# Glazing over grisaille. A multi-band record of pigmented and dyed oil glazes

Aránzazu Llácer-Peiró[3], Serena Hirsch[4], M. Antonia Zalbidea-Muñoz[2], Miquel Àngel Herrero-Cortell [1], Laura Fuster-López[3]

[1] *Departamento de Comunicación Audiovisual, Documentación e Historia del Arte, UPV*

[2] *Departamento de Conservación y Restauración de Bienes Culturales, UPV*

[3] *Instituto Universitario de Restauración del Patrimonio*

[4] *Centro Conservazione e Restauro "La Venaria Reale"*

*Corresponding author: Miquel Àngel Herrero-Cortell*

**ABSTRACT**

The present paper addresses the visual and technical study of historical glazes, both organic and inorganic, applied over monochrome grisaille. These glazes were commonly used in painting between the 15th and 17th centuries. The aim of this work is to record the behaviour of these materials when applied as glazes over grisaille (grey tones underneath), as their diverse nature gives very different results. In order to carry out this evaluation, two mock-up panels were prepared in which a wide range of greys were created using lead white and lamp black in varying proportions.

These grisailles served as a base for the application of 32 glazes made with different pigments, lakes and dyes, allowing for a variety of chromatic nuances that made it possible to evaluate material, visual or perceptual aspects. Along the paper, it is possible to observe how glazes can alter, modulate or accentuate the underlying colour, and vice versa, how the underlying colour can affect the appearance of the glaze (not only in the visible band, but also in the UV and IR bands). These mock-ups were created using already obsolete techniques and materials, with the aim of replicating the painting processes of the 15th to 17th centuries with the greatest possible methodological fidelity. This approach allowed the results of the application of glazes to the underlying grisaille to be evaluated visually and empirically.

The resulting layers of paint were characterised in two ways: by colorimetric measurements and by imaging in the visible, UV and IR bands using a multi-modal approach (VIS, UVL, UVR, IR, IRFC). This article is part of a broader research project that includes other works derived from the study of glazes as the focus of its field of study [1].

**KEYWORDS** Glazes, grisailles, multi-band technique, pigments, colorants.

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## 1. Introduction

The grisaille technique appeared in the Middle Ages to create three-dimensional and volumetric effects in figures and representations and remained popular until the 18th century. Although initially associated with black-and-white painting, from the 15th century onwards, it was used as a tonal primer for fully colouristic paintings, using only one white and one black pigment. Sometimes, however, it involved a very subtle use of colour to lightly tint the gradiations of grey. This method, carried out in several stages, involved the application of glazes or translucent layers of colour over a black and white model (hereafter referred to as grisaille) to define both the shadow and light areas. (Mayer, 1985; Villarquide, 2004; Zalbidea, 2014). The result is the product of the gradual chromatic layering of glazes (Torres, 2015). References to this painting technique can be found in various sources and treatises. For example, both Leon Battista Alberti (1434) and Giovanni Battista Armenini (1586) refer to this technique in their respective treatises on painting. Alberti claims that: "…with white and black, light and shade are expressed in painting, and the other colours become the matter to which the various accidents of brightness or darkness are added" (Alberti, 1435 [according to the edition by Rejón de Silva, 1784, p. 245]). On the other hand, Armenini in *De' veri precetti della pittura* [1586] expands on this concept, stating that: "by virtue of white and black, which create the species of these colors, one draws out everything that is necessary." (Armenini, 1999, pp. 84-85).

## 2. Materials and methods

The samples were prepared using techniques and materials that faithfully reproduce the painting processes used in the centuries under study. Two panels were prepared with different shades of grey, obtained by mixing lead white and vine black in different proportions.

A total of 32 glazes were applied on two panels over a monochrome grisaille ground (Figures 1 and 2). The support used consisted of two panels measuring 35 x 35 cm, prepared with a ground of gypsum, calcium carbonate, and rabbit-skin glue (Santos, 2005). The grisaille paintings on which the glazes were applied were created by combining lead white and lamp black, bound with linseed oil and mixed in various proportions to obtain a wide range of greys. All the pigments were bound according to historical procedures obtained from original sources. The pigments used in the grisaille (white and black) and the pigments, lakes, and dyes used in the glazes, are listed in Table 1.

At the top of each test panel, an area without any glaze application was left to serve as a control for comparison ("Register"). The pigments, dyes, and lakes used in the glazes were bound with a medium composed of linseed oil and mastic resin, which ensures a suitable balance between absorption and drying, thereby achieving the desired visual effect (Bomford et al., 1995; Zalbidea, 2014).

The varnish used as a medium was prepared with a ratio of two parts linseed oil to one part mastic resin, following the recipe of the monk Theophilus (12th century) as described in his treatise "De diversis artibus" (Dodwell, 1961); this recipe has been reproduced by Zalbidea Muñoz et al. (2022), and by Zalbidea Muñoz and Giner (2017).

Regarding the inorganic pigments, those that are more transparent to create translucent layers have been chosen. The selected dyes and lakes generally have a translucent quality, making them ideal for use as glazes, while other pigments with an opaque nature or with high hiding power were not considered. Taken together, the selected materials form a basic palette that woudl have been used from the 15th to the 17th century.

**Table 1. Pigments, colorants and lakes used for the grisailles**

| Nº | Pigment | Company | Reference |
|---|---|---|---|
| | **GLAZES** | | |
| 1 | Lead white | Kremer | 46000 |
| 2 | Reseda | Kremer | 36262 |
| 3 | Lead tin yellow | Kremer | 10100 |
| 4 | Saffron | Artisanal production | |
| 5 | Yellow ochre | Kremer | 40010 |
| 6 | Aloe | Kremer | 38010 |
| 7 | Stil de grain | Kremer | 37394 |
| 8 | Minium | Kremer | 42500 |
| 9 | Madder Lake Coral | Kremer | 372051 |
| 10 | Dark brown madder lake | Kremer | 372141 |
| 11 | Carmine naccarat | Kremer | 42100 |
| 12 | Cochineal+soda carbonate | Artisanal production | |
| 13 | Cochineal+alum + soda carbonate | Artisanal production | |
| 14 | Cochineal+alum+sodium bicarbonate | Artisanal production | |
| 15 | Blue Bice | Kremer | 10184 |
| 16 | Azurite | Kremer | 10200 |
| 17 | Ultramarine blue | Kremer | 10510 |
| 18 | Esmalt | Kremer | 10000 |
| 19 | Indigo | Kremer | 36002 |
| 20 | Pastel blue | Artisanal production | |
| 21 | Copper acetate + reseda | Artisanal production | |
| 22 | Copper acetate | Kremer | 44450 |
| 23 | Chrysocolla | Kremer | 10350 |
| 24 | Malachite | Kremer | 10310 |
| 25 | Sap green | Artisanal production | |
| 26 | Celadonite | Kremer | 11010 |
| 27 | Ochre havane | CTS | 275 |
| 28 | Van Dyck brown | CTS | 9260 |
| 29 | Dark purple madder lake | Kremer | 37218 |
| 30 | Vivianite | Kremer | 104000 |
| 31 | Bitumen | | |
| 32 | Atramentum | Kremer | 12030 |
| | **MONOCHROMATIC BASES** | | |
| | **Pigment** | **Company** | **Reference** |
| | Lead white | Kremer | 46000 |
| | Vine Black, German | Kremer | 47000 |

*Table 1. Pigments, dyes and lakes used in the grisailles*

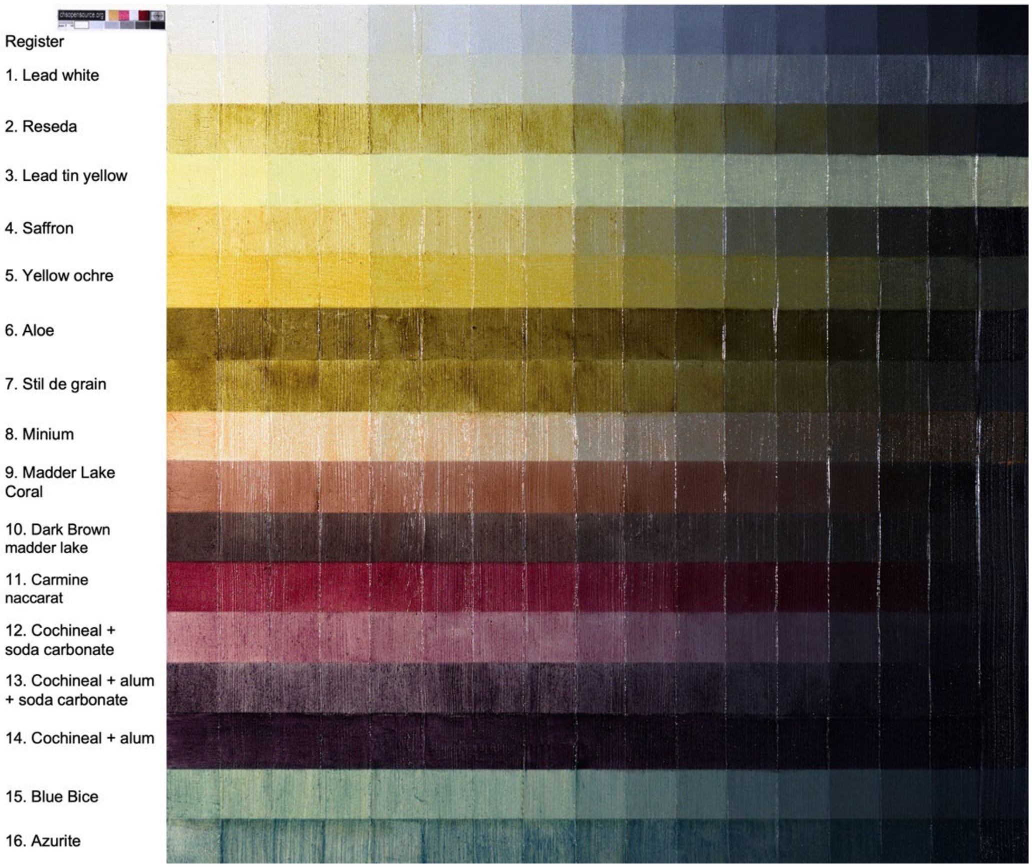


*Fig 1. Visible image (VIS) of Test Panel 1.*

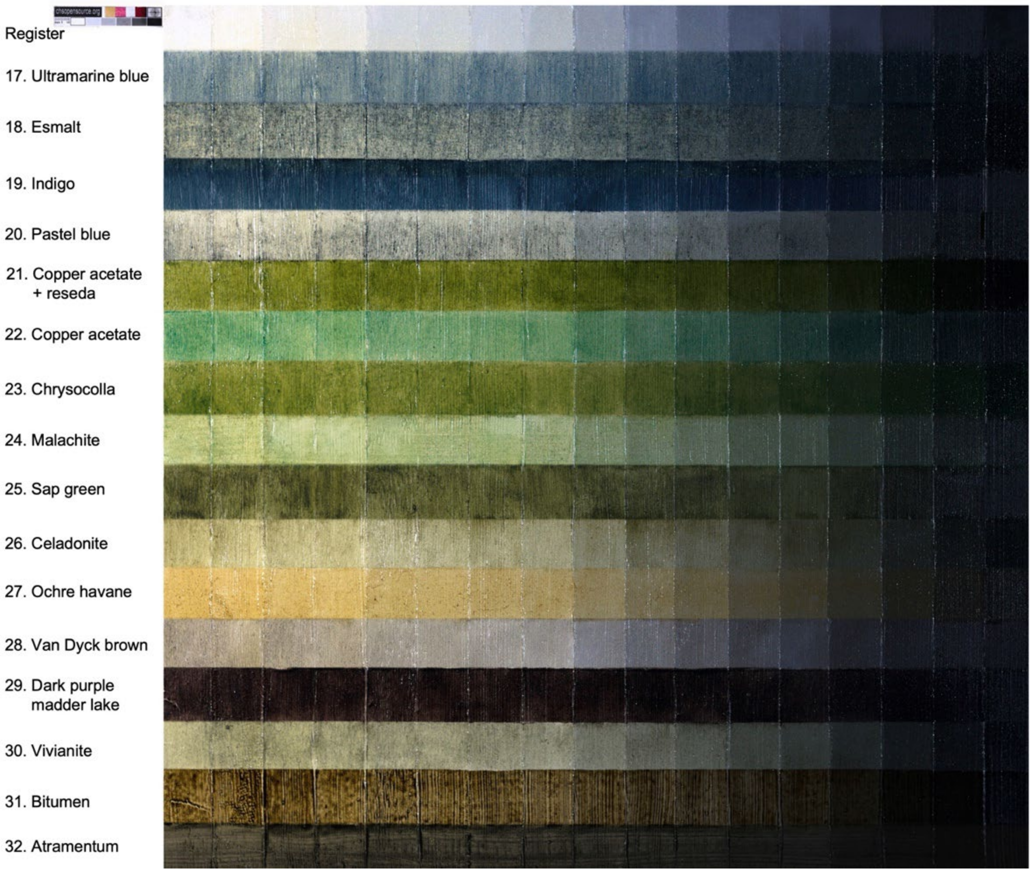


*Fig 2. Visible image (VIS) of Test Panel 2.*

It was found that the quantification of the mixtures of varnishes, pigments, and dyes with the binder is extremely complex due to the influence of environmental conditions on the result. They were worked and adjusted on the palette to obtain the right fluidity and opacity, avoiding excess oil and ensuring that the pigment did not overly cover the underlying grisaille too much. This experimental phase was mainly based on sensory perception and organoleptic evaluation, considering factors such as colour, the rheological behavior of the paint, and its handling properties.

The characterisation of these glazes has been approached using non-invasive techniques such as colorimetry and multi-band imaging technique. Surface microscopy and FORS spectroscopy were also performed, the results of which are not included in this article. Colorimetry allows for the quantitative, numerical, and objective characterisation of the properties of a colour based on three parameters: hue, lightness, and saturation (Salinas and Hatchondo, 2005). The exact chromatic composition of the glazes was recorded through colorimetric analysis. This digitisation system is as a fundamental tool in the strategies for the conservation and dissemination of cultural heritage, as it allows the identification and monitoring of the chromatic changes that materials undergo due to different factors (Pereira, 2018).

The measurements were conducted using the i1Pro X-Rite® spectrophotometer with D50 illumination, in accordance with the CIE 015:2018 standard, which has long been widely recognized and adopted, particularly in the field of graphic arts, as a reference standard. [2]. The measurement area diameter was 4.5 mm, without a specular component (SCE), in CIELab space. The data were captured using the i1Profiler® v1.8.2 software. Three measurements were taken per area, and the results were averaged (Table 2 and 3).

| **Colorimetric data of TEST PANEL 1** | | | | | | |
|---|---|---|---|---|---|---|
| Colorant, pigment, lake | Slab area | **L*** (brightness) | **a*** (positive value = degree of red negative value = degree of green) | **b*** (positive value = degree of yellow negative value = degree of blue) | **C*** CROMA (saturation) | **hº** (tone) |
| Register | 1 | 92 | -0,11 | 17,84 | 17,84 | 90,36 |
| | 2 | 70,7 | -2,31 | 2,8 | 3,63 | 129,55 |
| | 3 | 28,76 | -0,53 | -1,48 | 1,57 | 250,34 |
| 1. Lead white | 1 | 91,17 | 0,29 | 23,81 | 23,81 | 89,3 |
| | 2 | 72,01 | -3,17 | 9,98 | 10,47 | 107,61 |
| | 3 | 42,81 | -2,06 | 0,35 | 2,09 | 170,44 |
| 2. Reseda | 1 | 83,91 | 2,66 | 46,9 | 46,98 | 86,75 |
| | 2 | 60,65 | 2,05 | 40,91 | 40,96 | 87,13 |
| | 3 | 28,98 | -0,68 | 6,5 | 6,53 | 95,95 |
| 3. Lead tin yellow | 1 | 89,4 | -2,56 | 45,47 | 45,54 | 93,23 |
| | 2 | 75,89 | -6,15 | 29,91 | 30,54 | 101,62 |
| | 3 | 61,34 | -5,9 | 20,14 | 20,99 | 106,34 |
| 4. Saffron | 1 | 85,04 | 6 | 47,1 | 47,48 | 82,74 |
| | 2 | 65,09 | 1,78 | 34,21 | 34,26 | 87,02 |
| | 3 | 20,34 | -1,38 | 6,5 | 6,65 | 101,97 |
| 5. Yellow ochre | 1 | 83,72 | 9,29 | 52,92 | 53,73 | 80,04 |
| | 2 | 66,13 | 3,95 | 39,74 | 39,93 | 84,33 |
| | 3 | 32,79 | -1,3 | 13,2 | 13,27 | 95,63 |
| 6. Aloe | 1 | 54,51 | 16,47 | 51,01 | 53,61 | 72,11 |
| | 2 | 44,19 | 10,87 | 40,17 | 41,61 | 74,86 |
| | 3 | 17,88 | 1,31 | 9,58 | 9,67 | 82,22 |
| 7. Stil de grain | 1 | 65,59 | 14,37 | 54,65 | 56,5 | 75,27 |
| | 2 | 48,75 | 11,37 | 36,61 | 38,33 | 72,75 |
| | 3 | 24,8 | 1,14 | 7,31 | 7,4 | 81,16 |
| 8. Minium | 1 | 85,67 | 10,5 | 30,95 | 32,68 | 71,26 |
| | 2 | 66,11 | 3,59 | 17,35 | 17,72 | 78,32 |
| | 3 | 29,27 | 7,52 | 10,09 | 12,58 | 53,29 |
| 9. Madder Lake Coral | 1 | 67,62 | 23,65 | 27,32 | 36,14 | 49,12 |
| | 2 | 52 | 17,67 | 18,75 | 25,76 | 46,69 |
| | 3 | 16,72 | 4,57 | 4 | 6,07 | 41,15 |
| 10. Dark brown madder lake | 1 | 41,33 | 20,15 | 14,54 | 24,85 | 35,82 |
| | 2 | 42,2 | 10,81 | 9,97 | 14,7 | 42,69 |
| | 3 | 20,41 | 5,97 | 3,52 | 6,93 | 30,51 |
| 11.Carmine naccarat | 1 | 50,01 | 48,59 | 18,63 | 52,04 | 20,97 |
| | 2 | 39,35 | 36,78 | 10,09 | 38,14 | 15,34 |
| | 3 | 15,71 | 10,48 | 2,07 | 10,69 | 11,16 |
| 12.Cochineal + soda carbonate | 1 | 69,38 | 24,15 | 13,71 | 27,77 | 29,58 |
| | 2 | 56,93 | 13,87 | 5,54 | 14,94 | 21,77 |
| | 3 | 18,42 | 4,07 | -0,47 | 4,1 | 353,38 |
| 13.Cochineal + alum + soda carbonate | 1 | 44,73 | 19,63 | 3,74 | 19,98 | 10,78 |
| | 2 | 42,75 | 11,68 | 0,58 | 11,69 | 2,82 |
| | 3 | 14,53 | 3,63 | -1,1 | 3,79 | 343,19 |

| Colorimetric data of TEST PANEL 1 | | | | | | |
|---|---|---|---|---|---|---|
| Colorant, pigment, lake | Slab area | L* (brightness) | a* (positive value = degree of red negative value = degree of green) | b* (positive value = degree of yellow negative value = degree of blue) | C* CROMA (saturation) | hº (tone) |
| 14.Cochineal + alum + sodium bicarbonate | 1 | 31,9 | 26,34 | -0,07 | 26,34 | 359,83 |
| | 2 | 23,34 | 19,34 | -0,93 | 19,36 | 357,23 |
| | 3 | 14,74 | 4,34 | -1,38 | 4,55 | 342,32 |
| 15.Blue Bice | 1 | 73,56 | -12,38 | 16,34 | 20,5 | 127,14 |
| | 2 | 63,96 | -9,25 | 8,85 | 12,8 | 136,29 |
| | 3 | 28,44 | -3,53 | 0,06 | 3,53 | 178,98 |
| 16.Azurite | 1 | 76,45 | -8,27 | 13,41 | 15,75 | 121,66 |
| | 2 | 51,06 | -12,54 | 2,78 | 12,85 | 167,51 |
| | 3 | 22,96 | -5,22 | -1,83 | 5,53 | 199,34 |

*Table 2. Colorimetric data obtained from Test Panel 1.*

| Colorimetric data of TEST PANEL 2 | | | | | | |
|---|---|---|---|---|---|---|
| Colorant, pigment, lake | Slab area | L* (brightness) | a* (positive value = degree of red negative value = degree of green) | b* (positive value = degree of yellow negative value = degree of blue) | C* CROMA (saturation) | hº (tone) |
| Register | 1 | 90,93 | -0,34 | 15,19 | 15,2 | 91,29 |
| | 2 | 70,11 | -2,31 | 3,51 | 4,2 | 123,42 |
| | 3 | 29,26 | -0,6 | -0,47 | 0,76 | 218,21 |
| 17. Ultramarine blue | 1 | 65,54 | -6,95 | 9,54 | 11,8 | 126,07 |
| | 2 | 52,94 | -7,22 | 2,78 | 7,74 | 158,97 |
| | 3 | 21,33 | -2,08 | 0,01 | 2,08 | 179,86 |
| 18. Esmalt | 1 | 61,71 | -4,11 | 15,71 | 16,23 | 104,67 |
| | 2 | 49,22 | -5,02 | 4,89 | 7,01 | 135,79 |
| | 3 | 19,71 | -1,73 | 0,87 | 1,94 | 153,31 |
| 19. Indigo | 1 | 32,78 | -7,73 | -4,19 | 8,8 | 208,48 |
| | 2 | 32,46 | -6,35 | -0,65 | 6,38 | 185,85 |
| | 3 | 23,22 | -0,64 | -1,81 | 1,92 | 250,58 |
| 20. Pastel blue | 1 | 77,31 | -1,64 | 23,25 | 23,31 | 94,04 |
| | 2 | 63,88 | -3,3 | 9,49 | 10,04 | 109,16 |
| | 3 | 23,25 | -1,17 | 1,24 | 1,71 | 133,33 |
| 21. Copper acetate + reseda | 1 | 62,45 | -5,03 | 49,15 | 49,41 | 95,84 |
| | 2 | 45,29 | -8,09 | 42,46 | 43,22 | 100,79 |
| | 3 | 12,2 | -3,96 | 12,08 | 12,71 | 108,14 |
| 22. Copper acetate | 1 | 62,92 | -22,4 | 33,82 | 40,57 | 123,53 |
| | 2 | 54,24 | -17,87 | 24,15 | 30,04 | 126,49 |
| | 3 | 17,76 | -6,54 | 4,44 | 7,91 | 145,86 |
| 23. Chrysocolla | 1 | 59,85 | -9,48 | 41,93 | 43 | 102,74 |
| | 2 | 51,03 | -9,14 | 33,58 | 34,8 | 105,23 |
| | 3 | 21,63 | -9,55 | 12,06 | 15,38 | 128,38 |
| 24. Malachite | 1 | 71,23 | -9,27 | 37,76 | 38,89 | 103,8 |
| | 2 | 62,14 | -8,56 | 21,85 | 23,46 | 111,39 |
| | 3 | 28,07 | -3,71 | 5,18 | 6,37 | 125,6 |
| 25. Sap green | 1 | 56,7 | 1,23 | 35,65 | 35,67 | 88,03 |
| | 2 | 42,79 | -0,66 | 24,49 | 24,5 | 91,54 |
| | 3 | 22,87 | -0,48 | 2,99 | 3,03 | 99,07 |
| 26. Celadonite | 1 | 68,02 | 2,17 | 35,68 | 35,75 | 86,52 |
| | 2 | 58,45 | -1,59 | 22,57 | 22,63 | 94,03 |
| | 3 | 21,96 | -1,81 | 5,37 | 5,67 | 108,65 |
| 27. Ochre havane | 1 | 75,93 | 9,12 | 40,62 | 41,63 | 77,34 |
| | 2 | 61,4 | 3,17 | 26,28 | 26,46 | 83,11 |
| | 3 | 25,43 | -0,26 | 6,68 | 6,68 | 92,19 |
| 28. Van Dyck brown | 1 | 67,35 | 4,24 | 21,42 | 21,83 | 78,81 |
| | 2 | 60,65 | -0,24 | 8,8 | 8,8 | 91,54 |
| | 3 | 26,69 | 0,21 | 1,05 | 1,07 | 78,67 |
| 29. Dark purple madder lake | 1 | 31,18 | 13,95 | 12,99 | 19,06 | 42,95 |
| | 2 | 23,92 | 9,51 | 7,81 | 12,31 | 39,4 |
| | 3 | 16,71 | 1,46 | 0,73 | 1,63 | 26,6 |
| 30. Vivianite | 1 | 72,94 | -0,01 | 29,6 | 29,6 | 90,02 |
| | 2 | 58,31 | -3 | 17,22 | 17,48 | 99,88 |
| | 3 | 21,95 | -1,61 | 3,6 | 3,94 | 114,02 |
| 31. Bitumen | 1 | 53,25 | 12,71 | 39,28 | 41,29 | 72,07 |
| | 2 | 43,79 | 7,21 | 27,46 | 28,39 | 75,28 |
| | 3 | 13,6 | 1,48 | 6,85 | 7,01 | 77,84 |
| 32. Atramentum | 1 | 59,13 | 3,2 | 22,55 | 22,77 | 81,91 |
| | 2 | 40,61 | 0,95 | 13,55 | 13,58 | 85,98 |
| | 3 | 14,72 | -0,17 | 1,85 | 1,86 | 95,38 |

*Table 3. Colorimetric data obtained from Test Panel 2*

This study adopts a scientific and technical approach utilizing the multi-band technique, which captures images across different bands of the electromagnetic spectrum using the same device. The various images obtained through this technique provide valuable insights when analyzed individually. However, by comparing the results from the joint interpretation of these images, preliminary conclusions can be drawn regarding the presence or absence of certain materials, as well as their characteristics. (Herrero-Cortell et al., 2018; Artoni et al., 2019).

Photographs taken in the visible spectrum (VIS) provide information about chromaticity, tonality, and surface condition. Conversely, infrared (IR) photography reveals underlying drawings and the behaviour of pigments under infrared radiation, identifying possible pentimenti (Cosentino, 2016). Ultraviolet (UVL) photography, on the other hand, detects retouches, overpaints, as well as varnishes and pigments that fluoresce (Cosentino, 2015a). False color infrared photography (IRFC) helps to identify pigments by combining infrared and visible images. Although they do not provide definitive conclusions, they do support or generate hypotheses about the presence of certain materials (Cosentino, 2016).

A modified Nikon® D800 full-spectrum camera was used to capture the images, allowing information to be collected in the visible spectrum, part of the infrared spectrum, and part of the ultraviolet spectrum. For visible photography, an X-Nite CC1 filter was used to block out the IR and UV range. Pro-Foto 1250 W halogen lamps were used for lighting. The X-Nite CC1 filter was again used for visible photography under UV excitation (UVL). The light source was a 365 nm ultraviolet lamp with a pass filter for the UV range only (200-400 nm). For infrared (IR) photography, the Heliopan-1000 filter was used.

## 3. Results and discussion

### 3.1. *Colorimetry*

Measurements were taken in three representative areas: the lightest, the middle, and the darkest (Figure 3). The data obtained are presented in Tables 2 and 3, and they illustrate the changes experienced by each glaze applied over the grisaille.

#### *3.1.1. Hiding Power and Brightness*

Pigments differ in their ability to cover the underlying color. lead tin yellow (3), dark brown madder lake (10), cochineal (14), indigo (19), and dark purple madder lake (29) have a high hiding power. This visually perceptible characteristic (Llácer-Peiró et al., 2023) is also reflected in the colorimetric data, as the data indicate that this deviation is much less significant compared to the other glazeseven if there is a considerable change in brightness from areas over white grisailles to darker areas, (Figure 3). On the other hand, Reseda (2), Saffron (4), Minium (8), and Pastel Blue (20) have a more limited opacity (as noted by Díaz, 2022; Llácer-Peiró et al., 2023), resulting in a significant change in the brightness of the grisailles as the underlying colour becomes darker (Figure 3).

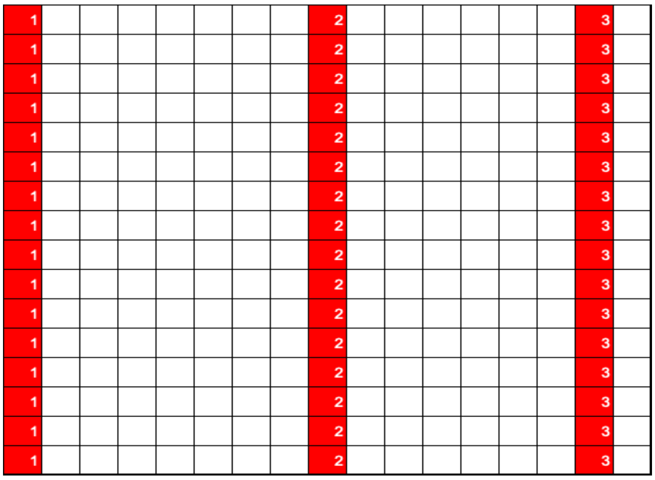

*Fig 3. Localisation of the areas where colourimetry has been carried out on the panels*

#### *3.1.2. Effect on the underlying color*

Glazes are significantly influenced by the underlying color. The a* coordinate shows a tendency for most glazes to shift towards green tones (-a*) as the tone of the underlying grisaille becomes darker. In this regard, red glazes such as madder lake coral (9), dark brown madder lake (10), carmine naccarat (11), and Cochineal (12, 13, and 14) are the ones with the most significant shift towards green tones (-a*), although this change is not visually perceptible. Only glazes made with blue pigments (15-22 and 24) and, exceptionally, malachite (24) show a tendency towards red tones (+a*). The b* coordinate indicates a shift towards blue tones for all the glazes (-b*), made of yellow pigments such as reseda (2), saffron (4), yellow ochre (5), aloe (6), stil de grain (7), and ochre havane (27) showing the greatest increase. The indigo glaze (19) is the only one that shows a slight shift towards yellow tones (+b*).

#### *3.1.3. Tonal changes*

While all pigments and dyes show changes depending on the underlying colour, some of them show significant chromatic transitions. For example, Lead White (1) has colorimetric values that indicate a significant tonal shift from yellow to green, although visually, bluish tones are perceived in the darker areas of the glaze. Another relevant case is cochineal 12 and 13, whose hues vary from reddish tones when the glaze is applied over light tones to bluish shades in darker areas. Blue bice (15) and azurite (16) also undergo a significant change from green to bluishtones as the underlying grisaille darkens.

*3.1.4. Colour dominance*

Although visual perception may suggest a predominant colour, colorimetric data reveal the true chromatic composition of the glaze. For example, Blue Bice (15) and Azurite (16) may appear bluish visually, but colourimetry shows a predominance of green and yellow hues.

### 3.2. *Multi-band technique*

The two mock-ups (Figures 1 and 2) were subjected to multiband imaging (VIS, IR, UVL) and false-color infrared (IRFC) to observe the behavior of the different materials studied. In particular, the aim was to show how the presence of different levels of grey used as grisaille can influence pigments, lakes, or dyes applied as glazes, even beyond the visible range. The results of the multiband imaging techniques used are detailed below.

3.2.1. VIS

Visible images (Figures 1 and 2) were used as a reference for UVL, UVR, IR, and IRFC images to observe the color based on the underlying grisaille. Where an underlying white layer is present, the colors appear very bright and clear. Over darker grey levels, the color tends to become less saturated until it appears almost completely black, which is confirmed by the colorimetric results. The exception to this is lead tin yellow (3), which retains its dominant color component over the underlying color due to its high opacity.

*3.2.2. UVL*

The phenomenon of UV-induced luminescence may depend on many factors such as the thickness of the brushstroke, the presence of an underlying material that may have its own luminescence, the type of binder or the presence of any varnish (Herrero-Cortell M. Á. *et al*., 2022).

Some pigments emit their own characteristic luminescence, such as lead white (1), which tends toward a light blue tint, or ultramarine blue (17), which has a bluish appearance. (Herrero-Cortell M. Á. *et al*., 2022).

Observation of the UVL images (Figures 4 and 5) shows that the different shades of grey under the pigment layers do not significantly alter the characteristic luminescence of the material. In fact, where the grisaille has light grey tones, the colours show almost unchanged and clearly distinguishable luminescence. With darker shades of grey, the luminescence is less pronounced but still clearly visible. Only in the case of some pigments, especially greens and blues, the last square in the row, where the grisaille is very dark, tends to be difficult to interpret. Finally, it should be noted that copper acetate + yellow (21), copper acetate (22), and dark purple madder lake (29) do not emit any luminescence, regardless of the grey tone of the underlying background, and therefore appear black (Fuster-López et al., 2023). Although lead white (1) and lead tin yellow (3) have a similar response to the visible light, their behavior in UVL photography is the opposite: lead white (1) is luminescent while lead tin yellow (3) is absorptive. (Díaz, 2022).

*3.2.3. UVR*

The image obtained with reflected UVR is useful for the identification of white pigments, such as zinc white or titanium white, which are highly absorbent. Similarly lead white and lithopone can be identified due to their high reflectivity (Cosentino, 2015b). However, this technique is not particularly useful for identifying other pigments. The presence of an underlying grisaille (Figures 6 and 7) does not significantly affect the result. In fact, the analysis of each colour row shows grey levels that are largely independent when moving from lighter to darker hues. It is interesting to note that the last three squares correspond to very dark grey tone, result in a slight change in the contrast. Lead white (1) always appears as a light grey tone and only tends to darken slightly in the presence of darker backgrounds.

*3.2.4. IR*

By observing the IR images, it is possible to see what is underneath the different color fields, based on their transparency to IR radiation (Cosentino, 2015b).

In this case (Figures 8 and 9), most of the pigments analysed appear quite transparent to IR radiation. In fact, the observed grey levels are mainly due to the different backgrounds used to create the underlying grisaille (white to black). Most of the organic pigments (2, 4, 5, 6, 7, 9, 10, 12, 13, 14, 19, 20, 25) exposed to IR radiation appear as transparent materials, allowing perfect observation of the underlying grisaille gradations. Only in the case of *Atramentum* (32) were contrasts between the different glaze layers visible in IR (Llácer Peiro, 2021).

Copper acetate + yellow (21), copper acetate (22), chrysocolla (23), malachite (24) and aloe (6) show an intermediate behavior and therefore the levels of grey that are observed follow the trend of the underlying grisaille, but the tone that is observed is partially influenced by the pigment itself.

Interestingly, lead tin yellow (3) has a high hiding power, and does not allow the observation of the grisaille obtained with dark tones (Kühn, 1968).

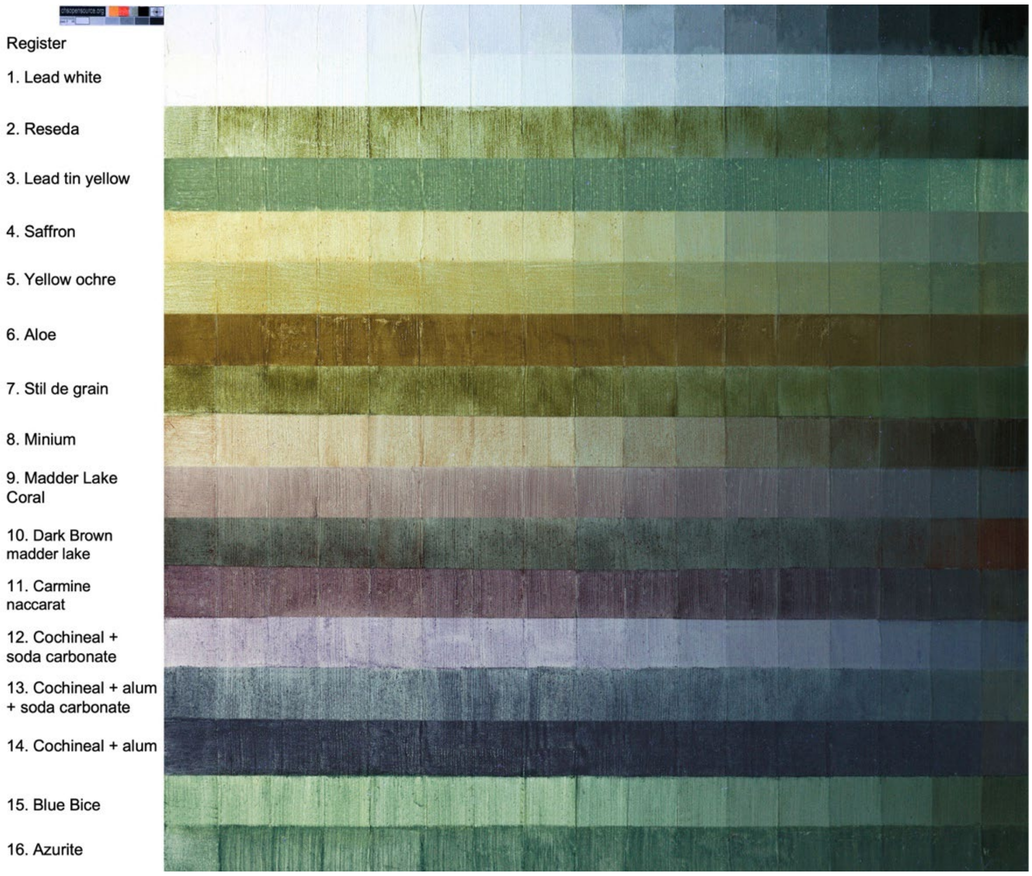


*Fig. 4. UVL image of Test Panel 1.*

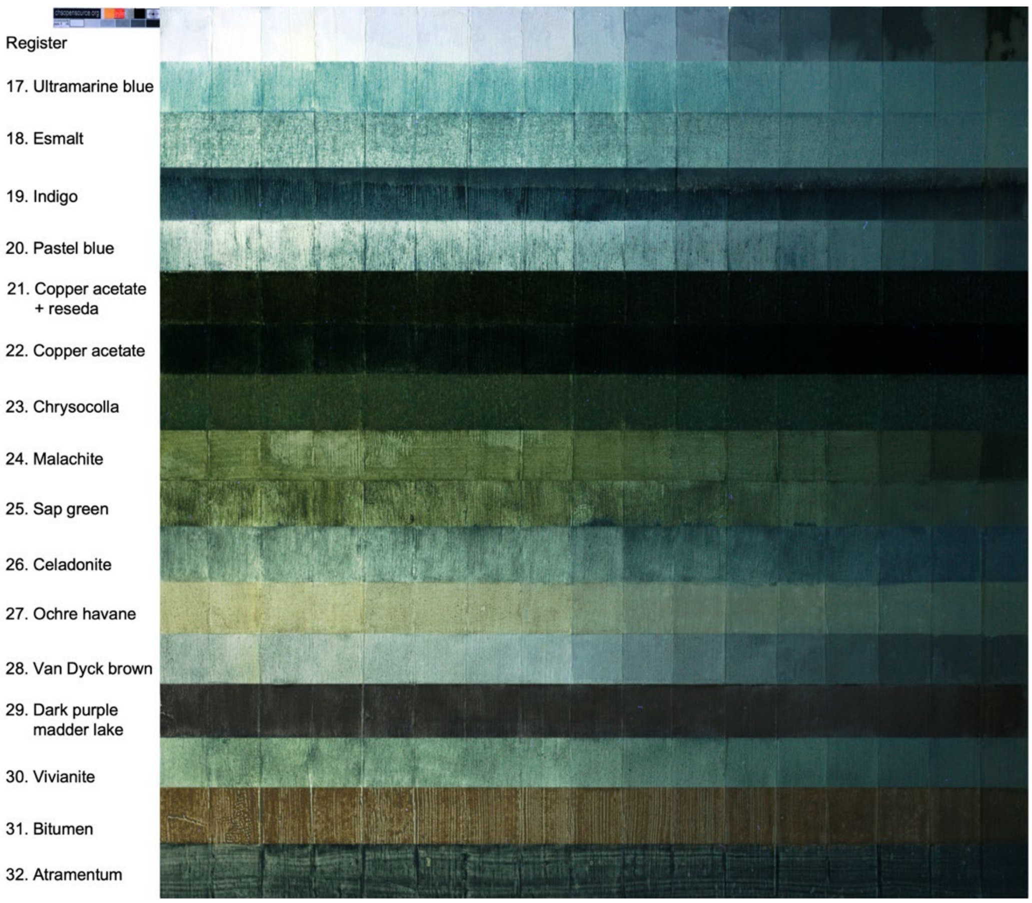


*Fig. 5. UVL image of Test Panel 2*

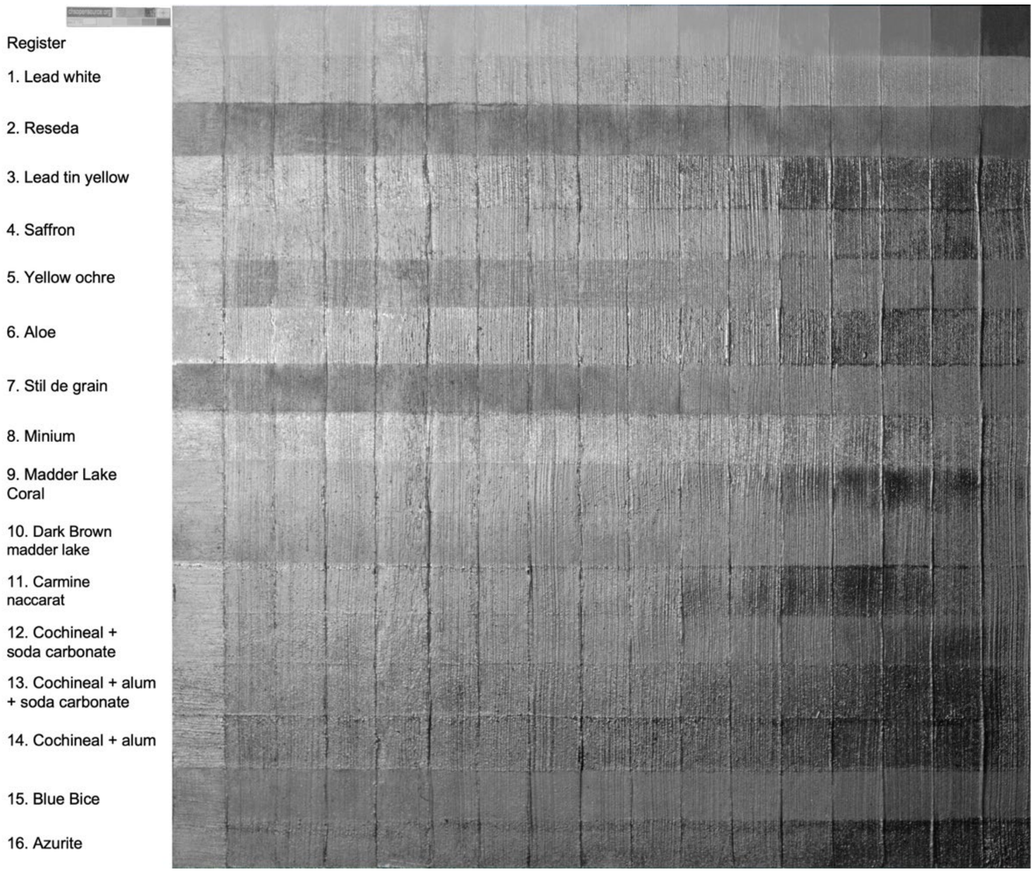


*Fig. 6. UVR image of Test Panel 1*

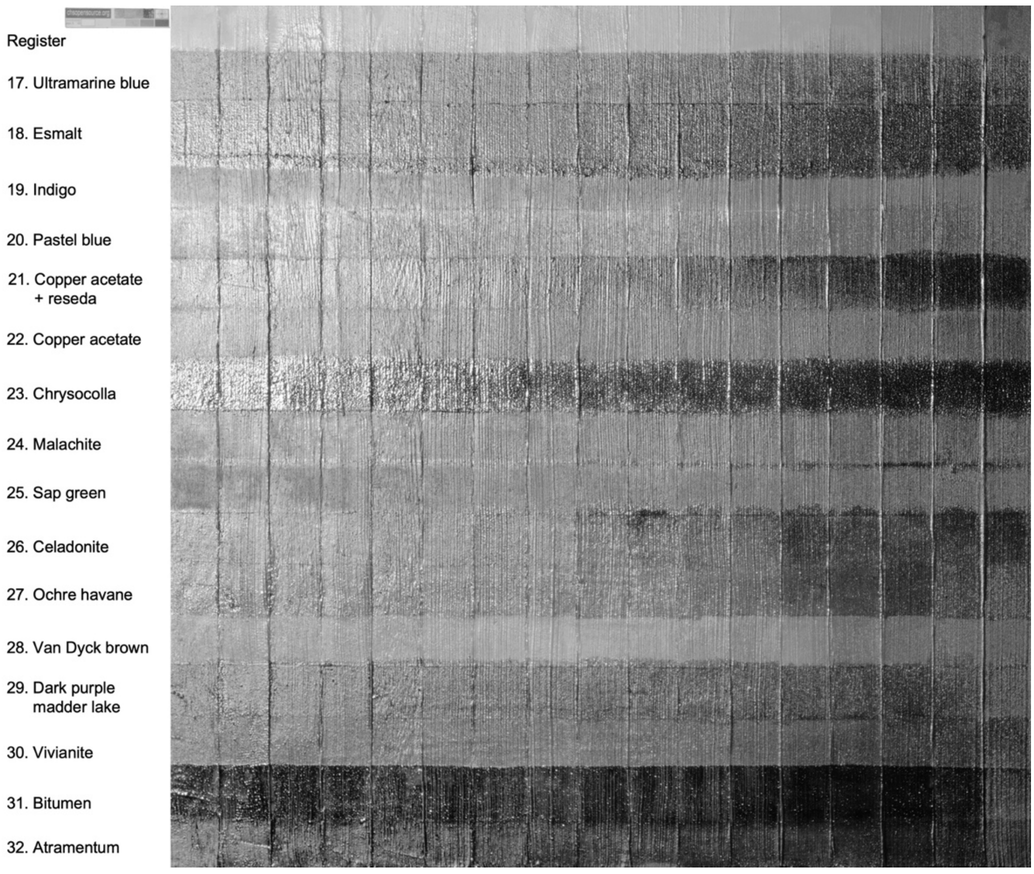


*Fig. 7. UVR image of Test Panel 2.*

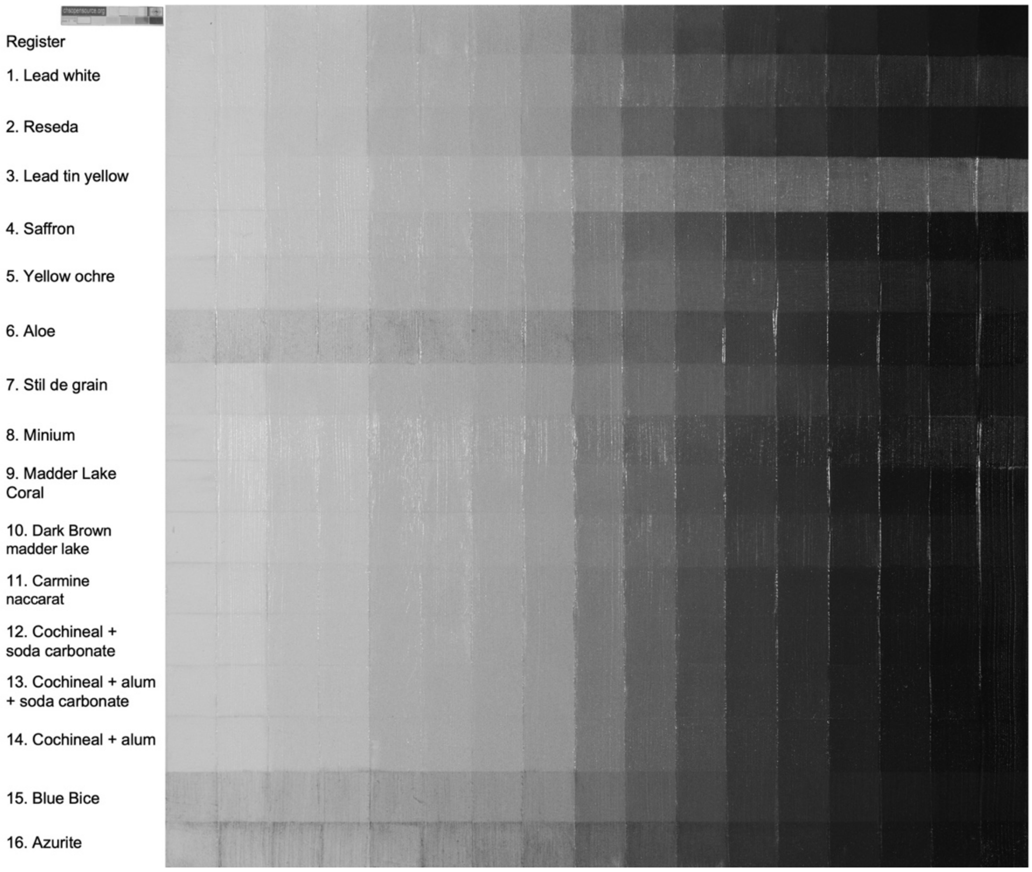


*Fig. 8. IR image of Test Panel 1.*

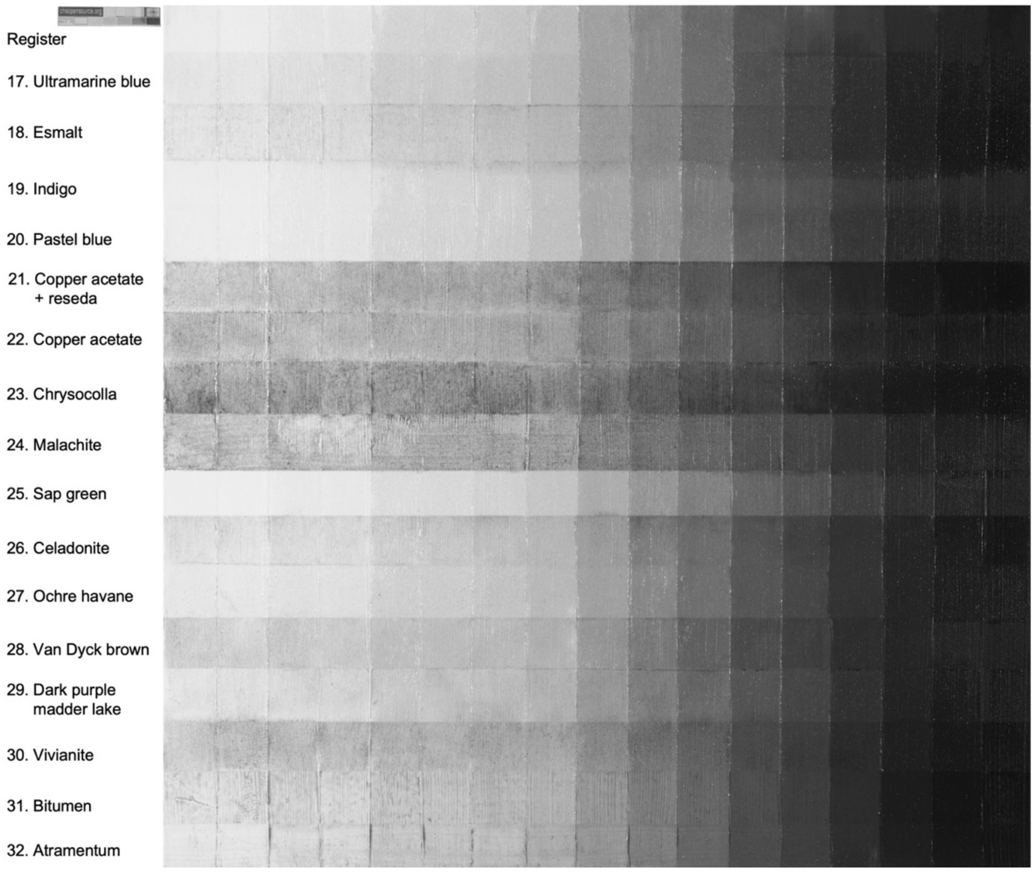


*Fig. 9. IR image of Test Panel 2*

### *3.2.5. IRFC*

False colour infrared is a technique that makes it possible to discriminate between pigments that have similar optical behaviour under visible illumination but different IR reflectance (Aldovrandi & Picollo, 2007).

Observing the images in IRFC (Figures 10 and 11), it can be seen that the color areas obtained on a light ground do not show significant changes in the characteristic false colour. The colours superimposed on darker grisaille, tend to be less and less saturated becoming almost black, as can be seen in the last two areas of each row. Once again, lead tin yellow (3), thanks to its hiding power, allows the characteristic false colour to be observed even over areas of very dark grey.

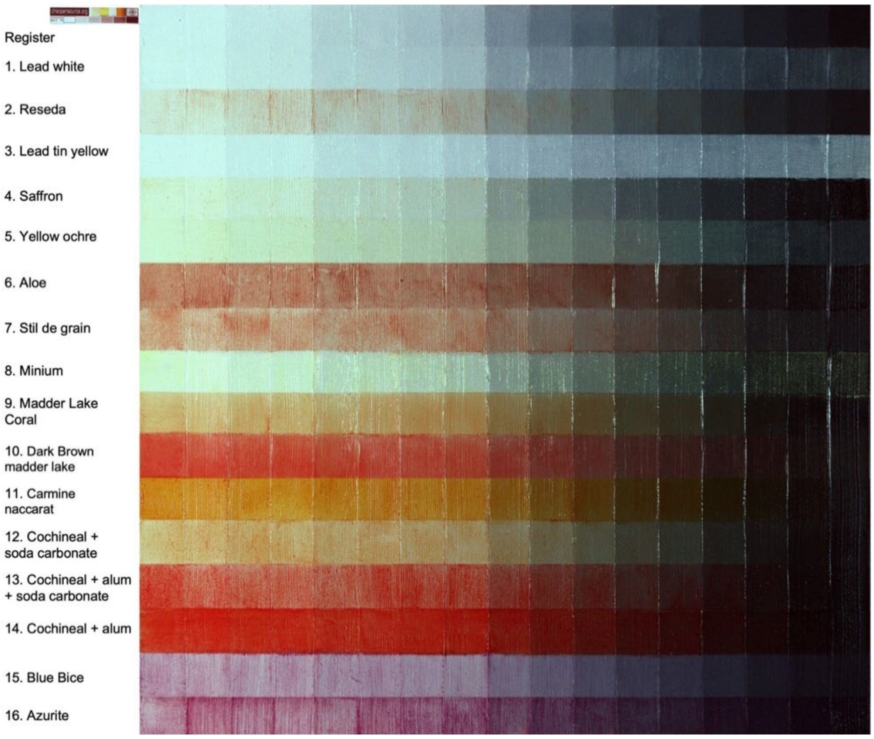


*Fig. 10. IRFC image of Test Panel 1*

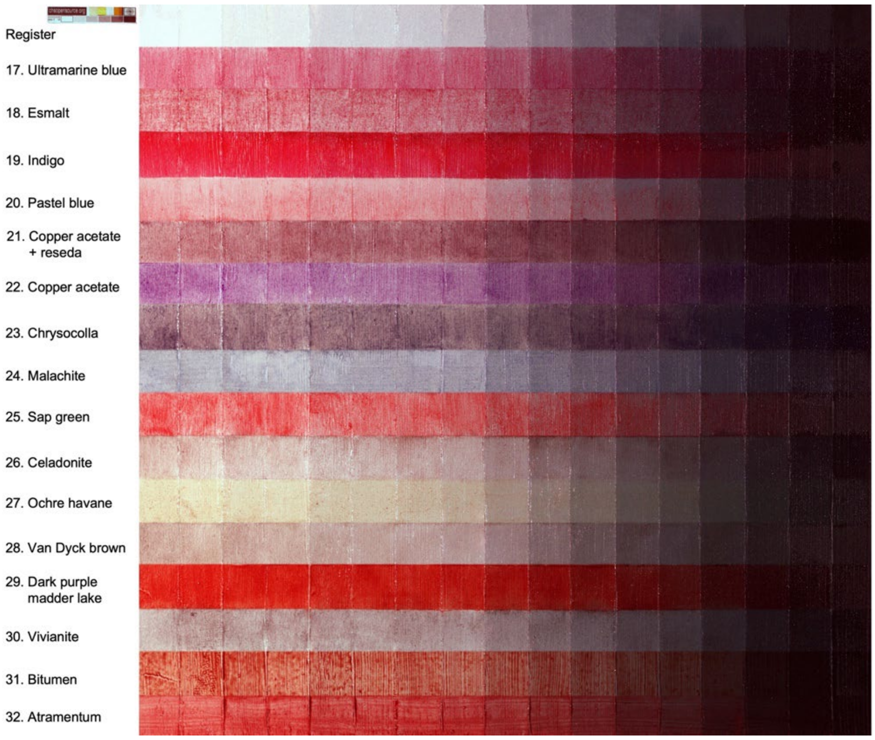


*Fig. 11. IRFC image of Test Panel 2*

## 4. Conclusions

This text presents a study of the use of historical glazes - both organic and inorganic-, applied over monochrome grisailles as used in painting between the 15th and 17th centuries. To achieve this, a visual analysis was carried out using a wide range of pigments, lakes and dyes to obtain different chromatic nuances. The main objective was to evaluate the impact of monochromatic underlying grisailles on the upper glazes.

All the processing and creation work on the pictorial material was characterised both visually and quantitatively by means of colourimetric measurements and multi-band techniques. Colorimetric analysis revealed an inverse relationship between hiding power and changes in luminosity. That is, opacity correlates with less variation in luminosity. On the other hand, glazes were found to shift colour being the most common shifts towards green tones. Significant tonal changes were observed in some pigments, such as chromatic transitions from yellows hues to greens (lead white) or from reds to blues (cochineal 12 and 13).

Finally, it should be noted that, although visual perception may suggest a predominant colour, the colorimetric data revealed the true chromatic composition of the glazes, highlighting that some pigments have a colour dominance different from that perceived, as seen with blue bice (15) and azurite (16). The observation of the multi-band images showed how the colour of the glazes changed depending on the grisaille underneath. UVL and UVR did not show any significant changes in the hues of the various pigments, except for areas on very dark grisailles where the colour tended to turn to black. In addition, many colours were quite transparent to the IR radiation, allowing the underlying grisaille to be seen. Finally, the IRFC showed an overall effect of the dark grisaille on the individual pigments, which in most cases makes it difficult to identify them.

This study has shown that grisailles have a significant impact on the perception of the glazes applied over them. These varnishes modify and nuance the tones upon which they are applied, hence the importance of considering these layers in the conservation of paintings.

## 5. Conflict of interest declaration

The authors wish to state that no financial or personal interests have affected the objectivity of the study, and that no conflicts of interest exist.

## 6. Funding source declaration

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## 7. Short biography of the author(s)

**Aránzazu Llácer-Peiró -** Research Technician pursuing the PhD in Conservation at Instituto Universitario de Restauración del Patrimonio (Universitat Politècnica de València) on the study of drying pigments through a multi-analytical approach.

**Serena Hirsch -** Master degree in Science and Materials for Conservation and Restoration of Cultural Heritage from the University of Florence. She conducted her MA thesis research on diagnostic techniques, in particular on multi-band imaging applied to paintings. She currently works as a scientific assistant at La Venaria Reale Conservation and Restoration Centre.

**Mª Antonia Zalbidea-Muñoz -** Professor in the Department of Conservation and Restoration of Cultural Heritage at the UPV, field in which she holds a doctorate degree. She has directed her research towards the procedural, material and conservative aspects of mural paintings, as well as to the use of varnishes and dyes in paintings. She is currently a member of the project team: B*yzantine illuminated manuscripts in Spain: work, context and materiality - MABILUS* (MICINN-PID2020-120067GB-I00).

**Miquel Àngel Herrero-Cortell -** He holds a PhD in Art History. He has a degree in Fine Arts from the Polytechnic University of Valencia (UPV) and a degree in Art History from the University of Valencia (UV). He holds a Master's Degree in Conservation and Restoration of Cultural Heritage and a Master's Degree in Artistic Production. He has developed his work as a researcher focusing on the field of materials and painting techniques, as well as on painting diagnosis. He is currently lecturer at the Universitat Politécnica de València.

**Laura Fuster-López -** Professor at the Conservation Department in the Universitat Politècnica de València (Spain). After several research fellowships at Europe and the United States, she got her PhD in Conservation from UPV where she coordinates the area on the study of the mechanical and dimensional properties of cultural materials since 2007. She has been involved in numerous international R+D projects always with a special focus on understanding the mechanisms involved in paintings behavior and degradation.

## Notes

[1] Below are the works derived from the study of glazes:

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[2] For more information, see Melgosa, M. (2020). "Revisión de algunos conceptos de ciencia del color relacionados con la iluminación" Luces CEI No. 70, 16-21.

## Licensing terms



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