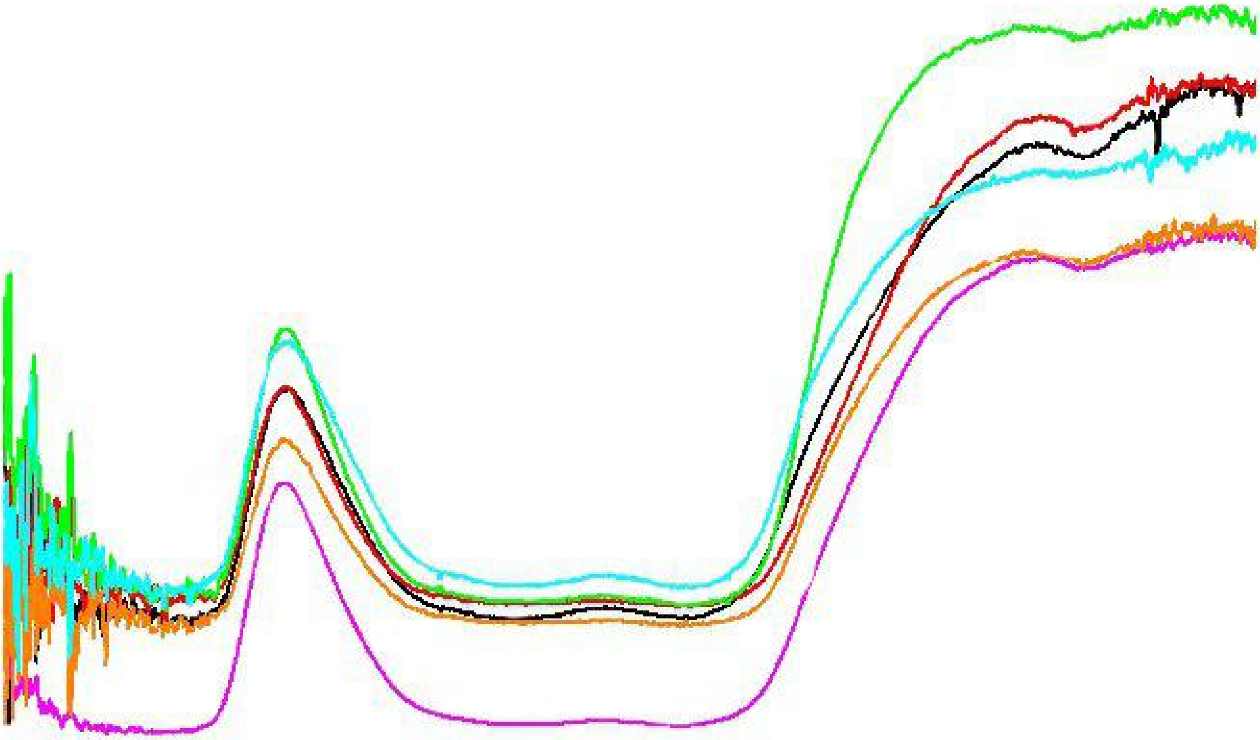
# FORS SPECTRAL DATABASE OF HISTORICAL PIGMENTS IN DIFFERENT BINDERS

*Antonino Cosentino*



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# FORS spectral database of historical pigments in different binders

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## ABSTRACT

*This paper presents the development of a Fiber Optics Reflectance Spectra (FORS) database of 54 historical pigments commonly used in art work. The database is available on-line and stores a large collection of spectroscopic data that can be freely downloaded. The database was built by collecting the reflectance spectra of the pigments both in pure powder and applied with gum Arabic, egg tempera, linseed oil and fresco, aiming to provide a knowledge base for the evaluation of the effect of different binders on the pigments' spectral features. The obtained results confirmed the effectiveness of the FORS system used for the non-invasive identification of pigments in different binders. Its small dimensions, low cost and other significant features such as instrument mobility and rapid data collection make it well adapted to the specific needs of professional art examination in the field. The paper highlights the great potential of this database for pigment identification purposes, and its usefulness to provide, for the first time, the additional possibility to freely download all spectroscopic data that would be of significant value as a reference for other FORS researchers in this field.*

## 1. Introduction

The identification of pigments in polychrome artworks is of great interest to obtain a deep knowledge of the raw materials and the painting technique applied, as well as to provide useful information to art historians and conservators to select the proper conservation procedures and correctly define restoration plans. In many cases, however, sampling cultural artifacts is not permitted and, therefore, the application of non-invasive techniques is the only diagnostic tool. In the analysis of polychrome artworks, among the techniques available in portable version, Fiber Optics Reflectance Spectroscopy (FORS) has been established as a powerful one for the identification of pigments. A FORS spectrum shows for each wavelength, 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 FORS spectra can provide information useful for the characterisationof pigments since the light that is not reflected is absorbed or transmitted depending on the chemical composition of the material tested. Pigments' identification procedures using reflectance spectroscopy involve a spectral database and can be achieved by comparing the spectral features (characteristic wavelengths) of the investigated unknown spectrum with the ones available in the database.

The peculiar advantage of this method with respect to the other spectroscopies most commonly used, such as XRF and Raman, is that the FORS equipment can be assembled with relatively low cost components: a light source; a spectrometer; a probe; and two fiber optics, one to illuminate the sample and the other to collect the diffused light (Figure 1). If the FORS system is limited to the visible spectrum, including just a small portion of the near infrared and the near ultraviolet, between 360 nm and 1000 nm, then the cost of the equipment is considerably low. However, if a wider spectral range is desired, more sophisticated and, thus, expensive equipment is required, in order to achieve greater accuracy and sensitivity in the far infrared. Specific advantages of the assembled system presented in this paper are its low weight and small dimensions, which are very important features for art diagnostics professionals. Indeed, on site art examination is extremely valuable and so the equipment portability is of the highest importance such as, for example, examination of mural paintings on high scaffoldings. Portability is also extremely valuable for traveling professionals who must bring the equipment to the site.

Other advantages are the speed in data collection and the modularity of the system. The same spectrometer could be used to set up other type of experiments simply by providing it with the right probes and sources (such as transmittance and fluorescence spectroscopies and colorimetry).

FORS has been widely employed by scientists for art diagnostics for almost three decades. In 1987, a research article introducing the application of FORS technique to the analysis of artworks was published [1], and in 1997 the application of this method for the identification of pigments and the monitoring of color changes on the Brancacci Chapel Frescoes in Florence was reported [2]. Later on, the IFAC (Institute of Applied Physics NelloCarrara) online database of FORS spectra of pigments was published [3]. This was the first and is still currently the most complete database in existence; however, their spectra are not downloadable. IFAC's database provides FORS spectra in the 270-1700 nm range for pure pigments or mixed with different binding media (egg tempera, mastic varnish and linseed oil). Some of the pigments were also applied as glazes over paint layers or metal leaf. In the recent literature a great number of research works have been reported demonstrating the use of FORS technique for the identification of pigments and natural dyes on a great variety of art works such as paintings and mural paintings [4-8], as well as on other polychrome artworks such as illuminated manuscripts [9].Furthermore, the method proved effective to identify natural dyes in historical textiles [10] and was recently applied for the evaluation of plastics degradation in modern artworks [11].

This paper presents the development of an online database of downloadable FORS spectra of 54 historical pigments in powder and mixed with gum Arabic, egg tempera, linseed oil and fresco. The database covers the 360–1000 nm spectral range and it is accessible as CSV files downloadable from http://e-conservation.org/issue-2/36-FORS-spectral-database. An extract from the spectra database is presented and discussed in this paper, aiming to provide a knowledge base for the assessment of the effect of different binders on the pigments' spectral features, as well as to evaluate the capabilities of the miniaturized and low cost FORS system used.

## 2. Experimental

### *2.1. Instrumentation*

For the collection of the reflectance spectra, a portable Ocean Optics USB4000 spectrometer with a 3648-element Toshiba linear CCD array, a diffraction grating with a working range of 360-1000 nm and resolution of 1,5-2,3 nm (FWHM) was used. The instrument is equipped with an HL-2000-FHSA halogen lamp, a reflection probe R400-7-UV/VIS and an integrating sphere ISP-R

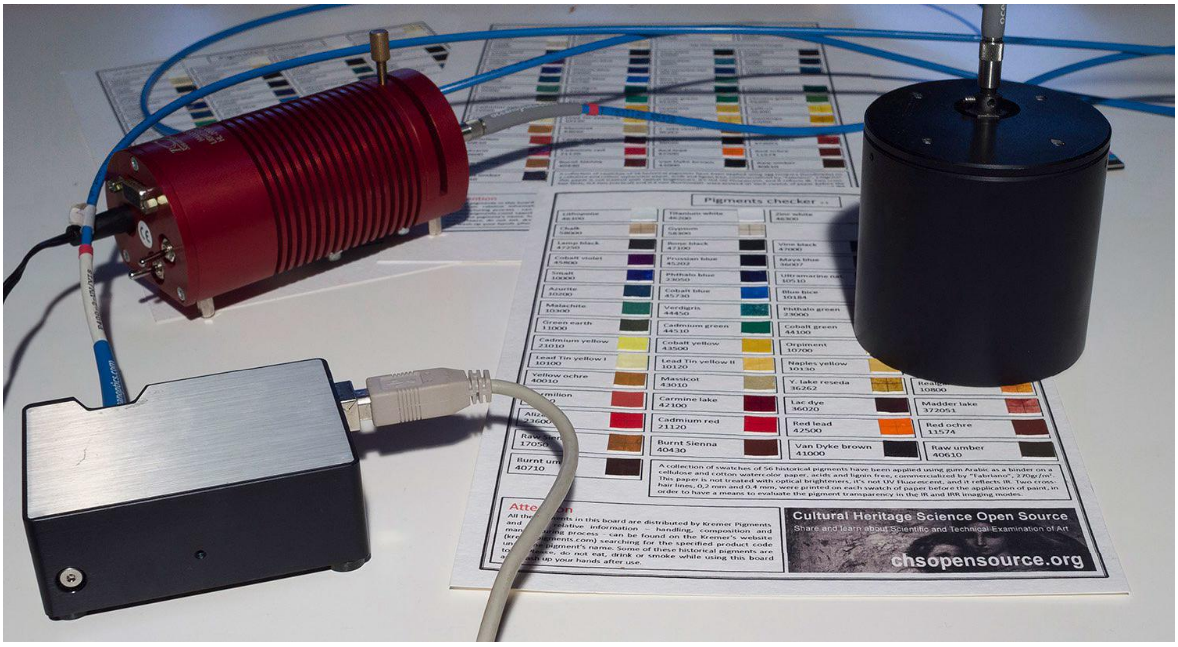

*Figure 1. Miniaturised FORS system (from left to right): halogen lamp, USB4000 spectrometer and integrating sphere.*

(Figure 1). The R400-7-UV/VIS consists of a tight bundle of 7 optical fibers (400 µm in diameter) in a stainless steel ferrule - 6 illumination fibers around one read fiber. The diffuse light is collected at the same angle of the incident light, but the probe can be tilted by the operator to get readings at 0/0, 45/45, decreasing the reflected component, or any arbitrary angle. The integrating sphere averages the diffused and the reflected components, providing a spectrum which is characteristic of the material analyzed and does not depend on the specific measuring angle. Spectra have been acquired with the following parameters: integration time: 5 sec (integrating sphere); 5 msec (reflection probe); scans to average: 4; boxcar width: 5. The integrating sphere ISP-R has been used to acquire all the spectra stored in the database while the reflection probe has been used only on the set of pigments laid with gum Arabic. Spectra have been collected at 45/45.

### *2.2. Pigments*

Fifty-four historical pigments have been tested, all commercially available from Kremer Pigments (Germany). Information regarding their composition and manufacturing processes is available on the company website. Table I shows the name and product code of each pigment. These were analyzed as powder and when grinded using a glass muller with gum Arabic, egg tempera and linseed oil as binders. They were applied with a brush on watercolor paper made of cellulose and cotton, acids and lignin free, commercialized by "Fabriano", 270 gr/m$^2$. These test plates are called "pigment checkers" and are visible in Figure 1. The reflectance spectrum of the paper was tested and it is flat without relevant features (Figure 2). The pigments were also applied with fresco technique, on a preparation of marble powder and lime plaster ($Ca(OH)_2$) in ratio 2:1. FORS spectra of all the binders and the watercolor paper are shown in Figure 2.

## 3. Results and Discussion

An extract of the developed database is presented below and the spectra acquired are discussed in groups of color. This database aims to complement the IFAC one by providing the FORS spectra of some additional pigments: Egyptian blue, Maya blue, phthalo blue, cobalt violet, cadmium green, cobalt green, phthalo green, lithopone, cobalt yellow and gamboge. Furthermore, to the best of the author's knowledge, the FORS spectra of the following pigments are also here reported for the first time: cobalt violet, cadmium green, cobalt yellow and gamboge.

### *3.1. White Pigments*

Among the whites, titanium white and zinc white are known for their strong UV absorbance [12] which is evident in the FORS spectra and remains unchanged regardless of the binder (Figure 3). Lithopone is a mixture of barium sulfate, a good flat reflector [13, 14], and zinc sulfide, which is responsible for absorption bands in the 650-800 nm region [15] (Figure 4). Lead white, as well as gypsum, has a flat spectrum [16] but it appears to be strongly modified by the absorbance in the blue and UV region when mixed with egg tempera and linseed oil (Figure 5).

### *3.2. Blue Pigments*

The database presents the FORS spectra of 11 blue pigments. Azurite shows the characteristic and well documented reflectance maximum at about 450 nm [2] and its FORS spectra are not affected by the binders (Figure 6). On the other hand, egg tempera and linseed oil shift the position of the 480 nm peak for blue bice, the synthetic form of azurite (Figure 7), in higher wavelengths as a consequence of their absorbance bands.

Smalt is characterized by an absorbance band that is divided in three sub-bands [6] with minima at 540 nm, 590 nm and 640 nm (Figure 8). The above mentioned three minima are well defined only in the spectrum of powder smalt, while when any type of binder is added the minima at 590 nm and 640 nm cannot be distinguished.

Cobalt violet has an absorbance band divided into two sub-bands with minima centered near 490 nm and 580 nm which are well defined in any binder (Figure 9). Applied as fresco, the spectrum is strongly modified and this could be attributed to an actual reaction of the pigment with the lime. Indeed, only few pigments are inert enough to be actually useful for fresco.

Egyptian blue shows two absorption bands near 800 nm and 630 nm, and is also characterized by the presence of a peak at 950 nm which could be assigned to its infrared fluorescence [17], and is visible with every binder (Figure 10). Phthalo blue has a minimum at 920 nm [18] which is visible in all binders, except fresco (Figure 11).

FORS can easily differentiate between indigo and Maya blue pigments; the first one is characterized by the presence of a broad absorption band in the 420-730 nm range, while Maya blue shows a more narrow absorption band between 540 nm and 730 nm followed also by a stronger and sharper positive slope [19] (Figure 12).

### *3.3. Green Pigments*

The reflectance spectra of eight green pigments were recorded. Green earth shows two broad reflectance maxima near 560 nm and 810 nm attributed to celadonite [7] and even if weak, they are evident with each binder used (Figure 13). The spectrum of malachite is recognizable by its large absorbance band between 600 nm and 900 nm [4] and is barely affected by the binder (Figure 14). Figure 15 demonstrates the FORS spectra of malachite mixed with an increasing amount (by weight) of lead white (0%, 20%, 40%, 60%) and the pigment is still identifiable. Cadmium green shows two characteristic minima at 620 nm, 710 nm and a stronger one at 920 nm, which can be observed in every binder (Figure 16). Cobalt green also exhibits a characteristic

*Table I. Distribution by color of the 54 historical pigments (Kremer Pigments) studied in this paper and respective pigment code.*

| White | Yellow | Red | Green | Blue | Brown | Black |
|---|---|---|---|---|---|---|
| Lead white, 46000 | Cadmium yellow, 21010 | Alizarin, 23600 | Cadmium green, 44510 | Azurite, 10200 | Burnt Sienna, 40430 | Ivory black, 12000 |
| Zinc white, 46300 | Cobalt yellow, 43500 | Cadmium red, 21120 | Chrome green, 44200 | Blue bice, 10184 | Burnt umber, 40710 | Vine black, 47000 |
| Lithopone, 46100 | Lead Tin yellow I, 10100 | Red lead, 42500 | Cobalt green, 44100 | Cobalt blue,45730 | Van Dyke , 41000 | Bone black, 47100 |
| Titanium white, 46200 | Lead Tin y. II, 10120 | Red ochre, 11574 | Green earth, 11000 | Egyptian blue, 10060 | Raw Sienna, 17050 | Lamp black, 47250 |
| Gypsum, 58300 | Massicot, 43010 | Vermilion, 10610 | Malachite, 10300 | Indigo, 36005 | Raw umber, 40610 | |
| Chalk, 58000 | Naples yellow, 10130 | Madder lake, 372051 | Phthalo green, 23000 | Maya blue, 36007 | | |
| | Orpiment, 10700 | Lac dye, 36020 | Verdigris, 44450 | Prussian blue, 45202 | | |
| | Saffron, 36300 | Carmine lake, 42100 | Viridian, 44250 | Smalt, 10000 | | |
| | Yellow ochre, 40010 | Realgar, 10800 | | Ultramarine, 10510 | | |
| | Yellow Lake, 36262 | | | Phthalo blue, 23050 | | |
| | Gamboge, 37050 | | | Cobalt violet, 45800 | | |

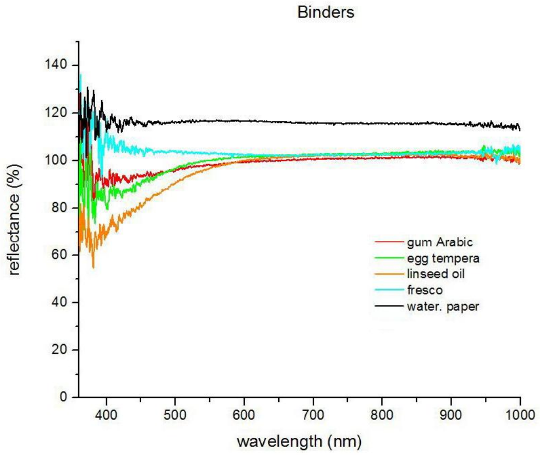

*Figure 2. FORS spectra of the binders and the support watercolor paper.*

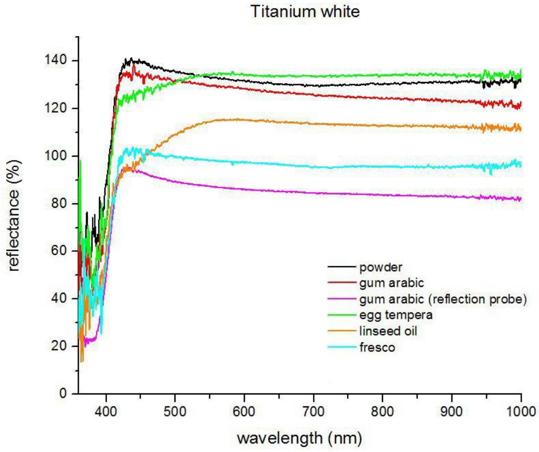

*Figure 3. FORS spectra of titanium white.*

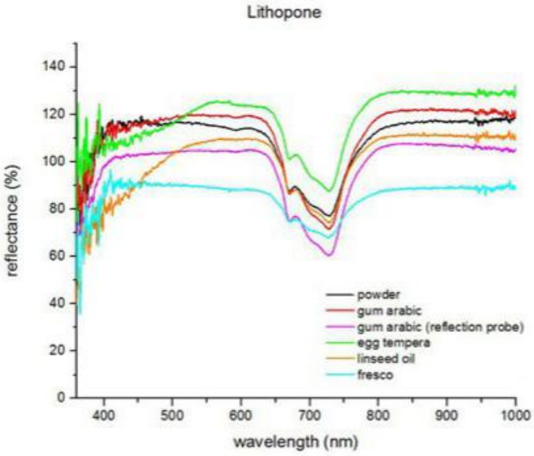

*Figure 4. FORS spectra of lithopone.*

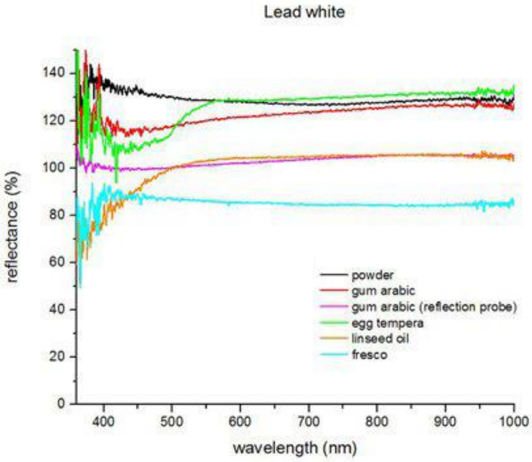

*Figure 5. FORS spectra of lead white.*

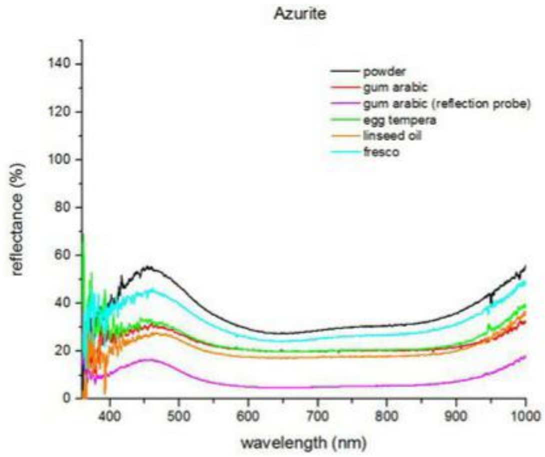

*Figure 6. FORS spectra of azurite.*

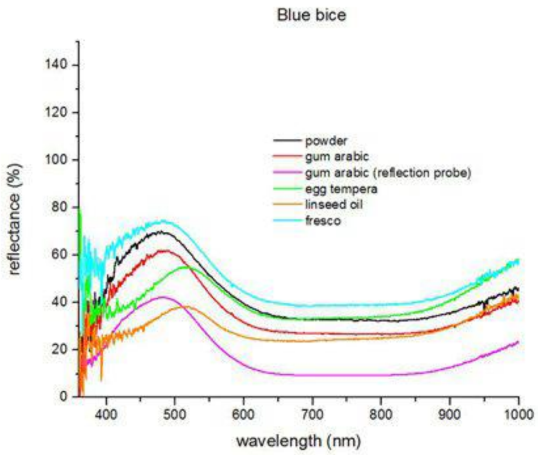

*Figure 7. FORS spectra of blue bice.*

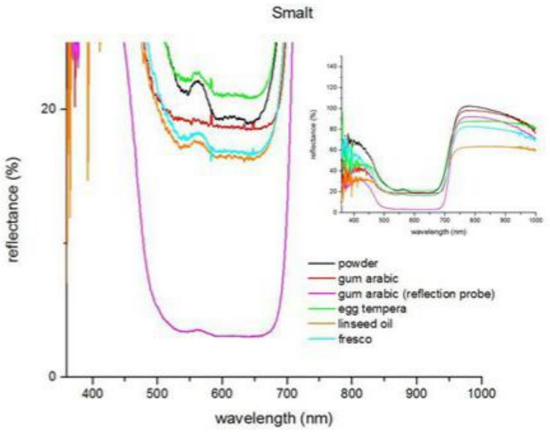

*Figure 8. FORS spectra of smalt: full scale spectrum (right); zoomed in on the structured absorbance band (left).*

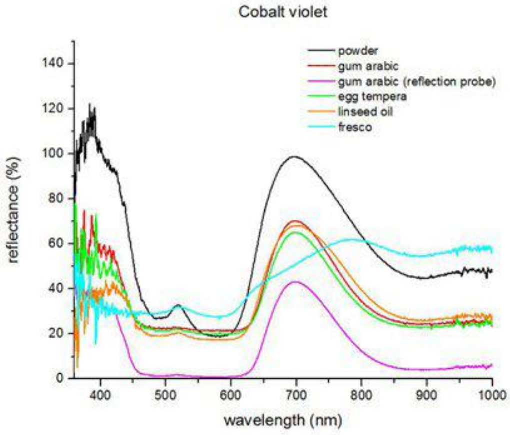

*Figure 9. FORS spectra of cobalt violet.*

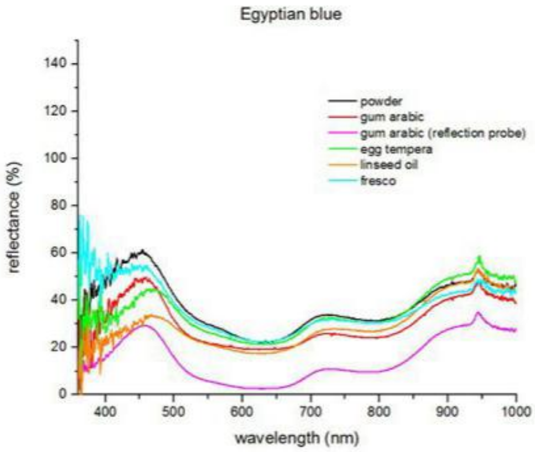

*Figure 10. FORS spectra of Egyptian blue.*

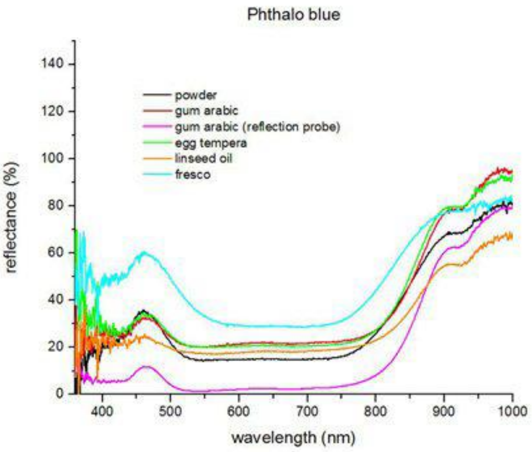

*Figure 11. FORS spectra of p blue.*

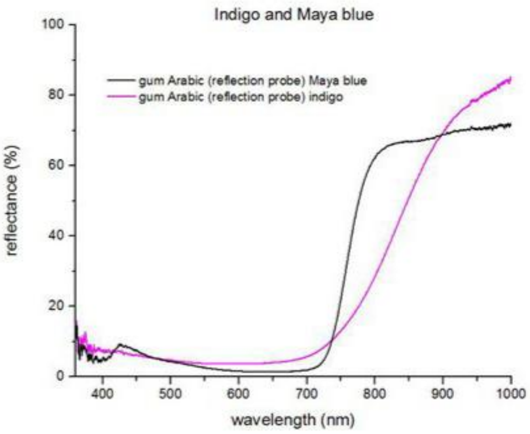

*Figure 12. FORS spectra of indigo and Maya blue.*

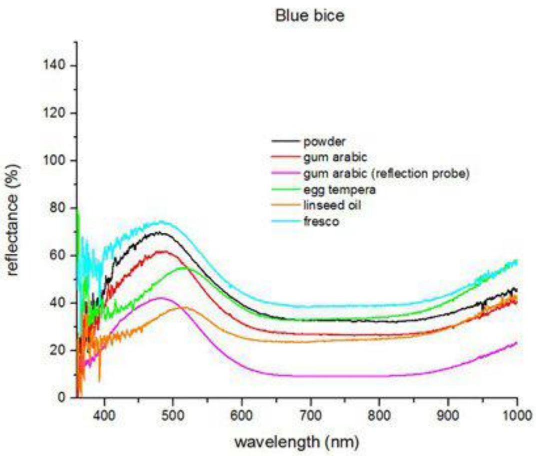

*Figure 13. FORS spectra of green earth.*

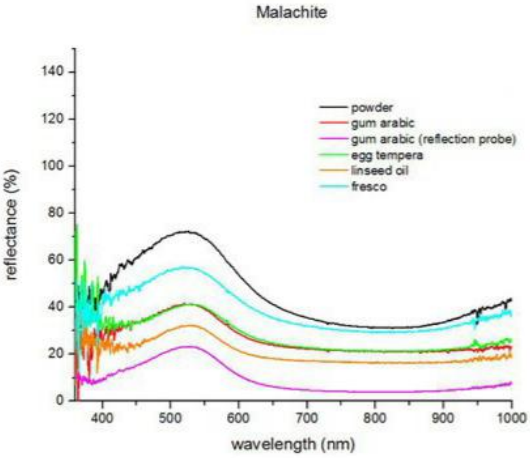

*Figure 14.FORS spectra of malachite.*

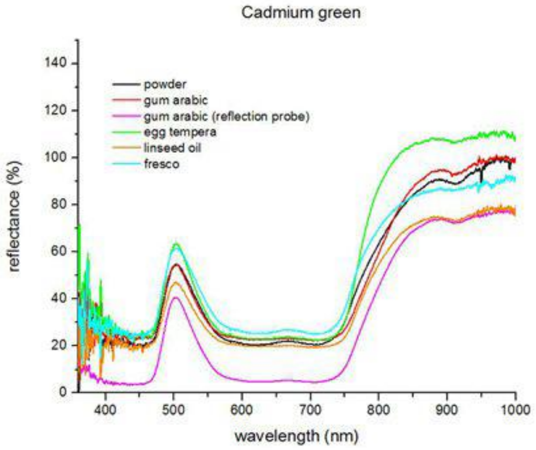

*Figure 16. FORS spectra of cadmium green.*

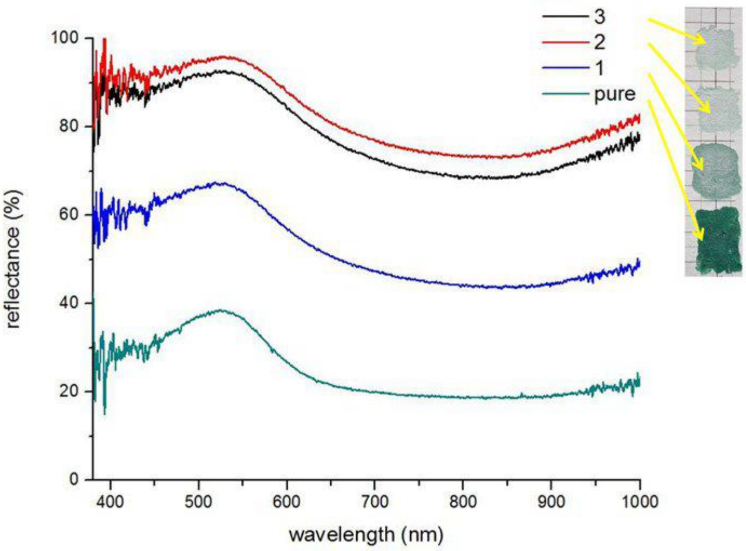

*Figure 15. FORS spectra of malachite mixed with lead white in gum Arabic.*

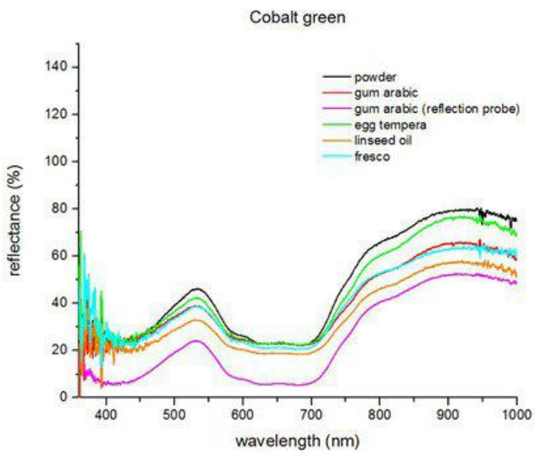

Figure 17. FORS spectra of cobalt green.

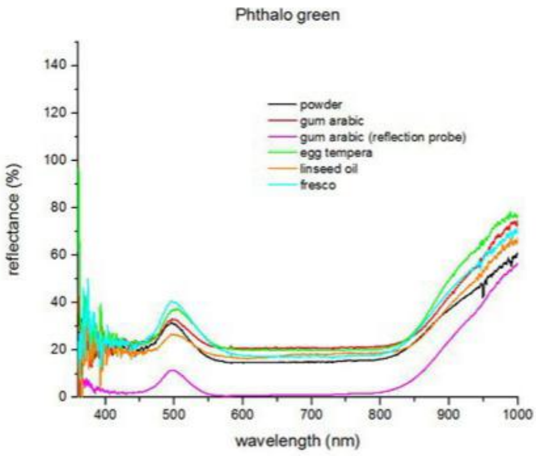

Figure 18. FORS spectra of phthalo green.

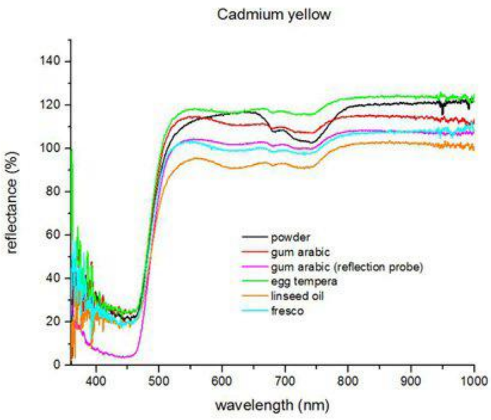

Figure 19. FORS spectra of cadmium yellow.

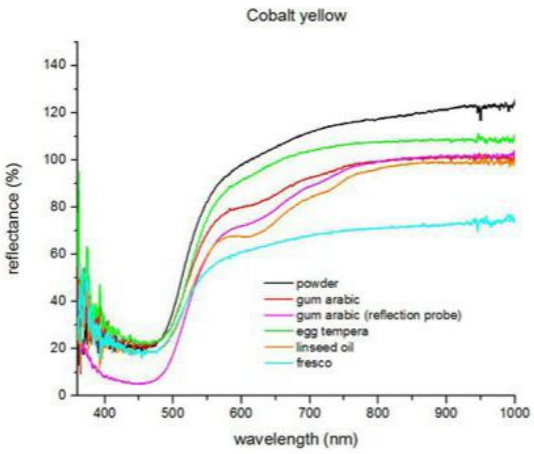

Figure 20. FORS spectra of cobalt yellow.

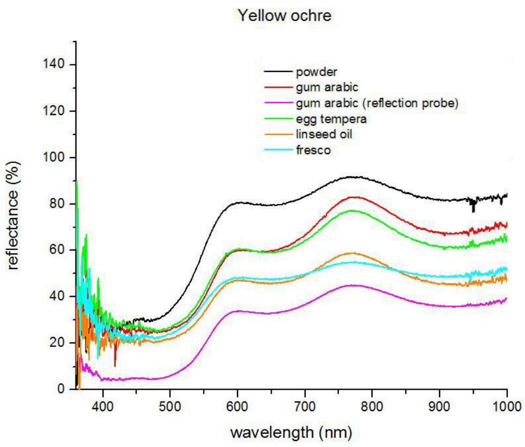

Figure 21. FORS spectra of yellow ochre.

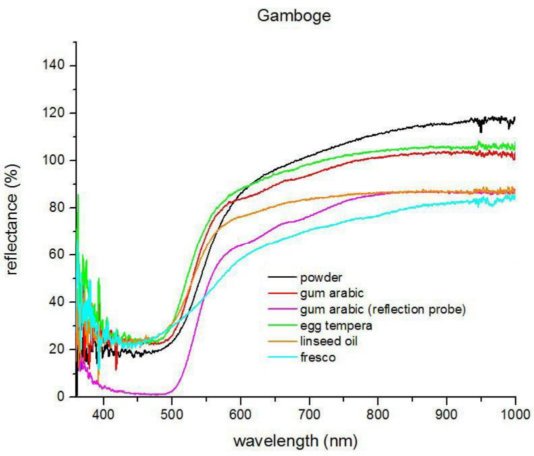

Figure  22. FORS spectra of gamboge.

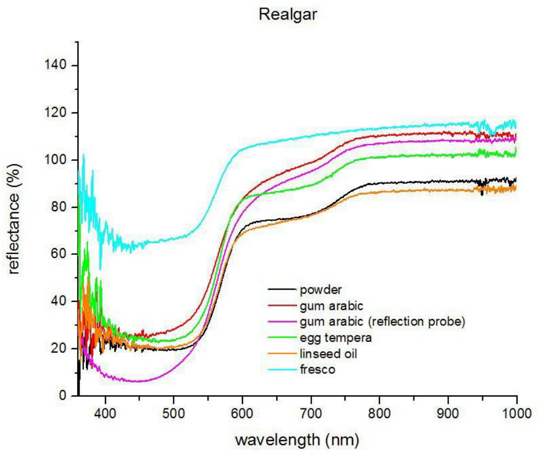

*Figure 23. FORS spectra of realgar.*

absorbance in the infrared at 820 nm [3], which even weak is still detectable in all binders (Figure 17). Phthalo green is reported to present a weak secondary peak at 700 nm [13] but this peak was not observed in our sample (Figure 18).

### *3.4. Yellow Pigments*

Cadmium yellow contains zinc sulfide and therefore its reflectance curve presents similar spectral features between 650 nm and 800 nm with the respective ones observed in lithopone as expected (Figure 19).

Cobalt yellow is characterized by two absorbance bands at 620 nm and 700 nm (Figure 20), which are visible only with the gum Arabic and linseed oil binders. Iron-containing pigments such as yellow ochre are identified by their characteristic S-shape and the presence of two broad absorption bands near 660 nm and 930 nm which could be attributed to goethite [7] and are detectable in every binder (Figure 21). Gamboge shows two very weak absorbance bands at 620 nm and 670 nm, which are visible only with the gum Arabic binder (Figure 22).

### *3.5. Red Pigments*

Realgar has a characteristic inflection point at 740 nm [3], visible in all binders but fresco, due to a reaction with lime (Figure 23). FORS is very sensitive to the presence of lakes and dyes [20, 21] and it is very useful for the identification of glazes. Figure 24 shows the FORS spectra of 4 red lakes

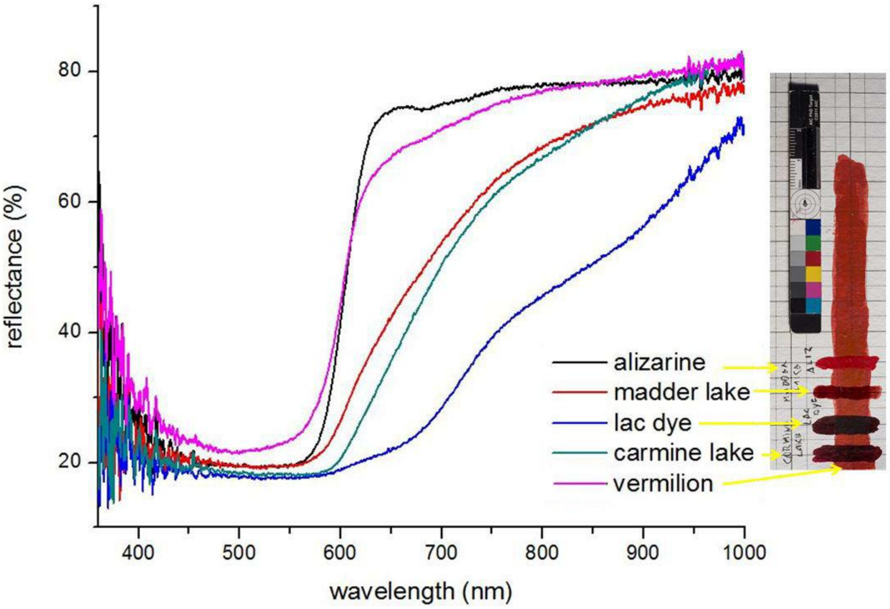

*Figure 24. FORS spectra of four red lakes glazed over vermilion.*

glazed over vermilion. As expected, their FORS spectra are not modified by the vermilion painted underneath.

### *3.6 Black and Brown Pigments*

The four black pigments could not be differentiated. Among the browns only raw Sienna and burnt Sienna are identified by their characteristic S -shape [7].

### 3.7. System Performance

The signal obtained using the integrating sphere exhibited a fair amount of noise in the UV and blue regions, as well in the near-IR end of the spectral range. The reflection probe provided much better spectra across the entire investigated range, and due to its lighter weight and better handling, it seems to be the better solution for on-site examination. Both probes allowed the detection of the strong UV absorbance band of titanium white and zinc white, while the weak absorbance bands present in cobalt blue at 480 nm and 495 nm were identified only with the reflection probe. The performance in the visible range was good with both probes; the characteristic S-shape of iron-containing pigments such as red and yellow ochre and sienna was detected with high accuracy. In some cases, the weak sub-bands present in the spectra of the pigments in powder were still recognizable in the spectra of the pigments laid with the binders, as shown for cobalt violet. In other cases, the very weak sub-bands could be lost in the spectra of the pigments after being laid with a binder, as shown for smalt. This example highlights the limits of this low-cost FORS system compared to the more sophisticated one used for the construction of the IFAC database which allowed the detection of the sub-bands of smalt even in the cases where it has been mixed with binders or other pigments.

In the near-infrared region up to 1000 nm, the reflection probe performance was still good. For example, the absorption bands of zinc sulfide present in lithopone and cadmium yellow from 650-800 nm, and the cadmium green minima at 620 nm and 710 nm, were well defined in every binder. The absorbance band of phthalo blue at 920 nm and the weak absorbance of cobalt green at 820 nm were visible in all binders, as well.

## 4. Conclusions

This new and available on line FORS spectral database of 54 historical pigments in powder and mixed with different binders is a very useful and helpful addition to the already created databases of reflectance spectra existing on line. FORS researchers working in the field of Cultural Heritage Science can significantly benefit from the added possibility to freely download all spectroscopic data that is provided for the first time, and use it as a powerful tool for pigments identification purposes as well as to evaluate how different binders influence the spectral features of the pigments.

The database shows that this system can produce spectra comparable with those of the referenced literature and it is an effective FORS system for the non-invasive identification of pigments in different binders in the 360-1000 nm spectral range.

Other additional value is that the spectra were acquired with a miniaturized and low cost FORS system designed for portable field use. Its small dimensions and speed in data collection make this system valuable for professionals involved in art examination in the field.

**Acknowledgments**
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