# Effect of Particle Size on Pigments Colour

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Received 2 February 2016; revised 6 May 2016; accepted 6 May 2016

*Abstract: The historical pigments, contrary to modern ones, are not constituted by particles having all the same size and this influences the colour of the paint layers. The hiding power and colouring power of a pigment depends, in fact, on its particle size. The aim of this study was to evaluate the influence of particle size on optical characterization of paintings in terms of reflection of light and related colour specification. Starting from the qualitative observation, we have attempted to quantify the pigments colour variations induced by grinding and then attributable to granularity. Powdered pigments of principal colours have been selected in specific particle size range by mechanical sieving. The measurements were performed both on pigment pellets and on paintings realized with binder casein. All samples were characterized by an optical and colorimetric point of view through spectrophotometric analysis and for the surface morphological observation through scanning electron microscopy.* © 2016 Wiley Periodicals, Inc. Col Res Appl, 42, 236–243, 2017; Published Online 2 June 2016 in Wiley Online Library (wileyonlinelibrary.com). DOI 10.1002/col.22062

*Key words: particle size; pigments; colour; spectrophotometric analysis; SEM observations*

## INTRODUCTION

The relationship between colour and particle size is well known, and it is the object of many studies in several fields including food,[1] inks,[2] sediments,[3] and teeth.[4]

The particle size of pigments[5] is relevant for the conservation and restoration of polychrome artefacts in terms of its role in colour changes. The knowledge of the optical characteristics of pigments used by craftsman in earlier times represents an important starting point for the study and characterization of paintings. In ancient time, the pigments, depending on their nature, were often used in the form of powder with particles that, depending on their physical structure, could be distinguished by primary particles, conglomerates and aggregates. The optical properties of a pigment and in particular the hiding power, the tinting strength, and the colour depend on the dimensions and form of its grains. Usually, the pigments show up in the form of conglomerates from which, depending on the grinding degree, particles of different form and dimension are obtained.[6]

The hiding power is the pigment capacity to make opaque the medium in which it is dissolved. The hiding power is proportional to the difference between the refractive index of the pigment and that of the dispersing medium, and it is also in relation to the size and shape of the particles. It is known that for a given size, spherically shaped particles have higher hiding power. The ability of a pigment to impart colour to the medium in which it is applied is called tinting strength. Considering the colour perception, a pigment can be instead defined in terms of hue, brightness and saturation, which are parameters depending on incident light reflection and on selective absorption of different wavelength photons.[7,8] A pigment has a tinting strength and a specific hiding power; however, the degree of fineness can affect the saturation as the amount of white light reflection from its surface is greatly increased relative to the amount of absorbed light.[9]

Unlike the modern ones, the pigments used in the past, ground by hand, were not constituted by particles

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TABLE I. Materials object of the study with the corresponding ID supplier's code, state, colour index and composition.

| | Materials | ID supplier code | State | Colour index | Composition |
|---|---|---|---|---|---|
| **BLUE** | Azurite natural standard | K10200 | Powder 0-120 $\mu$m | PB 30.77420 | $2CuCO_3 \cdot Cu(OH)_2$ |
| | Cobalt blue pale | K45714 | Powder | PB 28.77346 | $CoAl_2O_4$ |
| | Indigo pale blue | K36005 | Powder | NB 1.75780 | Precipitated with $Al(OH)_3$ |
| | Lapis Lazuli | K10520 | Powder | PB 29.77007 | $Na_2O \cdot 3Al \cdot 6SiO_2 \cdot 2Na_2S$ |
| **GREEN** | Chrysocolla | K10350 | Powder | PB 31.77437 | $CuSiO_3$ |
| | Malachite natural | K10300 | Powder 0-120 $\mu$m | PB 30.77420 | $2CuCO_3 \cdot Cu(OH)_2$ |
| | Green earth | K17400 | Powder | PG 23.77009 | Al, K, Mg, Ca, and Fe silicates |
| | Viridian green | K44250 | Powder | PG 18.77298 | $Cr_2O_3 \cdot 2H_2O$ |
| **RED** | Red bole | ZC0009 | Powder | PR 102.77015 | Natural earth |
| | *Caput mortuum reddish* | K48700 | Powder | PR 101.77491 | Natural iron oxide |
| | Sinopia | ZC0008 | Powder | PR 102.77491 | Natural earth |
| **YELLOW** | French ochre JCLES | K40040 | Powder | PY 43.77492 | $SiO_2 + Al_2O_3 + Fe_2O_3$ |
| | Yellow ochre | ZC0784 | Powder | PY 43.77492 | Natural earth |
| | Raw Sienna | K40400 | Powder | PY 43.77492 | Natural earth |

having all the same dimensions. Depending on the particle size, it can be distinguished as 'fine grain' pigments with dimensions of grains smaller than 1 μm, 'medium grain' if the dimensions fall within the range between 1 and 10 μm, and 'coarse grain' if they are constituted by particles with diameter greater than 10 $\mu$m. The particle dimensions of the most used artistic pigments cover a range from 30 to 40 $\mu$m with some larger or smaller particles. The dimension of the particles determines smoothness, gloss and uniformity of the paint layer. Pigments consisting of coarse grain particles induce very saturated colour but have poor hiding power unlike those with fine grain, which instead have greater hiding power. In a film that consists of pigments mixed with a binder there are larger and irregular particles. Indeed, the light easily penetrates through the different paint layers, and then, the contribution of the support to the light reflected is greater. Instead, for some pigments, very thin and homogeneous grains have good hiding power, but little tinting strength. This evidence is not generally applicable, in fact, for other pigments, as colour saturation is not decreased by the grinding and they maintain both a good hiding power and a good tinting strength even in the case of smaller particles.[9]

Since the Middle Ages, artists are concerned with the problem of which is the more suitable particle size for paint. As written in important medieval treatises, the blue and green pigments have the property of changing colour, the latter becoming less intense as they were ground.[10]

This study is aimed to confirm that the particle size is an important parameter in the colour specification of historical pigments, above all for chromatic changes evaluation. Colours and pigments manufacturers do not pay specific attention to this aspect in the formulation of the pigments most used in the olden time and useful to conservation and restoration purposes.

The specific objective of the work was to investigate by visible spectrophotometry, a not invasive and non destructive technique, the optical characteristics of historical pigments of principal hues. The main attention is paid to spectral reflectance factor (SRF%) behaviour changes varying the particle size with specific attention to the related chromatic differences evaluation.

## MATERIALS AND METHODS

### Pigments

The natural and synthetic inorganic pigments listed in Table I are selected for the study because their use is documented in historical fonts and in restoration manuals.[11–17] The blue indigo natural organic dye was also studied because it is widely used by painters in the past.

The materials used in this study have been prepared by the Kremer[18] and Zecchi[19] companies, and were formulated according to old recipes. The pigments used in the past, in fact, are usually prepared through grinding, calcinations and natural and vegetal elements cooking.[10] Only cobalt blue and viridian green have been synthetically prepared.[20,21]

The materials examined in this work are representative of the main hue of the artist's palette and are listed in Table I along with the corresponding ID supplier's code, the state, the colour index and the composition. The ID code Z or K indicates whether the material was supplied by Zecchi and Kremer. They were in the form of powder, the dimension range was sometimes indicated by the suppliers (Table I).

In general, the procedure adopted for the particle size pigments selection includes a first step of grinding in agate mortar to simplify the second step of mechanical sieving by stainless steel mesh of different sizes.

For each pigment, besides the sample 'as is' (size 0), the samples were obtained with a particle size in the ranges listed below and renamed according to the laboratory procedure:

- Size 0: mixed grain
- Size 1: $45 < \Phi < 75$ $\mu$m
- Size 2: $38 < \Phi < 45$ $\mu$m
- Size 3: $20 < \Phi < 38$ $\mu$m
- Size 4: $\Phi < 20$ $\mu$m

There was no case in which the powder particle size greater than 75 $\mu$m was obtained. For some pigments (cobalt blue pale, chrysocolla, and indigo pale blue), the material provided by the companies did not allow to select the entire first particle size range indicated.

The pigments were examined both in the form of pellets and in the form of paints. The pellets were obtained for all samples under hand pressure of the powder to avoid any change of orientation, space and then colour. For all paints, casein (ID code Z2050) was used. This historical binder[11] is a phosphoprotein obtained from milk in the form of colloidal dispersion. The pigment powder is mixed with the casein in a ratio respectively of 1: 3 and the mixture was then painted on canvas prepared using synthetic gypsum (ID code Z4700).[19]

### Spectrophotometric Analysis

To investigate the relationship between the optical properties of the pigments analyzed and the grain size, this study was carried out with the aim of highlighting any changes on the SRF factor in the paint layer and in the pellet obtained with the different size classes selected from each pigment.

The analysis was conducted using a Konica Minolta spectrophotometer, model CM-2600d with measurement geometry *d*/8°, selecting an area of 6 mm in diameter (small average value [SAV]). The results are reported for to 10° standard observer, and the D65 illuminant was selected. The values were obtained from repeated measures (five different acquisitions) and the elaboration regarded SPEX/100 data (SPecular component EXcluded and UV included). The acquisition step was made with the SpectraMagic® software, whereas Origin® software (OriginPro 8) was used for data processing. The PH3DRA laboratories routine protocol[22] was used for spectrophotometric measurements by selecting homogeneous areas both on painted layer and on pellet. In the latter case, the measurement was made using the CM-A149 Dust Cover Set to protect the integrating sphere, ensuring at the same time the optical contact between the spectrophotometer and the sample.

The scale adjustment was carried out using a simulating perfect reflective standard as a reference for the maximum brightness 'white standard' (CM-A145) and a black box that simulates a body perfectly absorbent as 'black standard' (CM-A032).[23]

The results were elaborated with attention to the values of SRF% versus wavelength in blue (400–500 nm), green (500–600 nm), and red (600–700 nm) regions and the chromaticity coordinates in the CIELAB space of the both planes ($a^*$,$b^*$) and ($C^*$,$h$). Starting from the coordinates $a^*$ and $b^*$, the change of colour was quantified by the coordinates chroma $C^*$ $\{C^* = [(a^*)^2 + (b^*)^2]^{1/2}\}$ and hue angle $h$ $[h = \tan^{-1}(b^*/a^*)]$ because these cylindrical coordinates allow to better evaluate the colour differences. In fact, in ($C^*$, $h$) plane, the simultaneous control of the hue (linked to $h$) and colour saturation (linked to $C^*$) variations is possible.

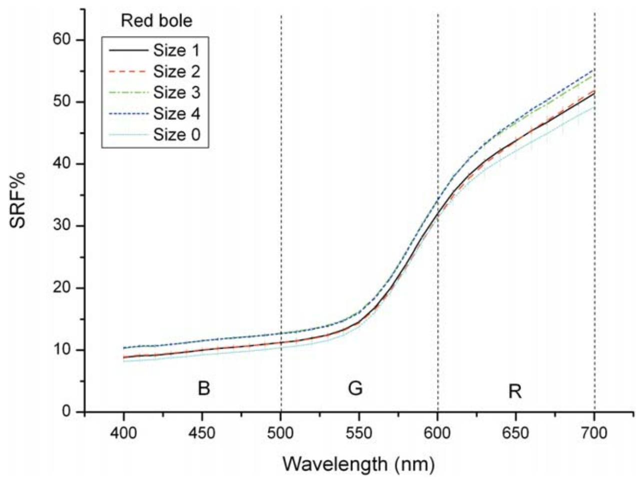


Fig. 1. The trend of spectral reflectance factor (SRF%) obtained for the red bole pigment.

The value of chroma $C^*$ is 0 at the center and increases according to the distance from the center. Hue angle $h$ is defined as starting at the $+a^*$ axis and is expressed in degrees: 0° would be $+a^*$ (red), 90° would be $+b^*$ (yellow), 180° would be $-a^*$ (green), and 270° would be $-b^*$ (blue).

### Morphological Observations

The colour of paint depends on the different spatial orientation of the pigment particles and by their shape. In fact, the average position of the first reflecting face of the grains is decisive for the light reflection. To link the spectrophotometric results and the influence of grain size in appearance of paintings obtained by different pigments mixed with a fixed binder ratio, morphological observations by scanning electron microscopy (SEM) were performed. The shape of pigment grains and their arrangement in the dry paint were observed through Zeiss Gemini 1530 SEM. The system is equipped with E-T secondary electron and a Schottky field emitter. Accelerating voltage voltage is from 0.2 to 30 kV with 1 nm resolution at 20 kV and 2.1 nm resolution at 1 kV.

## RESULTS AND DISCUSSION

The spectrophotometric measurements, carried out on all pigments listed in Table I, were useful to assess the possible change of optical characteristics varying the particles dimension. The analysis regarded the trend of SRF, for a qualitative influence in the Blue (B), Green (G), and Red (R) regions, and the derivative of SRF, $d$(SRF%), as a function of the wavelength ($\lambda$) for detecting any change of characteristic values of each pigment. The SEM images have the aim to support the assessments made by spectrophotometric study.

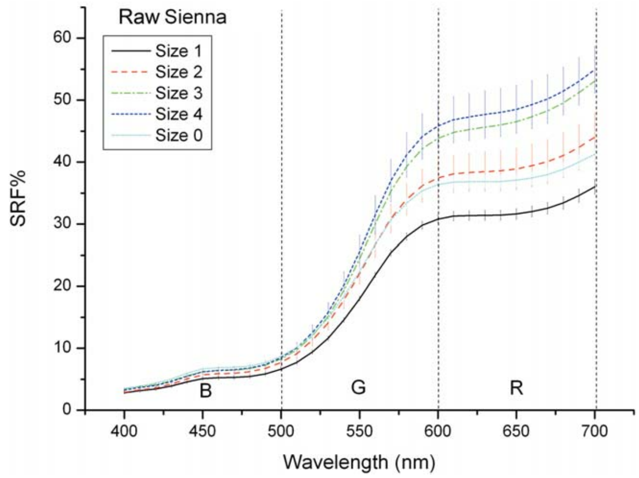


Fig. 2. The trend of spectral reflectance factor (SRF%) obtained for the raw Sienna pigment.

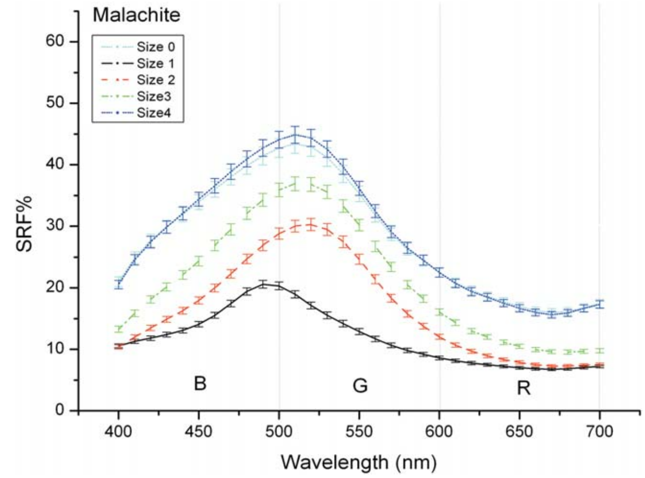


Fig. 4. The trend of spectral reflectance factor (SRF%) obtained for the malachite pigment.

### Spectral Reflectance Factor (%) Analysis

The visible spectrophotometry is a technique of optical investigation based on the measurement of the SRF of the sample analyzed in function of the wavelength (range 400–700 nm) of the incident radiation. The SRF is expressed as the percentage ratio between the intensity of the reflected and the incident radiation.

The SRF% trend as a function of grain size is different for pellets and for painting samples. The general result obtained on pellets for all the analyzed pigments consists in an increase of SRF% with the decrease of particle size. This evidence is shown, for example, for a pigment for each hue in the following figures: the red bole for red (Fig. 1), raw Sienna for the yellow (Fig. 2), the cobalt blue pale for blue (Fig. 3), and the malachite natural for green (Fig. 4) pigments. Instead, in the case of paintings, with the decrease in the particle size, the SRF% values are reduced (Fig. 5).

This general behavior observed was expected in terms of optical changes due to the medium presence. Considering a fixed size fraction, the different behavior is in fact imputable to the presence of a medium in the paintings (casein) with a refractive index much higher than that of air (the 'medium' in pellets).[9]

If you compare the trend of SRF% for paintings obtained with different sized pigment powders (as shown in Fig. 5), we observe a specular behavior with respect to the trend of SRF% of the same pigment in the form of pellets (see Fig. 3).

### Derivative of Spectral Reflectance Factor *d*(SRF%) Analysis

As shown by Bacci *et al.*,[24] to evaluate the colorimetric aspect better, the *extrema* points of the first derivative of the spectral reflectance curve were analyzed. This points were identified starting from $SRF\% = SRF\%(\lambda)$ curves (see Figs. 1–4) after derivative calculation on the $d(SRF\%) = d[SRF\%(\lambda$, where lambda indicates the wavelength in nm,)] trend (Figs. 6–9).

Considering the size 4 ($\Phi < 20$ $\mu$m) as the particle size of reference, the colour changes were evaluated in terms

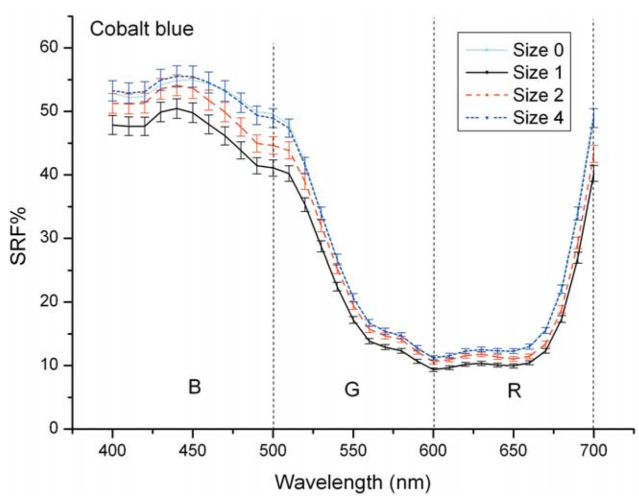


Fig. 3. The trend of spectral reflectance factor (SRF%) obtained for the blue cobalt pigment.

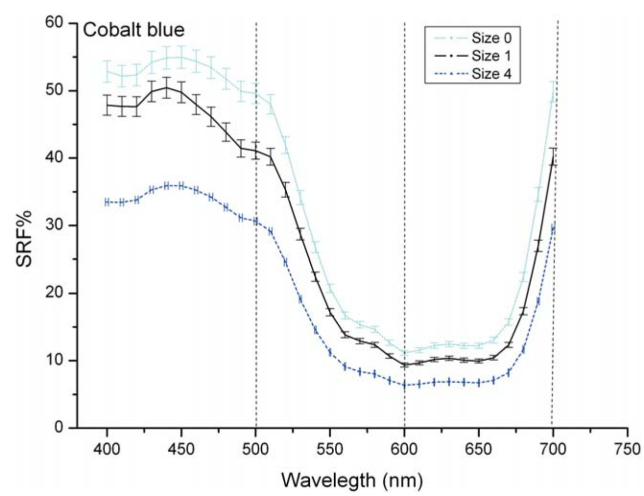


Fig. 5. Reflectance curve for the blue cobalt painting.

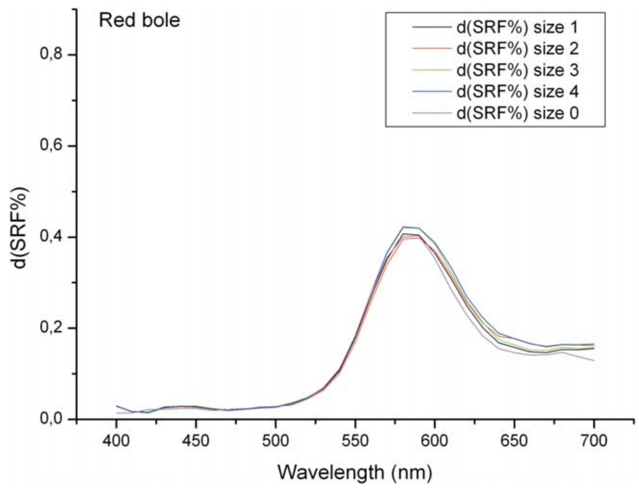


Fig. 6. The trend of derivative *d*(SRF%) obtained for the red bole pigment (*d*/8° – SPEX – SAV – 10°).

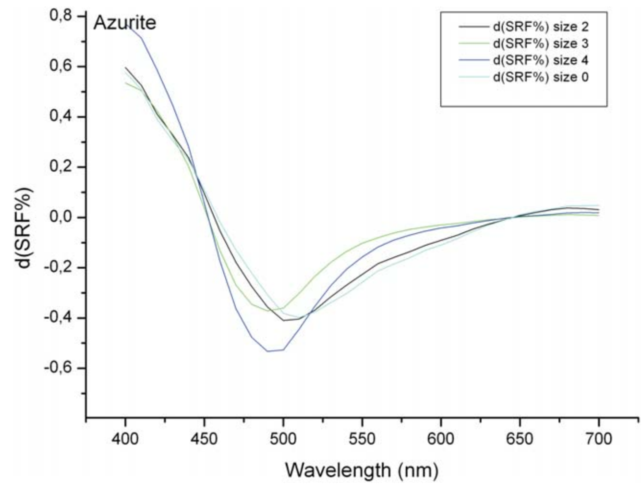


Fig. 8. The derivative *d*(SRF%) obtained for the azurite natural standard pigment (*d*/8° – SPEX – SAV – 10°).

of *extrema* points shift (Table II). As mentioned in the 'Pigments' section, for azurite it was not possible to select sufficient quantities of sample in the particle range size 1.

No shift is detected for the red and yellow pigments. This shows that the colour of the pigments is not substantially modified to vary the size of the grains.

Otherwise, the green and blue pigments, such as malachite natural and azurite, show a little shift when compared with size 0 values (Table II). This evidence suggests that supplied powder before sieving is largely composed of 20 $\mu$m less sized grains. The shift becomes, however, more relevant with respect to size 1 for the malachite natural and to size 2 for the azurite.

The comparison between the SRF of the pigment particle size prior to selection (no grinding) and the SRF of the particle size varies in samples obtained from it (only screening), allowing to assume that the sample on the market is mainly composed of grains $<20$ $\mu$m.

The optical properties changes induced by grinding were individuate thanks to *d*(SRF%) shift values on all pigments and they were quantified considering C* and h variations. According to Hunter *et al*.,[25–27] the value of $\Delta a^*$ and $\Delta b^*$, which is visible to the naked eye, the colour variation is 5. Starting from this consideration, the equivalent values of $C^*$ and $h$ were equal to 7 and 45°, respectively. A colour variation induced by grinding will be significant if $\Delta C^* > 7$ and $\Delta h > 45°$.

The chromatic variations of each pigment were calculated using the powder size 0 as reference because this dimension range corresponds to the product sold by the manufacturer (Table III). In Table III, the values are listed with the size of the considered class given in subscript: for example, $\Delta C_1^*$ and $\Delta h_1$ values correspond to variations of chromatic coordinates of size 1 samples relative to the data of size 0 class.

For all the hues, grinding does not induce changes detectable by the human eye in terms of hue ($\Delta h < 45°$). The same result was obtained for colour saturation of yellow and red pigments ($\Delta C^* < 7$). Otherwise, the pigments green and blue show a significant variation in the

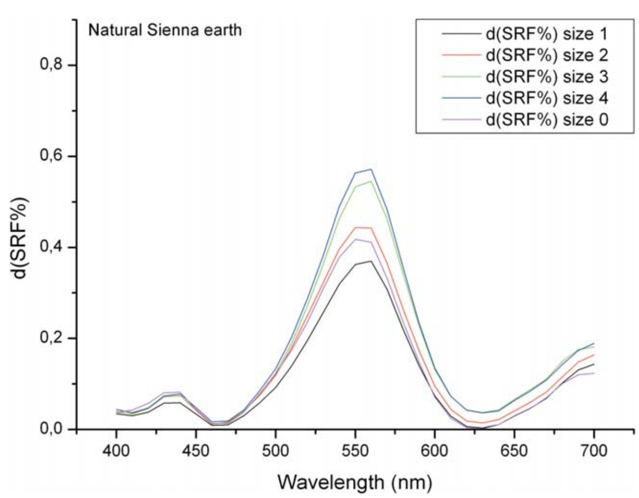


Fig. 7. The derivative *d*(SRF%) obtained for the raw Sienna (*d*/8° – SPEX – SAV – 10°).

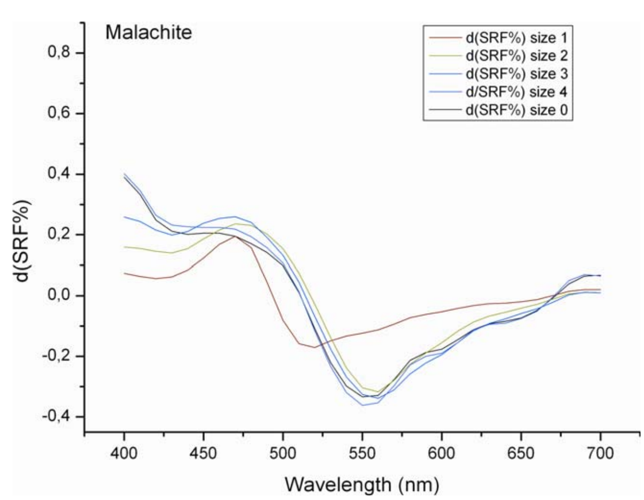


Fig. 9. The derivative *d*(SRF%) obtained for the malachite natural pigment (*d*/8° – SPEX – SAV – 10°).

TABLE II. Zero points position (nm) and its shift with respect to size 4 sample for the pigments shown in Figs. 6–9.

| | | Shift (nm) | | | |
|---|---|---|---|---|---|
| Pigments | *Extrema* point (nm) | Size 0 | Size 1 | Size 2 | Size 3 |
| Red bole | 585 | 0 | 0 | 0 | 0 |
| Raw Sienna | 560 | 0 | 0 | 0 | 0 |
| Azurite natural standard | 458 | −2 | – | −6 | −6 |
| Malachite natural | 510 | 0 | +17 | +7 | +4 |

saturation. These colour changes may be related to the chemical composition and/or to the mineralogy of the pigment.

### Scanning Electron Microscope Observations

SEM is a technique widely used in the field of cultural heritage.[28] In this case, the aim of the SEM observations is the evaluation of the pigment grains spatial distribution in the analyzed paint surface obtained with different grinding. In particular, morphological observations of the surface were made to support the spectrophotometric evidences. The particles distribution in the first paint layer has, in fact, an important role for the specular and diffuse reflection of the light that contribute to the colour perception in a decisive manner.

Scattering of light is closely related to the refractive index changes on the incidence surface. In general, a painting is a rough surface, constituted by pigment grains incorporated in a polymer matrix constituted by the binder. With an equal amount of binder, if the grains size are small, the painting appears smoother and more homogeneous when compared with one in which the grains are larger. Therefore, the larger the pigment grains, more optically inhomogeneous is the painting surface. This means an increased diffuse reflection of the incident light when compared with the specular one.

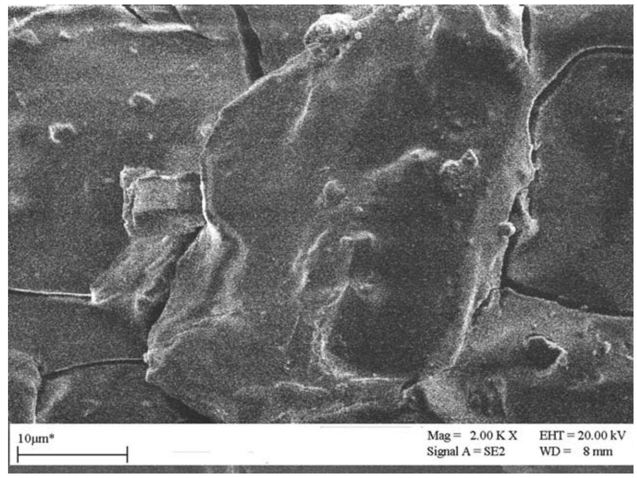


Fig. 10. Morphological observation of malachite natural paint sample (size 1).

SEM observations showed the difference among the paintings obtained with different grain-sized samples with a constant binder–pigment ratio. The painting sample of malachite natural is reported in Figs. 10–13, which show the difference due to the dimension grain. The size 1 samples have a more indented surface, and this leads to a light with more diffuse reflection and a greater SRF%. The different optical behavior is then imputable to grain size.

## CONCLUSIONS

The optical and colorimetric characteristics of yellow, red, blue, and green pigments, of different particle sizes, were investigated by spectrophotometric analysis. The grain size selection methods were represented by mechanical and manual sieving after grinding in agate mortar of pigment powders.

Spectrophotometry is an ideal methodology for painting characterization because it is a non-invasive and non-destructive technique. This study assessed the relationship

TABLE III. Chromatic changes $\Delta C^*$ and $\Delta h$ calculated for the pigments studied.

| Hue | Pigments | $\Delta C^*_1$ | $\Delta h_1$ | $\Delta C^*_2$ | $\Delta h_2$ | $\Delta C^*_3$ | $\Delta h_3$ | $\Delta C^*_4$ | $\Delta h_4$ |
|---|---|---|---|---|---|---|---|---|---|
| **BLUE** | Azurite natural standard | – | – | −3.50 | −7.81 | −7.52 | −12.00 | −2.38 | 7.83 |
| | Cobalt blue pale | 0.38 | −5.55 | 0.38 | −4.21 | – | – | −0.04 | −1.56 |
| | Indigo pale blue | −0.46 | −32.60 | – | – | – | – | −1.67 | −29.60 |
| | Lapis Lazuli | 7.79 | 1.58 | 7.99 | 4.78 | 9.03 | 5.60 | 0.52 | 0.35 |
| **GREEN** | Chrysocolla | 0.31 | −24.64 | – | – | 3.17 | −1.03 | 0.16 | 0.93 |
| | Malachite natural | 3.90 | −9.60 | −7.41 | 14.18 | −6.21 | 10.27 | −1.47 | 1.17 |
| | Green earth | 0.49 | 3.68 | −0.24 | 3.44 | −0.83 | −7.82 | −1.10 | −0.04 |
| | Viridian green | 2.06 | −1.10 | 2.20 | −3.03 | 2.57 | −1.26 | 1.56 | −1.91 |
| **RED** | Red bole | 1.68 | 0.37 | 1.29 | 1.01 | 2.02 | 0.97 | 1.86 | 1.50 |
| | *Caput mortuum reddish* | 0.52 | −2.03 | −0.43 | −0.43 | −0.14 | −2.52 | −3.14 | −3.68 |
| | Sinopia | −0.79 | −0.19 | 2.80 | 2.35 | −0.57 | 0.60 | −1.53 | −0.06 |
| **YELLOW** | French ochre JCLES | 0.75 | 0.16 | −1.10 | 2.56 | −1.41 | 3.02 | 1.76 | 2.82 |
| | Yellow ochre | 1.47 | 0.51 | 1.70 | 0.40 | 1.40 | 0.21 | 1.98 | 0.17 |
| | Raw Sienna | 2.78 | 1.15 | −2.64 | 0.60 | −5.24 | 1.86 | −4.89 | 1.57 |

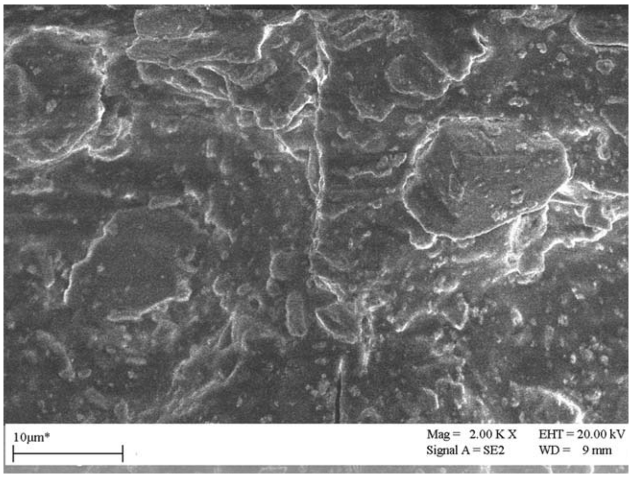


Fig. 11. Morphological observation of malachite natural paint sample (size 2).

between the particle size and the optical behavior of different pigments in terms of SRF% trend. Measurements were performed on different particle size classes in the form of pellets and of paintings made with casein.

The results obtained on the pellets showed for all analysed pigments an increase of SRF% with decreasing particle size. In contrast, the painting samples show an opposite trend because with the increase of the particle size, the SRF% values also increase.

The spatial distribution of grains in the surface layer of painting is observed through SEM to support the results obtained by spectrophotometric study. The different optical behavior of paintings depends on orientation and distribution of grains in painted layer.

The influence of grain size on the colour pigment was also quantified by studying the trend of the first derivative of the SRF% curve and by calculating colour differences $\Delta C^*$ and $\Delta h$. The data obtained confirm that yellow and red pigments are not affected by grinding degree, whereas green and blue lose their colour when ground too finely. This influence regards the colour saturation; in fact, green and blue are desaturated in finest sized classes. These evaluations will be further investigated considering the results also in terms of chemical composition of pigments belonging to the same hue class.[29]

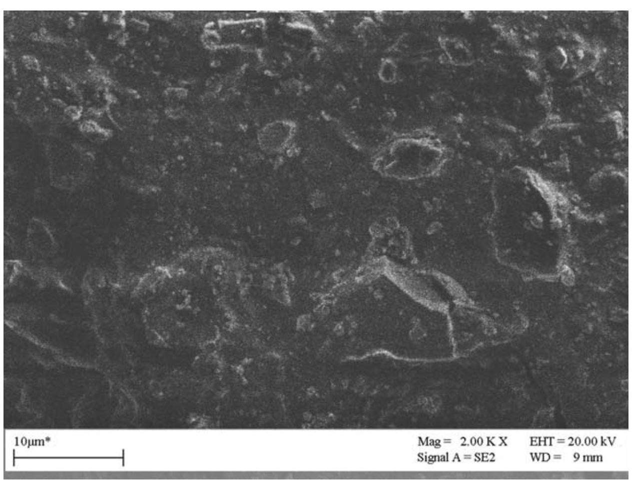


Fig. 12. Morphological observation of malachite natural paint sample (size 3).

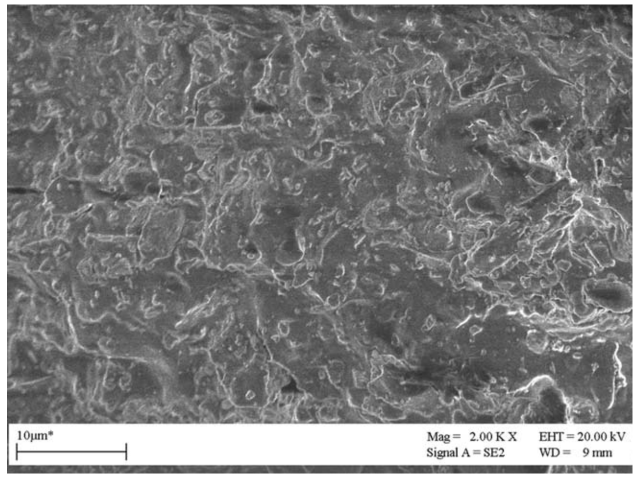


Fig. 13. Morphological observation of malachite natural paint sample (size 4).

## ACKNOWLEDGMENTS

The authors would like to thank professor Claudio Oleari for his permanent support, stimulating discussions and valuable suggestions. Thanks to Dr. Giuseppe Sciuto of CTM 8 Physics Laboratory of STMicroelectronics for the SEM observations.

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