

MULTISPECTRAL IMAGING OF PIGMENTS WITH A DIGITAL CAMERA AND 12 INTERFERENTIAL FILTERS

Antonino Cosentino

Abstract

This paper discusses a low-cost multispectral imaging system for the identification of pigments in artworks. It is composed of a full spectrum modified digital camera, a DSLR with the IR cut-off filter removed and sensitivity extended to about 360-1100 nm. A set of 12 interferential filters covering the range 400-805 nm completes the equipment. The system uses on-scene reflectance standards and the raw images are split in the 3 CFA (color filter array) components (RGB). An appropriate set of 12 RGB components was chosen to form the set of 12 spectral images to build up the reflectance imaging cube. This system was tested on a collection of 54 historical and modern pigments and their reflectance spectra were compared with a database of FORS spectra (360-1000 nm) of the reference pigments. The performance of this system was evaluated against a commercial spectral imaging system equipped with the same set of 12 filters, but mounting a conventional monochromatic high-sensitivity CCD. The performance of the digital camera system is comparable to that of the monochromatic CCD camera, but the latter provides more accurate spectra thanks to its higher linearity, especially at the edge of the spectrum and in the condition of low signal. The proposed system is of interest for the art conservation sector because of its low cost and because the same digital camera can be used for other technical photographic methods, reducing the weight and cost of the overall imaging equipment necessary. The proposed method implements a small number of filters and consequently it has limited analytical capacity. It must only be used for an initial mapping of the pigments and this preliminary identification must then be confirmed by elemental or vibrational spectroscopic methods.

1 Introduction

The identification of pigments in polychrome artworks is necessary to gain a deep understanding of the materials and the painting technique applied. Conservators and art historians can use this information to select the proper conservation procedures and to reconstruct the artists' workshop practices. In many cases, the application of non-invasive techniques is mandatory since physical sampling of the art works is not possible. Among the non-invasive techniques, reflectance spectroscopy allows for the identification of painting materials (pigments and binders) and has been employed for art diagnostics from the late 1980's¹⁻³. For each wavelength, this method shows the ratio between the intensity of the reflected light and the incident light, measured with respect to a standard white reference. This ratio is called reflectance and is given in percentage (%). The light that is not reflected is absorbed or transmitted depending on the chemical composition of the material tested. In the range of visible light, the absorption is due to electronic transitions, responsible in part for the color of the pigments; while in the infrared range it is due to vibrational overtones and combinations of the fundamental molecular absorption bands. Two databases of reflectance spectra for pigments are available on the internet: one is characterized for its completeness, showing spectra from 270 to the far infrared at 1700 nm⁴,

the other is limited to the near ultraviolet and near infrared, from 360 nm until 1000 nm, but it allows the spectra to be downloaded⁵. This feature is essential to compare the spectra of investigated unknown materials with those available in the database. All the FORS reference spectra presented in this paper belong to the freely available database. Reflectance spectroscopy systems have been welcomed in the art conservation sector because their cost is relatively limited, particularly if they are constrained to the 360-1000 nm range.

Reflectance spectroscopy for art examination has mostly been performed using fiber optics probes for the analysis of small spots on the order of few millimeters in diameter⁵ but it can also be implemented with imaging systems with the added advantage that the materials can be identified and mapped remotely. In this case, images of an object in a series of spectral bands are acquired, and once the images are registered and calibrated, they are uploaded in the reflectance image cube. This represents the pixels of each image in the X and Y axes, while the Z dimension denotes the wavelength of each spectral image. From the cube, it is then possible to reconstruct the reflectance spectrum for each pixel of the image. Such systems are generally composed of a monochromatic camera that can be either a CCD for about the 360 – 1100 nm range or an InGaAs camera⁶ for the 900 – 1700 nm range, or a combination of both. The camera is equipped with an appropriate wavelength selection system, such as series of bandpass interferential filters. These systems are called multispectral or hyperspectral imagers depending on the number of spectral images produced; generally less than a dozen for the first⁶⁻¹⁰, and many more for the hyperspectral systems which can make use of tunable filters (liquid-crystal tunable filters (LCTF)¹¹, acousto-optical tunable filter (AOTF)¹² or grating spectrometers¹³ to provide image cubes with hundreds of spectral bands. It's necessary to remember that multispectral imaging is also referred in literature¹⁴⁻¹⁶ to the collection of broad spectral bands images realized with different sensors and lighting sources, such as ultraviolet fluorescence photos, infrared reflectograms and x-ray radiographs, this is also commonly referred to as: diagnostic imaging. Reflectance imaging systems are successfully used in art examination to map and identify artists' materials in paintings (pigments^{6,8,17} and binders, such as animal glue and egg tempera¹⁶) and to enhance the reading of old documents¹¹. This work proposes a low-cost multispectral imaging system for the identification of historical pigments. It is composed of a DSLR digital camera and a set of 12 interferential filters. This filter set was also used with a monochromatic (grey-tones) filter-wheel CCD camera. This paper presents the results obtained with the DSLR camera and the CCD monochromatic camera, using the same set of filters to identify a collection of 54 historical pigments. The advantages related to the implementation of a DSLR camera rather than a monochromatic camera are significant. The same digital camera can be used for other technical photographic methods such as infrared photography, ultraviolet fluorescence or RTI (reflectance transformation imaging)¹⁹, making the overall imaging equipment lighter and more compact since just one camera is sufficient for all the imaging methods. Portability is a very important feature for art diagnostics professionals who must bring the equipment to the site. Another advantage is the higher pixel count of a digital photo camera, as compared to a monochro-

matic camera, and the better control over the exposure. The possibility to use a digital camera rather than a monochromatic one was already tested^{20,21} but the aim was to realize a system which took advantage of the CFA (color filter array) in order to get the multispectral images. This work shows a much simpler system based on in-scene black, white and grey reference targets. The goal for this system was to be an affordable and simple tool, and to have sufficient accuracy to be used in preliminary study of art works. Indeed, reflectance imaging spectroscopy, no matter how accurate the system is, doesn't provide conclusive identification in more difficult cases when pigments are mixed or glazed, and therefore invasive analytical examinations become necessary. Nonetheless, reflectance imaging spectroscopy can successfully assist with making conservation decisions and it provides important information about the materials used. The system illustrated in this paper uses just 12 filters and, as a consequence, its analytical capacities are limited. It must be used only for mapping the pigments, and to attempt a strictly preliminary identification which should be confirmed by other elemental or vibrational spectroscopies.

2 Experimental

The proposed multispectral system is composed of a DSLR Nikon D800 digital camera modified "full spectrum". Its CMOS sensor responds both to the near infrared and near ultraviolet ranges of the spectrum (approximately the 360-1100 nm range) and manufacturers install an IR cut-off filter in front of the sensor to reduce infrared transmission. This filter can be removed and the camera is said to be "full spectrum". Wavelength selection is provided by a set of 12 interferential filters commercialized by PixelTeq (center wavelength/bandwidth, nm): 425/50, 475/50, 532/16, 578/10, 620/10, 669/10, 680/10, 717/10, 740/10, 750/10, 780/20, 800/10. This set of filters was chosen to cover the VIS-NIR spectrum from 400 nm to 805 nm, since most of the characterizing spectral features of the pigments are located in this range. While a large number of narrow interferential filters provide higher spectral resolution it also implies higher costs and more technical difficulties; narrow bandpass filters need high intensity lighting, condition that could be either prohibitive for light sensitive art objects or unpractical for large art works such as frescoes. The camera mounted a Nikon Nikkor Micro 105 mm f2.8 D lens, equipped with a microscope objective adapter (diameter 0.7626 in 19 mm), to host the interferential filters. The reflectance spectra reconstructed from the 12 multispectral images acquired with this system will be referred to with the acronym DMSI-12 (D standing for digital camera) and will be represented in the figures with triangular dotted lines. This paper compares this DSLR system with the spectroCam VIS commercialized by PixelTeq, a standard multispectral imaging system with a monochromatic camera incorporating a high-sensitivity 5 MP CCD and covering the range 360 – 1000 nm. The spectral images and the reflectance spectra obtained with the spectroCam will be referred to as MSI-12 and the spectra will be represented in the figures with square dotted lines.

The reflectance calibration of the images was performed using in-scene reflectance standards. The AIC photo target²² was added to the scene and its white,

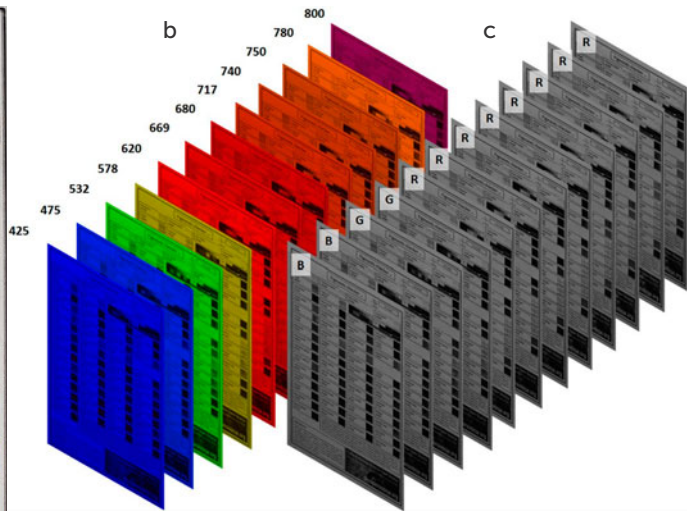


Figure 1: Pigments checker. a) RGB (visible) image, b) RGB images acquired with each of the 12 inter-ferential filters, c) selected RGB components images.

black and 4 grey patches were used to calibrate the images applying a multi-point 3rd degree polynomial calibration curve. These patches are manufactured by X-Rite® and they are identical to those used in X-Rite ColorChecker® and ColorChecker Passport®. The patches are identified by the following designations (white to black): white; N8; N6.5; N5; N3.5; and black. In the Munsell notation the corresponding chroma is 9.5, 8, 6.6, 5, 3.5, 2, their sRGB are 243, 200, 160, 122, 85, 52 and the reflectance across the 400-805 nm range covered by the interferential filters is uniform. The system was designed to register images just in the VIS-NIR range, discarding the UV. Consequently, standard halogen lamps (2 x 400 W) were used. In any case, the system can work with any other VIS-NIR lighting sources.

The DSLR camera images are split into their RGB components and calibrated and rendered as grey tones for the purpose of reconstructing reflectance spectra. It must be noted that it is possible to modify the detector of a digital color camera to become monochromatic by removing the CFA (color filter array) with the noticeable advantage of increasing the actual pixel

count. Unfortunately, the few companies that provide this service declare a low success rate and discourage this process. On the other hand, there is currently only one example of monochromatic photo-camera for the consumer level, the Leica M Monochrom, but it is very expensive and its cost compares with that of professional monochromatic cameras, while the goal of this work was to explore the possibility to use a consumer DSLR camera.

The Nikon D800 features a 35.9 x 24 mm Full Frame FX format CMOS sensor (Sony IMX094AQ), 4.88 µm pixel size. The photosensors of each pixel cannot distinguish the wavelength of the incoming light and they are covered with a CFA; tiny color filters placed over the pixels to select only red green or blue light. The CFA on the Nikon D800, as on the majority of digital cameras, implement the Bayer CFA scheme. Each two-by-two cell contains 2 green, 1 blue and 1 red filter. The raw image captured by the image sensor of the digital camera is converted to a full-color image by a demosaicing algorithm run by the on camera image

Blacks	Browns	Whites	
Ivory black, 12000	Burnt Sienna, 40430	Lead white, 46000	Table 1. Distribution by color of the 54 historical pigments (Kremer Pigments) studied in this paper and respective product code.
Vine black, 47000	Burnt umber, 40710	Zinc white, 46300	
Bone black, 47100	Van Dyke brown, 41000	Lithopone, 46100	
Lamp black, 47250	Raw Sienna, 17050	Titanium white, 46200	
	Raw umber, 40610	Gypsum, 58300	
		Chalk, 58000	
Blues	Greens	Reds	Yellows
Azurite, 10200	Cadmium green, 44510	Alizarin, 23600	Cadmium yellow, 21010
Blue bice, 10184	Chrome green, 44200	Cadmium red, 21120	Cobalt yellow, 43500
Cobalt blue, 45730	Cobalt green, 44100	Red lead, 42500	Lead Tin yellow I, 10100
Egyptian blue, 10060	Green earth, 11000	Red ochre, 11574	Lead Tin y. II, 10120
Indigo, 36005	Malachite, 10300	Vermilion, 10610	Massicot, 43010
Maya blue, 36007	Phthalo green, 23000	Madder lake, 372051	Naples yellow, 10130
Prussian blue, 45202	Verdigris, 44450	Lac dye, 36020	Orpiment, 10700
Smalt, 10000	Viridian, 44250	Carmine lake, 42100	Saffron, 36300
Ultramarine nat, 10510		Realgar, 10800	Yellow ochre, 40010
Phthalo blue, 23050			Yellow Lake res., 36262
Cobalt violet, 45800			Gamboge, 37050

processor. The images so created cannot be used to reconstruct reflectance spectra because the resulting color and brightness of each pixel depend on the intensity received by each of the 4 pixels in the pixel cell and how the algorithm mixes them. Consequently, in order to increase the linearity of the response the raw images were split into their 4 (BGRG) components using ddraw²³, an open-source raw images decoding computer program.

The multispectral imager was tested on a board, hereafter referred to as the "pigments checker"²⁴, composed of 54 swatches of historical pigments which have been applied using gum Arabic as a binder on cellulose and cotton watercolor paper, acids and lignin free, fig [1]. The pigments were mulled into the binder, which was added, as needed, for each pigment and applied with brush. No other means to control and measure thickness of the paint and binder-pigment ratio were implemented. All the pigments are commercially available from Kremer Pigments (Germany) and information regarding their composition and manufacturing processes is available on the company website. Table 1 shows the name and product code of each pigment.

The 12 raw photos were acquired with the same lens (aperture (f/3)) and lighting condition. The exposure was adjusted for each filter (filter wavelength, exposure): 425 nm (1/2 sec), 475 (1/4), 532 (1/4), 578 (1/4), 620 (1/8), 669 (1/8), 680 (1/8), 717 (1/8), 740 (1/8), 750 (1/8), 780 (1/8), 800 (1/8). The spectral response curves of the CFA filters have been reconstructed in order to verify their features across the VIS-NIR range. Some coarse assumptions were made in order to calibrate the images for this task, since the goal was just to achieve a qualitative reconstruction of the response curves in order to determine their maxima and their performance in the infrared, Figure 2. The images were calibrated assuming that the light collected is linearly proportional to the exposure. The images were also corrected for the actual bandwidth of each filter assuming that the transmittance of the filters is constant across their bandwidth and also across all the filters. The images were also corrected considering the spectral features of the lighting, and black body radiation at 2800 K was assumed for the two 400 W halogen lamps used. The reconstructed response curve for the blue CFA filter shows a flat maximum as a result of the large bandwidth of the two interferential filters covering the blue region (425(50) and 475 (50)). The response curves of the green and red CFA filters show a sharp maximum, respectively, on the 578 nm and on the 620 nm interferential filters. All the three response curves show a sharp and equal increase in the infrared

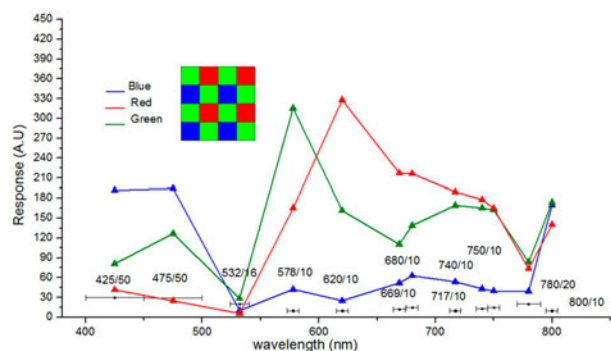


Figure 2: Reconstructed spectral response for the CFA on the Nikon D800 and, insert top left, Bayer CFA scheme for 4 pixels.

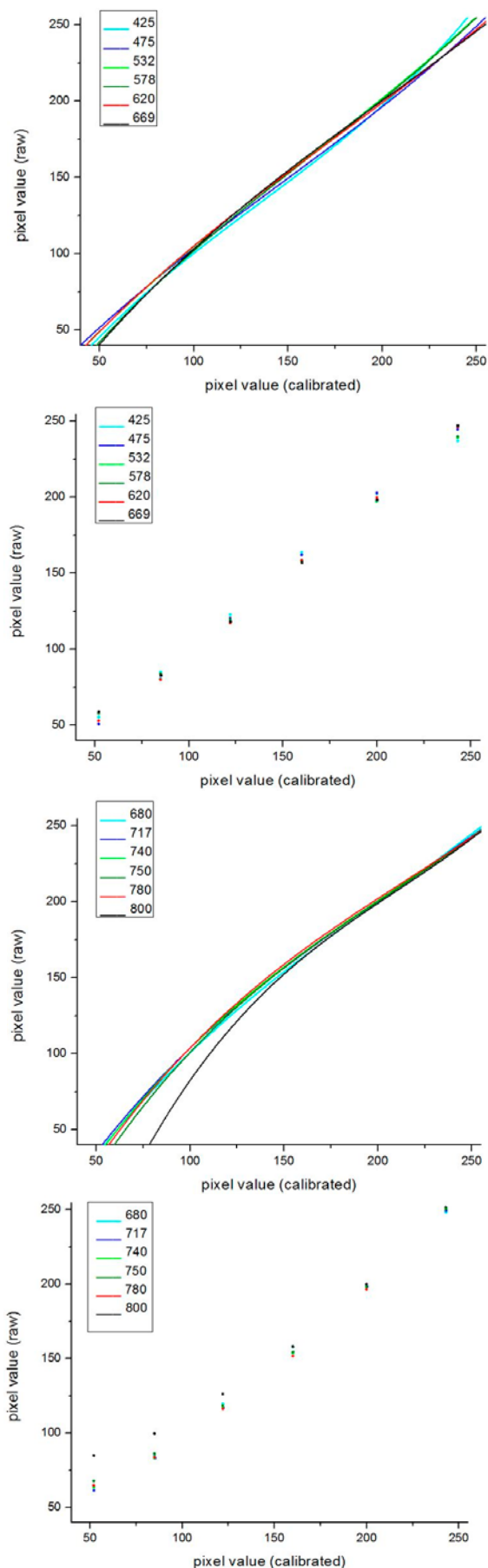


Figure 3: Calibration curves. Calibration curves and points for each filter.

(800 nm filter) since the CFA filters become transparent to the infrared.

These three response curves were able to verify that the splitting of the raw images was performed correctly and this permitted an informed choice of the set of 12 RGB split images used to build up the reflectance cube. An issue with the DSLR system is in identifying saturation. With a monochromatic camera it is immediate to verify that there are no saturated pixels in the image. On the other hand, in the RGB image, one channel could be saturated and it is not possible to detect it without splitting the channels first.

The chosen set of monochromatic images for each filter is (filter wavelength (RGB)): 425 (B), 475 (B), 532 (G), 578 (G), 620 (R), 669 (R), 680 (R), 717 (R), 740 (R), 750 (R), 780 (R), 800 (R), figure 2. This set of images were first registered and then calibrated. Since the linearity of the DSLR camera is not guaranteed, as for a scientific CCD camera, it was necessary to implement a multi-point 3rd degree polynomial calibration curve using the AIC photo target. Figure 3 shows that the linearity of the CMOS response was degraded just in the infrared region and for the black swatch and the darkest of the grey.

3 Results and Discussion

The goal of this study was to evaluate the use of a DSLR camera combined with a set of bandpass interferential filters as a reflectance imaging system useful for the identification of pigments. In the following discussion, the results obtained with such a system are evaluated against those collected using the same set of filters mounted on the PixelTeq spectroCam and the reference FORS spectra from the database.

With this filter set, the UV region was discarded and therefore it is not possible to register the UV absorption band that characterizes titanium white and zinc white. On the other hand, these two pigments and viridian are the only ones that show features in the near UV region and consequently the exclusion of this band was considered acceptable. Figure 4 shows the FORS, MSI-12 and DMSI-12 spectra of 3 important white pigments, zinc white, titanium white, and lead white. The MSI-12 and DMSI-12 spectra of the first two pigments don't register the UV absorption band and are not different from lead white that has a flat reflectance all over the UV-VIS-NIR range. The DMSI-12 spectra successfully represent the flat spectra of the white pigments because of the better linear response of the spectral images at the higher reflectance of the whites, as seen in the calibration curves, Figure 3.

In the blue region, the characterizing spectral features are broad and vary slowly, consequently it was chosen to cover this region with only 2 broad (bandwidth 50 nm) filters in the blue region, centered at 425 nm and 475 nm, and one green filter at 532 nm (bandwidth 16 nm). Azurite and ultramarine are the most heavily used historical blue pigments, and they have reflectance maxima very close to each other in the blue region at about 460 nm. These maxima are adequately reconstructed in the corresponding MSI-12 spectra. The DMSI-12 spectra feature the maxima in the blue region for both the pigments, figure 5.

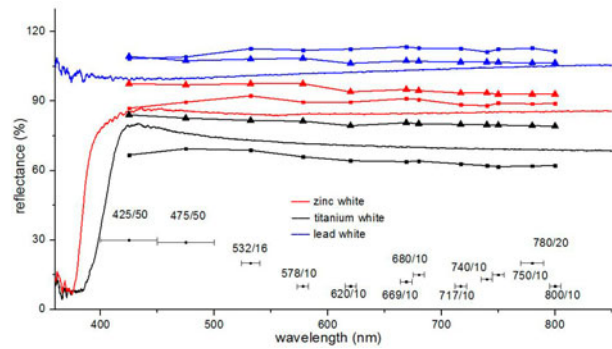


Figure 4: FORS (line), MSI-12 (squares) and DMSI-12 (triangles) spectra of zinc white, titanium white and lead white.

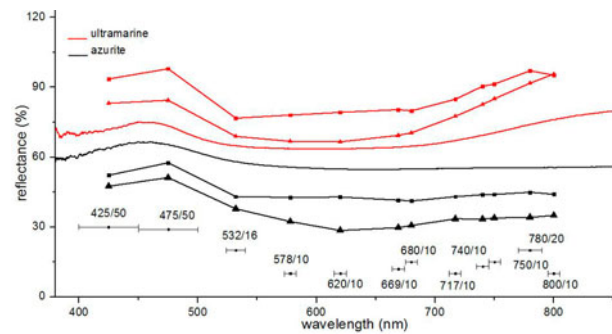


Figure 5: FORS, MSI-12 (squares) and DMSI-12 (triangles) spectra of ultramarine and azurite.

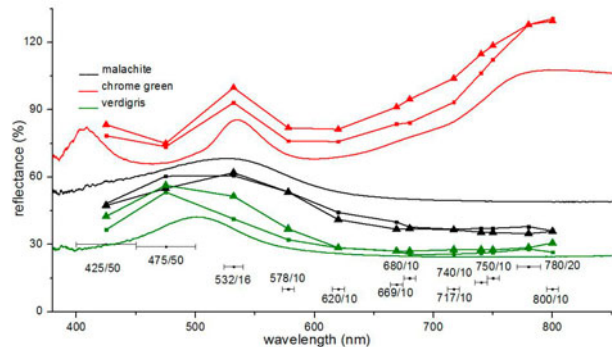


Figure 6: FORS, MSI-12 (squares) and DMSI-12 (triangles) spectra of malachite, chrome green and verdigris.

Figure 6 shows that the five filters at 425, 475, 532, 578 and 620 nm can reconstruct the maxima of three widely used green pigments both with the DMSI-12 and MSI-12 setup, even if some slight differences are observed. The sharp maximum of chrome green, as well as the broad one of malachite, are well represented by both the systems because these maxima fall on the narrow green filter at 532 nm. On the other hand, the broad maximum of verdigris is closer to the blue region, at about 500 nm and it isn't reconstructed with the same accuracy.

The region between the far red and the near infrared is covered with 8 filters: 7 filters (669, 680, 717, 740, 750, 800 nm) with bandwidth 10 nm and one filter centered at 780 nm with bandwidth 20 nm. The combination of these filters allows reconstruction of the absorption band in lithopone, a mixture of barium sulfate, a good flat reflector, and zinc sulfide, which is responsible for absorption bands in the 650-800 nm region, figure 7. Both DMSI-12 and MSI-12 correctly represents the features of lithopone, a flat spectrum with a large and deep absorption band across the red and the infrared. Both the systems also perform adequately on the

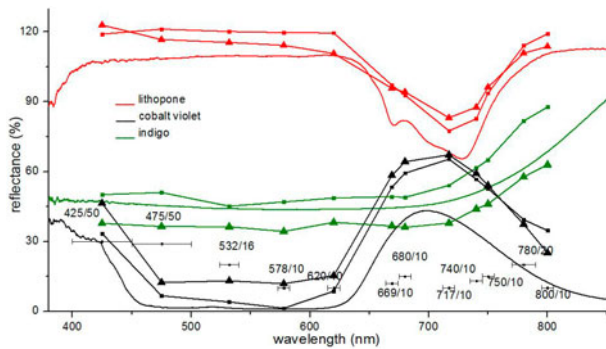


Figure 7: FORS, MSI-12 (squares) and DMSI-12 (triangles) spectra of lithopone, cobalt violet, and indigo.

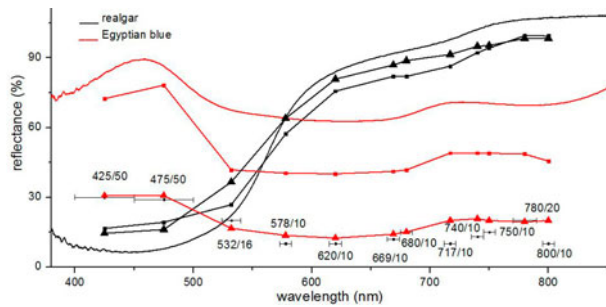


Figure 8: FORS, MSI-12 (squares) and DMSI-12 (triangles) spectra of realgar and Egyptian blue.

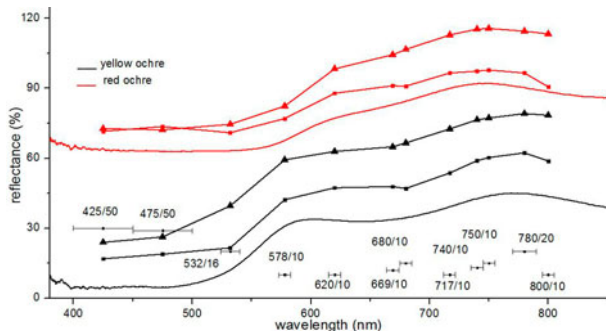


Figure 9: FORS, MSI-12 (squares) and DMSI-12 (triangles) spectra of yellow and red ochre.

infrared edge of the recorded spectrum. Figure 7 shows that they effectively reconstruct the absorption band of cobalt violet and the sharp reflectance inflection of indigo.

Another example of characterizing spectral features in the infrared edge is given by realgar, which has an inflection point at 740 nm; and Egyptian blue, which has two absorption bands near 630 nm and 800 nm, figure 8. The weak inflection point of realgar is represented by the MSI-12 but it is lost in the DMSI-12. On the other hand, the features of Egyptian blue are well represented by both the systems but DMSI-12 fails to reconstruct its maximum in the blue region, as was observed already in the case of ultramarine.

The most challenging task for these 12 filters was to successfully reconstruct the S-shape of yellow and red ochre which spans from the green region to the infrared, figure 9. Again, the DMSI-12 compares well with the MSI-12.

Another two examples are represented by cadmium yellow and cobalt blue. The first is identified thanks to the absorption bands of zinc sulfide in the infrared region and the sharp inflection point at about 490 nm,

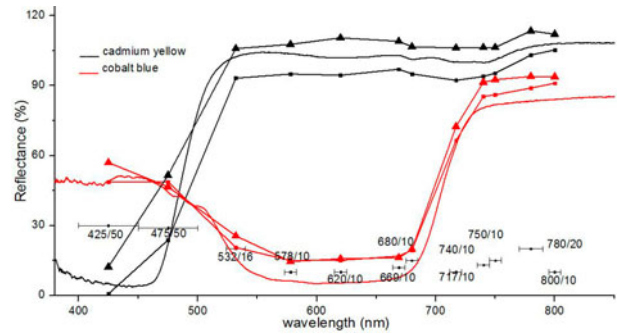


Figure 10: FORS, MSI-12 (squares) and DMSI-12 (triangles) spectra of cadmium yellow and cobalt blue.

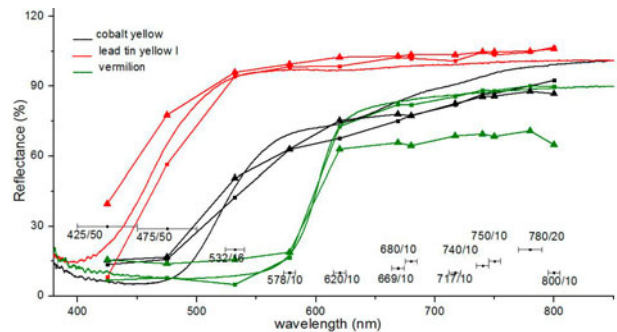


Figure 11: FORS, MSI-12 (squares) and DMSI-12 (triangles) spectra of lead tin yellow I, cobalt yellow and vermilion.

figure 10. The two systems both reconstruct the absorption bands, but the DMSI-12 is less accurate in representing the sharp inflection point. Cobalt blue is characterized by an absorption band in the 500 - 700 nm region and a flat reflectance from the blue region towards the UV, figure 10. Again, the DMSI-12 provides a comparable reflectance curve but fails to represent the flat reflectance in the blue region.

Regarding the reconstruction of sharp curves, figure 11 shows pigments with inflection points in the blue (lead tin yellow I at 465 nm), in the green (cobalt yellow at 525 nm) and in the red region (vermilion at 600 nm). Again, the DMSI-12 fails to match the MSI-12 spectrum in the blue-green region. The inflection point of lead tin yellow I is shifted toward the blue, as well as, that of cobalt yellow. As seen before, the reconstruction in the red-infrared region is much more accurate. The inflection point of vermilion overlaps flawlessly in both the methods, and for this spectrum, the only issue is an unexpected decrease in intensity observed at 800 nm.

4 Conclusions

This paper demonstrated that a DSLR camera can be used with a set of bandpass interferential filters and can constitute a reflectance imaging system useful for the preliminary identification of pigments. This study compared the results obtained with this system with those acquired with a system using the same set of filters but with a high sensitivity monochromatic camera. The examination of 54 historical pigments laid with gum arabic showed that the results are comparable. The monochromatic scientific camera guarantees higher linearity and it is therefore recommended for more accurate reconstructed reflectance spectra. On the other hand, the DSLR system is a competitive alternative especially for preliminary identification of pigments and for their mapping (classification).

The advantages of using a modified “full spectrum” DSLR camera are its low cost and the possibility to use the same camera for other imaging methods, such as technical photography and RTI. On the other hand, the comparison with a monochromatic camera exposed the difficulty in reconstructing the weakest spectral features, such as the small inflection point of realgar. The blue region is the part of the spectrum where the DSLR camera proved less accurate, but using more filters in this region will most likely solve the problem. In conclusion, while, as expected, the DSLR camera is less accurate than the monochromatic camera, a set of more filters, covering the blue region with more resolution, will reasonably provide much more accurate reconstructed reflectance spectra.

It must be pointed out that this study must be considered as a first step in developing this new and simple method and further research is needed. Indeed, the reflectance spectra of pigments are influenced by a number of parameters, such as the pigments’ particle size, their concentration in the medium, their use as glazes and the binding media. These issues are very relevant even for hyperspectral imaging and reflectance spectroscopy methodologies that provide a much higher spectral resolution than the system introduced in this paper.

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