so the order of the curves is twisted twice. The consequence on the image is that the grey values contrast representing each pigment will be maximal. We can then choose one wavelength in each of the three spectral zones, at places where the difference between the two is maximal. Figure 9 shows the two corresponding colors of the generated composite.

The colors of the two pigments are well distinct (dark blue for azurite and purple for lapis) so they can be separated easily. This is an example of the way we choose the spectral images composing our false color composite. The spectral bands were here chosen by hand but an algorithm could be done to maximize the false color efficiency.

The three variable composites

We study each category (blues, reds, yellows and green) separately. The first goal was to find one band combination that would separate all the pigments (in all the categories). But, because of the diversity of the spectral shapes, some colors recognition had low accuracy with only one false color image. We made tests to find the lowest number of false color necessary to obtain accuracy in pigment recognition. We found that generating 3 false color images allow us to distinguish most of the pigments of our database. The chosen band were :

- Composite FC1 (false-color #1) - bands #4,31,128 - can distinguish greens and some blues.
- Composite FC2 – bands #20,89,158 – can distinguish some blues and yellows.
- Composite FC3 – bands #50,60,128 – can distinguish reds.

For example, here is the result of FC1 and FC2 for the four types of blue pigments. In FC1, we see that azurite looks blue-green and lapis looks purple, whereas we cannot distinguish smalt from indigo; in FC2, azurite looks purple, lapis looks grey, smalt looks yellow-green and indigo looks orange so we can distinguish between the 4 pigments with FC1 and FC2 (figure 10). It is an improvement of IRFC photography because the latter could only distinguish azurite from the three others, and our methodology can easily separate the four pigments.

To generate the variable composites, we just have to save the spectral images in TIFF format, and then combine them on Adobe Photoshop to generate the RGB file. The explanations on the other categories of pigments can be found in [14].

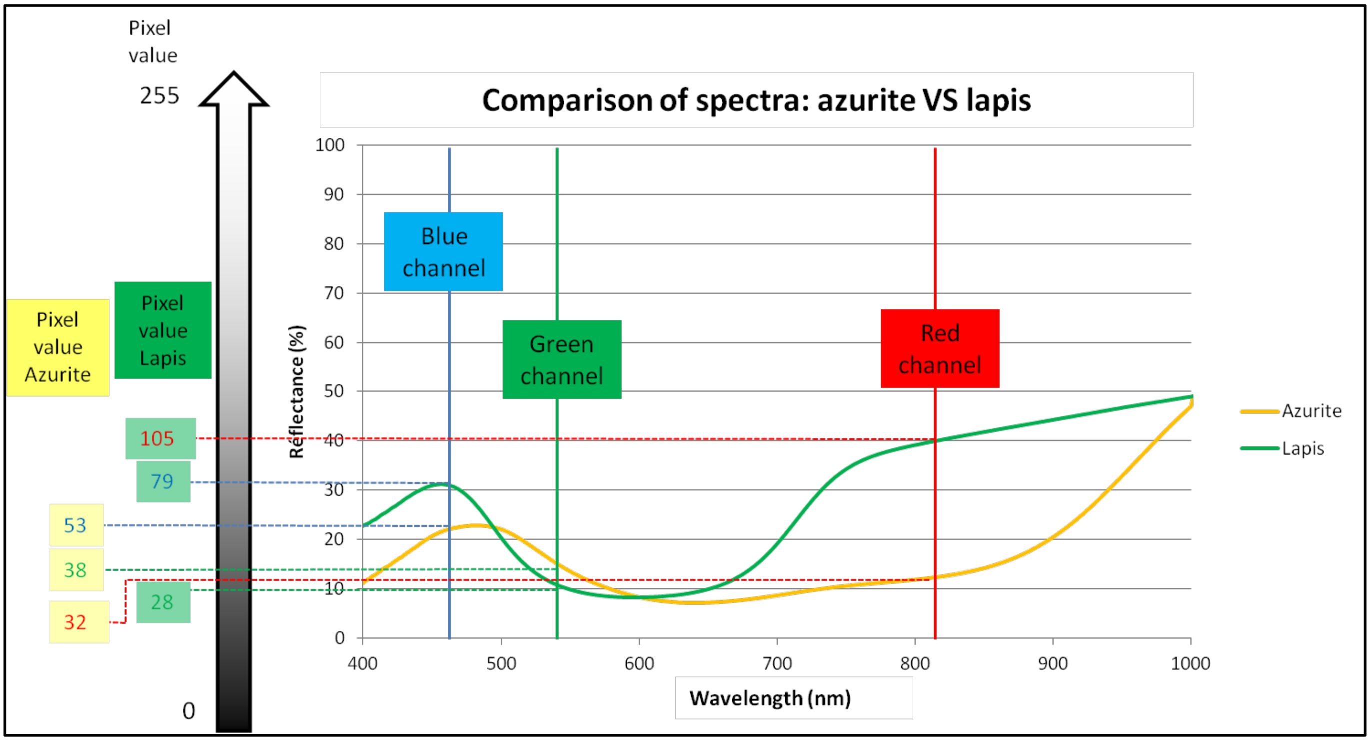


Figure 8 - Choice of spectral bands to distinguish azurite from lapis

Pigment	Azurite	Lapis
Pixels values (8 bit) (R,G,B)	(32,38,53)	(105,28,79)
Corresponding false color		

Figure 9 - Resulting false-color composite colors

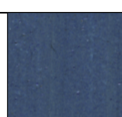
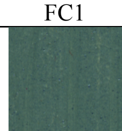
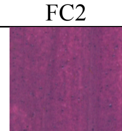
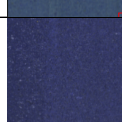
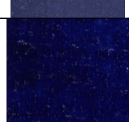
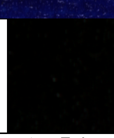
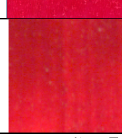
Pigment	Natural color	Composite FC1	Composite FC2
Azurite (+ white)			
Lapis (+ white)			
Smalt			
Indigo			

Figure 10 - Blue pigments - False-color composites FC1, FC2

Analyzing the blues a 17th century painting with both techniques to characterize pigments

We analyzed a painting of the 17th century French painter Eustache Le Sueur, called *Venus presents Love to Jupiter* (figure 11), painted around 1646 as a draft for the decoration of a famous private mansion in Paris, the Hotel Lambert.

Figure 11 - Venus presents Love to Jupiter, Eustache Le Sueur, 1646 © C2RMF, Laurence Clivet

Let's look to the blues of the paintings: the blue of Venus drapery and the one of the sky. We generate the FC1 and FC2 composites and looks to the colors (figure 12). The FC1/FC2 "sequence" of colors looks like lapis (purple on FC1 and blue-grey on FC2). We can then identify the blue pigment used by the artist as lapis lazuli. We also did some spectrophotometry points and put the spectra in our Matlab program. The results were, for Venus' drapery, a mixture of lapis with lead white (with around 20% lapis), which is consistent with our variable false color composite diagnosis.

We then confronted the results of the optical techniques to the traditional ways of pigment characterization: IRFC photography, optical microscopy and X-ray fluorescence. On IRFC photography, the color of the blue zones looks pink, so the "diagnosis" is the following: smalt, indigo or lapis. X-ray fluorescence mainly finds lead, iron, calcium and potassium (no cobalt which could lead to smalt), and by optical microscopy big blue grains, characteristically of lapis were observed. The blue pigment used by the painter is for good lapis. The results are very coherent and can be trusted for the blue pigments characterization on this painting. We also study the other pigments were and confronted them to traditional analyses. Our methodology correctly analyzes the reds and yellows. Results are consistent with other pigment analyses. The only limitation is the characterization of the greens, which can be misidentified by our hyperspectral methodology but could be improved in the future, maybe by adding infrared spectral bands to our false color composites.

Regular colors	FC1	FC2

Figure 12 - Blue zones of the painting, FC1 and FC2

Conclusion

Optical techniques can be very powerful to characterize pigments on paintings. After calibrating and transforming raw data to reflectance, the pigments can be identified (and sometimes quantified) with spectrophotometry by a Matlab program, with good results for pure pigments or simple mixtures (like the ones used on pre-18th century paintings). As in the case of hyperspectral imaging, we develop a new methodology to process the data in a simple way in order to characterize the pigments, by generating false color composites with hyperspectral images. The color bands are chosen in order to maximize the differences between the different pigments of a category (blue, red, yellow or green). The application of this new methodology to a painting of the 17th century yields reliable results, as we can see for the blue pigments of Venus presents Love to Jupiter by Eustache Le Sueur. The other colors too are well characterized by this methodology [14]. The only category of pigments that can present errors in the characterization by variable composites is the green pigments category. This is understandable because greens are more complex than the others, being possibly made by a green pigment or a pigment mixture (yellow+blue). This limit should be solved in the future developments.

This method, with that pigment database, is working to the 17e century paintings, and is not depending of the painter. Adding other pigments (appearing in the 18e, 19e century and after) allow us to use this method but the false color wavelength optimization should probably be done again, depending of the new pigment spectra's. We can apply this methodology to other periods with a bigger database and other spectral band choices, as well as to other types of artworks, like frescoes, manuscripts or sculptures with polychromy.

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