



EXPLORATORY ANALYTICAL STUDY OF A 20TH CENTURY PORTUGUESE MURAL PAINTING BY JULIO RESENDE (1917-2011)

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Abstract

This paper unveils for the first time the technical and material features of the mural painting entitled Pentecost's, executed by the Portuguese artist Julio Resende in 1955. The painting depicting twelve Apostles covers the altarpiece of a small church in the countryside of Évora (southern Portugal) and it was rediscovered in 2013 by art historians. The research was carried out with both non-invasive and micro-destructive techniques. In situ examination included technical photography in visible (Vis/Vis-RAK) and in infrared (NIR) light range, ultraviolet induced visible fluorescence (UVF), portable optical microscopy, visible spectrophotometry and handheld energy dispersive X-ray fluorescence spectroscopy (hXRF). Further analysis on paint layers micro-samples were undertaken by dark field optical microscopy (OM), scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDS) and micro-Fourier transform infrared spectroscopy (μ -FTIR). According to the acquired data, the mural was executed in a fresco technique (true and most likely lime fresco). Full size cartoons and handmade sketches were used for transferring the composition to the wall. No traces of organic binder were found with the analytical setup and the analysis of paint layers revealed the use of cobalt blue, a wide range of ochres, chromium green, green earth and barium white. The use of chrome orange and cadmium-based pigments are hypothesized.

Keywords: Julio Resende; Modern Mural Paintings; OM; SEM-EDS; μ -FT-IR

Introduction

Julio Martins Resende da Silva Dias (1917-2011) remains one of the most acclaimed Portuguese artists of the 20th century. His works are very diverse in typology and techniques, ranging from drawings, oil paintings, mural paintings, stained glass and tiles [1]. Stylistically, his art evolved from early Neorealistic artworks through phases of Neo-cubism and Non-figurativism to Action painting and Neo-figurativism [2]. Despite his large artwork production few scientific studies have been carried out and none from an archeometry perspective [3]. The present study aims to unveil for the first time the painting technique and pictorial materials used in his mural painting entitled *Pentecost's* for future conservation works (Fig. 1). On a broader scale, the study aims also to contribute to the still scarce literature concerning 20th century mural painting technology in national and international context.

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Fig. 1. Overall view of the mural painting *Pentecost's* with the location of micro sampling (ref. in black) and of h-XRF analyses (ref. in white). On the bottom, a detail of Julio Resende's signature and date of execution. Photo by Manuel Ribeiro 2018

The mural painting Pentecost's

Julio Resende only created four mural paintings throughout his almost 60-year-old career: two in Porto (Northern Portugal) in 1952 and 1962, one in Évora (Southern Portugal) in 1955 and the last one in Anadia (Northern Portugal) in 1966 [4]. The mural painting in this study is his second artwork which curiously, and for unknown reasons, remained unnoticed for fifty years in a small church in Évora's countryside. According to the art historian *L. Castro* [2], all four mural paintings were executed in a similar manner close to Cubism esthetic and constitute a brief but distinctive phase in Resende's art, which is related with the time he spent in the district of Évora.

The painting *Pentecost's*, rediscovered in 2013 by Art historians, with approximately 3.67 x 2.84m covers the altarpiece on the eastern wall of the church and depicts twelve apostles in accordance with the biblical episode described in the Act of the Apostles: "fiftieth days after the Easter The Apostles were celebrating Feasts of the Week in the Cenacle, when the Holy Spirit descended on them and the other followers of Jesus" [5]. Figure 1 shows an overall view of the painting and a detail of the Resende's signature and date of execution located in the right bottom corner.

Overall the painting is in a good state of conservation. However, lack of cohesion in the blues and green pigments has been noted, raising the hypothesis of the use of a *secco* painting technique. It is known that in the first half of the 20th century, mural painters have experimented techniques and materials unconventional to the traditional fresco technique [6-10]. A clear example is the mural painting known as *America Tropical* done by David Siqueiros in 1932 in

downtown Los Angeles [6]. This research intended to ascertain if it was also the case of *Pentecost's*.

Experimental

In situ research

Photo Documentation and Technical Photography (TP)

The primary stage of the research was visual inspection and photographic documentation of the mural. Visible (Vis) and visible racking light (Vis-RAK) photography were acquired with a Nikon D3200 24Mpx with a Nikkor 18-55mm, f: 3.5-5.6 GII objective and a Canon SIGMA24-35mm F2 DG HMA015. The overall photography of the painting for graphic documentation was achieved by mosaic methodology. The number of photos taken was 50 (5 rows with 10 photos each). The photos were assembled and edited in Adobe Photoshop CS5.5.

Racking light photography was achieved using illumination at an angle of 15-20° from the surface of the painting. The UV induced visible fluorescence photography (UVF) was also acquired with a Nikon D3200 24Mpx with a Nikkor 18-55mm, f: 3.5-5.6 GII objective. UVF allowed the detection and preliminary characterization of the surface coatings and fluorescent pigments.

The infrared photography in the near range (NIR) was implemented in order to disclose the possible presence of carbon-based under drawings. The photos were acquired with a Nikon D3100 digital camera modified for full spectrum equipped with 10.0-550mm f/3.5-5.6 lenses and a 14.2 Megapixel CMOS sensor. Three high-pass band filters – X-Nite 780nm, X-Nite 850 nm and X-Nite 1000nm – were used for the NIR images.

Raw image output was used in combination with a reference target QpCard101 v3 and AIC PhD target in order to get a more accurate and comparable color registration.

OSRAM 64575 Halogen lamps 1000W-230V Gx6.35 NAED 58525 (Color temperature: 3400 K) were used for Vis, Vis-RAK and IR photography. UV photography was carried out with a Labino® MPXL UV PS135 (35W PS135 UV Midlight 230V) with a UV filter included (310-400nm and a peak at 365nm); a Midlight distribution angle (beam) of 20° and a start –up time full power after 5-15sec. Technical photography was made by a professional photographer (Manuel Ribeiro).

Portable optical microscope

In situ observations and record of painting technical and material features was carried out with a portable Dino-lite ProX AM 4000 series with 50x and 430x magnifications.

Spectro-colorimetry

Spectro-colorimetry was used for a first characterization of the painting's current color palette. In total 258 measurements were taken on the painted surface which enabled the selection of further pigment analysis for hXRF. Data Color Check Plus II (Lawrenceville, NJ), equipped with an integrating sphere was used with the following working conditions: diffuse illumination 8 viewing (in accordance with the CIE standard No. 15.2. Colorimetry), SCE and Standard Illuminant/Observer D65/10. The aperture size used was USAV (Ø5 mm). The analyzed wavelengths were 360-750nm with 10 steps between measurements [11-15].

hXRF

The preliminary elemental composition of the paint layers was obtained by hXRF. A Bruker™ Tracer III SD® handheld X-ray fluorescence spectrometer (Bruker, Germany), equipped with a rhodium target delivering a polychromatic X-ray beam of 3 × 3mm and a silicon drift detector (XFlash®) was used to analyze a total of 83 paint areas covering the entire palette's color range. Spectra were recorded using a voltage and a current intensity of 40kV and 30µA, respectively, during a 30s real-time count. All spectra were recorded using S1PXRF software (Bruker™) and processed using Artax (Bruker™) software in order to obtain semi-quantitative data.

Laboratory research

Micro samples were collected from the blue, green, red, orange and brown paint layers for further characterization of paint layers (technique and painting materials) (Fig. 1). Ten powder micro samples were collected for μ -FT-IR analysis to ascertain the presence of organic binders. These samples were collected by gently scratching the surface of the painting with a scalpel. In turn, fifteen micro samples were collected for stratigraphic analysis in OM and VP-SEM-EDS. All the samples were collected on the edges of lacunae, cracks and erosions areas. Both kinds of micro-samples were used for pigment identification by means of VP-SEM-EDS and μ -FT-IR. Figure 1 shows the location of the micro sampling (ref. in black) and the h-XRF analyses (ref. in white) that are illustrated and discussed in the subsequent sections.

Cross sections

For cross-sections, the micro samples were embedded in an epoxy fix resin (Epofix Fix, Struers A/S, Ballerup, Denmark) and polished with 6000, 8000 and 12000 sandpapers in a rotating disc Drehzal Regler (Jean Wirtz, Dusseldorf, Germany).

Optical Microscope (OM)

The embedded cross-sections were studied with a Leica DM2500M reflected light optical microscope in dark field illumination mode. The observations were carried out in 100, 200 and 500x magnifications. Photographic documentation was made with Leica MC 170HD digital camera attachment (Leica microsystems, Wetzlar, Germany).

VP-SEM-EDS

A Hitachi™ S3700N variable pressure scanning electron microscope, coupled to a Bruker™ XFlash 5010 silicon drift detector, operated with an accelerating voltage of 20kV and under a 40Pa chamber pressure was used to perform EDS microanalysis, and to determine the morphological characteristics of the paint layers present in each cross section. The use of the variable pressure mode in the study of non-conductive specimen allows analyzing the samples without the metal coating. SEM images were acquired in backscattering (BSE) mode.

μ -FT-IR

A Bruker Tensor 27 Mid-IR (MIR) spectrometer was used for the identification of binders and pigments. The spectrometer is coupled to a HYPERION 3000 microscope and is controlled by OPUS 7.2 software (Copyright© 2012 Bruker Optics and Microanalysis GmbH, Berlin, Germany). It has a MCT (Mercury Cadmium Telluride) detector cooled with liquid nitrogen and allows spectra acquisition at different points of the sample. The samples were analyzed in absorbance mode using a 15x objective and an EX'Press 1.6 mm diamond compression microcell, STJ-0169. The IR spectra were plotted in the region of 4000-600 cm^{-1} , with 64 scans and 4 cm^{-1} spectral resolution. Peaks identification were made by comparison with bibliographic references [16, 17].

Results and discussion

Pictorial support

The first recognition of the plasters used as the pictorial support was made in situ by Vis and Vis-Raking light. Vis-raking light was particularly useful to ascertain the way the plaster was laid down progressively, mainly following the contours of the figures. A total of seven *giornata* (*giornate* in plural) – the Italian term that stands for “daily work” – were found in the *Pentecost's* mural painting, having been laid down, on top of an inner layer of plaster, from top to bottom and from left to right. Figure 2 shows the location and sequence order. The edges of the *giornate* are identified by the slight overlapping of the plasters. Interestingly, in one apostle the *giornata* is restricted to the face. The presence of *giornata* provides a significant insight to the artist's *modus operandi* and is a clear evidence of the use of a *fresco* painting technique that requires a damp plaster to paint.

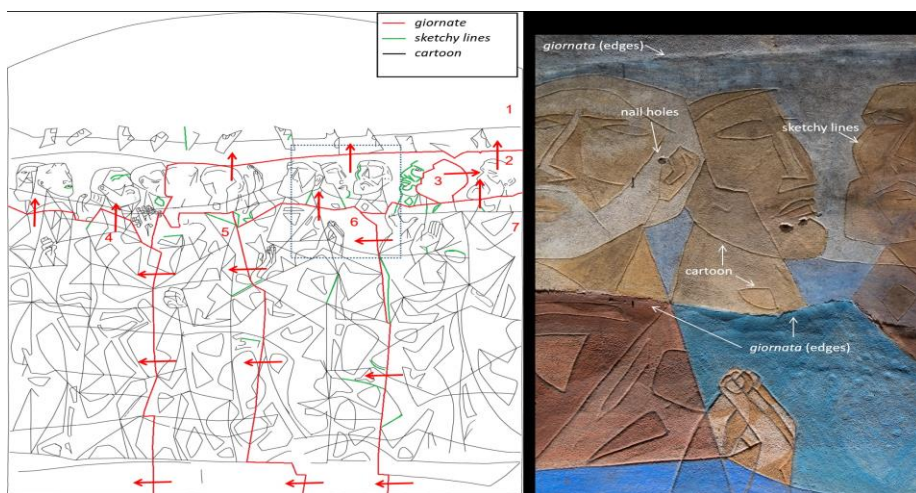


Fig. 2. Map of the *giornate* and a detail of the plaster's surface features in Vis-RAK. The arrows indicate the direction of overlapping plaster edges of the *giornate*

Other technical features of the plaster layering method were also recognized: a) tool marks, left by trowels used to spread the plaster and smooth the surface of the painting; b) different textures of the upper plaster, being the background of the figure's faces surface smoother than the rest of the composition and c) large amount of nail marks holes, which in some cases are still present. The distribution of the nail marks in all the surface of the painting raises the hypothesis of nails having been used as an aid to the transfer of the composition to the wall.

In terms of composition, the inner and upper plasters observed in the lacunae located on the edges of the painting are lime based mortars. Analysis of micro sample cross sections 8 and 18 by OM and VP-SEM-EDS revealed a brownish inner layer with coarse siliceous aggregates, corresponding most likely to quartz and K-feldspars, while the upper layer of plaster is white, very thin (around 4 μ m) with no aggregates and enriched in calcium (Fig. 3).

Preparatory drawings

Two types of drawings incisions became evident when using Vis-Raking light. The first and more predominant are rounded groove lines that indicate the use of full-size cartoons which were fixed to the wall and pressed through with a pointed tool when the upper plaster was still fresh (Fig. 2). The second type are shallow sketchy lines made with a point tool by free hand which were made after the previous ones to slightly change or add more details to the composition (Fig. 2). The edges of the sketchy lines occasionally have a grainy aspect which suggest that they were made in a drier surface. No clear evidence of under drawings made with carbon-based materials were detected with IR photography. **Paint layers (pigments and binders)**

In situ Vis-raking light observations and portable optical microscopy survey disclosed evident overlapping of paint layers which can shed light on the painting process used by the artist. In general, Julio Resende seems to have used a very simple paint structure. The lighter and more transparent background tones were laid down first to build up the main volume of the figures' cloaks and flesh tones. Next, Julio Resende painted the more opaque darker tones in the garments, the shadows and final "reprise" of the contours on the figures' anatomic details.

An overview of the current color palette plotted in the 2D CIE a*b* space is given in figure 4. Despite the contribution of a brownish dirt deposit on the painted surface, the results of 258 measurements show a broad chromophore content in the red, yellow, blue and green domains and the intermediate hues. The black dots displayed in figure 4 indicate the color regions of the OM microphotographs and hXRF analysis that are illustrated in figures 5 and 6.

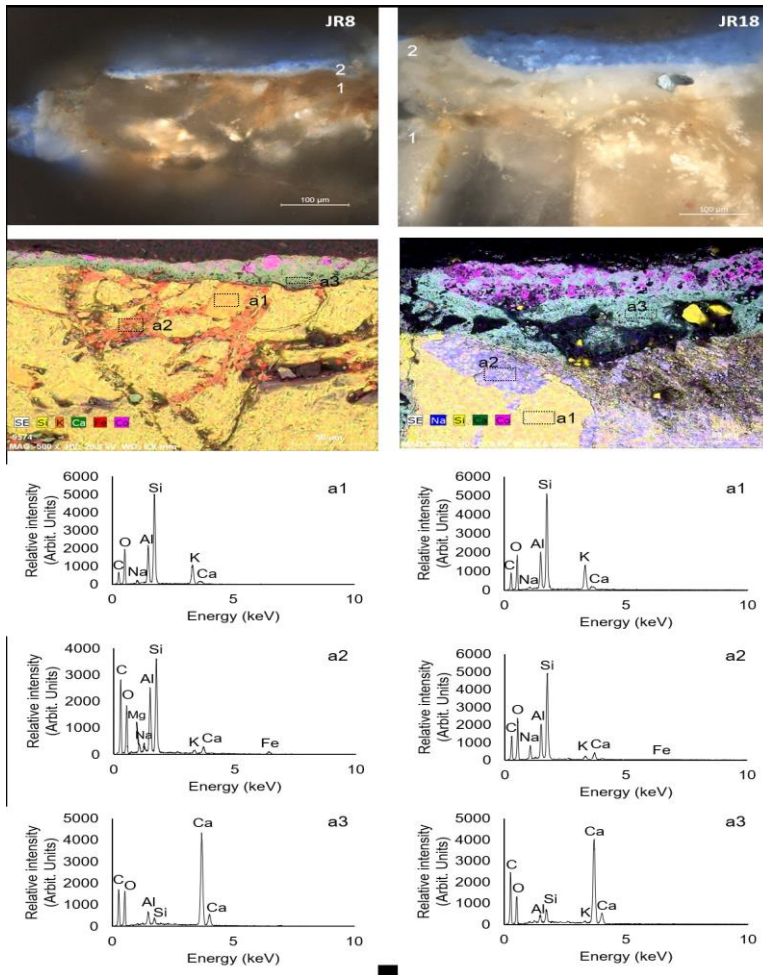


Fig. 3. Microphotographs in visible light and VP-SEM-EDS analysis of micro sample cross sections 8 (left) and 18 (right) where the two layers of plaster can be seen below the blue paint layer

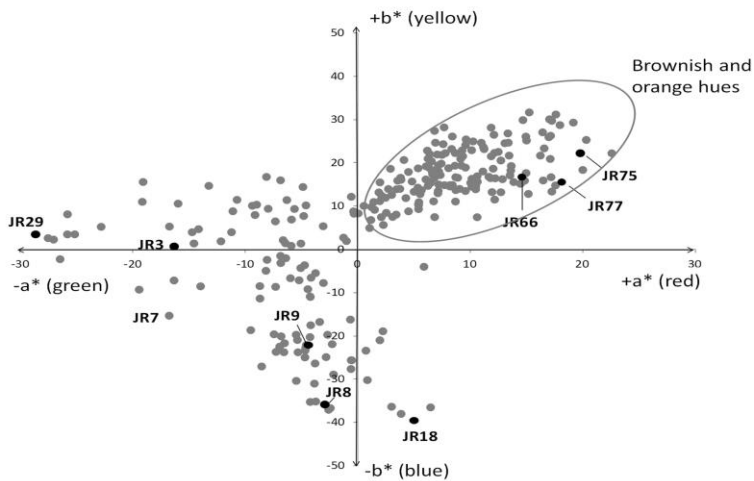


Fig. 4. Global view of the current chromatic palette projection in 2D CIE a*b* color space with the location of the microphotographs illustrated and discussed in the text

Blue and green pigments

The high amount and variety of $-a^*$ and $-b^*$ values displayed in Figure 4 shows a broad range of blue and green hues which were achieved by using different pigments, differences in pigment dilution, pigment mixtures and pigment overlaps (Fig. 5a and b).

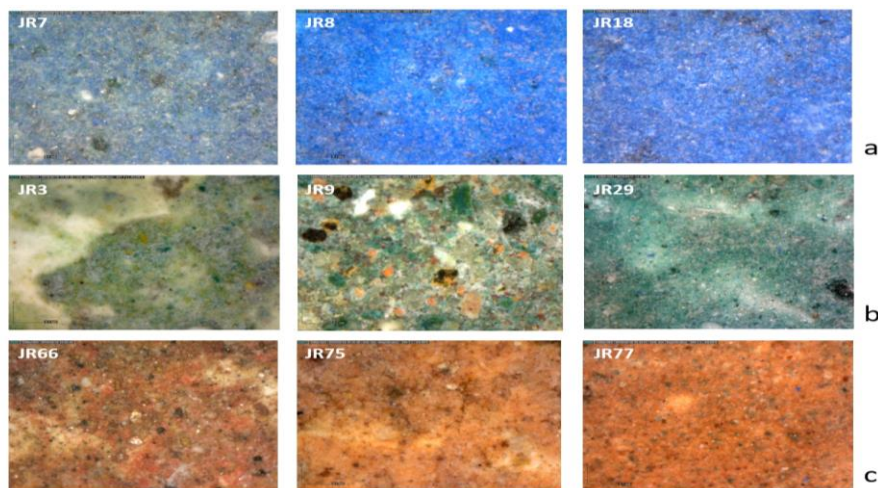


Fig. 5. Microphotographs in visible light with 435x magnification of: blue (a), green (b) and ochre-colored (c) paint layers.

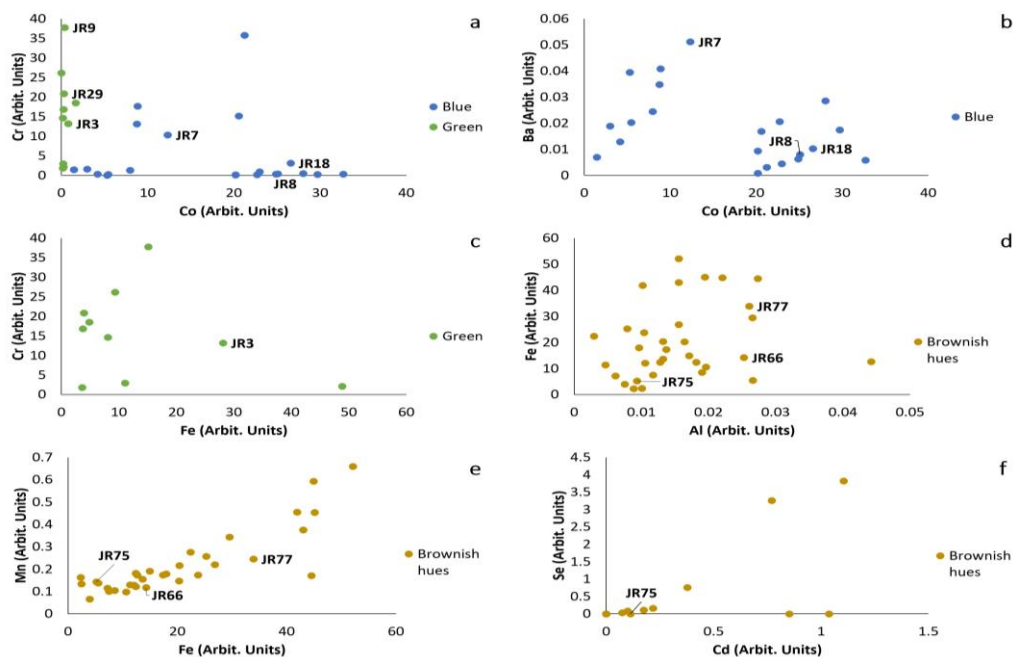


Fig. 6. a) hXRF Cr-Co plot indicating the use of Co and Cr to produce the blue and green pigments, respectively. In some cases both elements were found in the blue areas of the *Pentecost's* painting, which could indicate overlaying of paint layers or pigment mixing; b) hXRF Ba-Co plot indicating that barite was present, most likely as a filler, in the cobalt blue pigment; c) hXRF Cr-Fe evidencing that green earth pigments were also used to produce green hues, occasionally in conjunction with Cr green pigments; d) hXRF Fe-Al plot suggesting the use of earth pigments to produce brownish yellow to brownish red hues; e) hXRF Mn-Fe plot suggesting the presence of manganese oxides in the earth pigments used to produce the brownish yellow to brownish red colors; f) hXRF Se-Cd plot substantiating the occasional use of Cd pigments in the production of brownish yellow to brownish red hues

Cobalt was found in all the blue paint layers analyzed by hXRF (Fig. 6a). VP-SEM-EDS analysis of the blue particles in cross sections 8 and 18 (Fig. 3) have also shown Al and Co-rich areas. Cobalt blue pigment was used alone, but also with Cr and Ba-rich pigments, as evidenced by hXRF (Fig. 6b). In fact, both green and white pigments particles were found in conjunction with cobalt blue by OM in JR7 (Fig. 5a). The white Ba-rich particles were identified as barite by μ -FT-IR (Table 1).

Barite (BaSO_4), also known as the pigment barium white, has a weak covering capacity and, thus, in many occasions it is used not as a white pigment itself but as filler by paint manufacturers [15, 17]. This is most likely the case of the blue micro samples collected from mid and dark bluish and green tones (Fig. 1 and Table 1).

Chromium was identified in the green paint layers by hXRF and VP-SEM-EDS (Fig. 6a and 7). In addition, minor amounts of Fe (Fig. 6c), Ba, Co (Fig. 6b) and Pb were also detected in these paint layers. The use of OM revealed the presence of red, blue and orange particles together with Cr green pigments (Fig. 5b), which can explain the combined presence of these elements. Based exclusively on elemental characterization it is not possible to determine which type of chromium-based green pigment was used: chromium oxide (Cr_2O_3) and hydrated chromium oxide ($\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$), also known as viridian [18]. By μ -FT-IR another green chromophore was also identified mixed with Cr based pigments in the powder sample 2 (Table 1 and Fig.7).

Table 1. Summary of the μ -FT-IR results of the paint layers analyzed

Micro sample Ref	Colour	μ FT-IR (identification of mean chemical compounds)
2	Green (mid tone)	Celadonite (3601, 3557, 3533, 1075, 976, 959, 840, 800, 682 cm^{-1}); Calcite (2511, 1795, 1435, 874, 712 cm^{-1})
4	Green (dark tone)	Barite (1178, 1085, 983, 637, 611 cm^{-1}) ; Quartz (794, 783 cm^{-1}) ; Calcite (2510, 1794, 1420, 874, 713 cm^{-1})
6	Blue	Cobalt blue? (1079 cm^{-1}); Kaolinite (3694, 1046, 914 cm^{-1}) Gypsum (1165, 1113 cm^{-1}); Calcite (2510, 1794, 1417, 873, 712 cm^{-1}); Calcium oxalates (1625, 1318, 782 cm^{-1})
7	Blue/greyish (dark tone)	Kaolinite (1042, 914, 781 cm^{-1}); Gypsum (3404, 1622, 669 cm^{-1}); Calcite (2512, 1794, 1421, 874, 712 cm^{-1})
14a	Red (dark tone)	Kaolinite (3694, 3653, 3618, 1034, 914 cm^{-1}); Barite (1085, 637, 611 cm^{-1}) ; Quartz (1085, 797, 781 cm^{-1}) ;Gypsum (3405, 1619, 673 cm^{-1}) Calcite (2513, 1795, 1429, 874, 713 cm^{-1})
14b	Green	Barite (1080, 983, 639, 611 cm^{-1}); Gypsum (1164, 1112 cm^{-1}) Calcite (2512, 1795, 1418, 874, 713 cm^{-1}) ; Calcium oxalates (1625, 1319, 782 cm^{-1})
15	Green/blue	Barite (1177, 1072, 984, 639, 610 cm^{-1}); Quartz (798, 782 cm^{-1}) Calcite (2510, 1794, 1409, 872, 711 cm^{-1}); Calcium oxalates (1630, 1319, 782 cm^{-1})
17	Blue/green	Barite (1177, 1072, 984, 640, 609 cm^{-1}); Calcite (2511, 1795, 1420, 874, 712 cm^{-1}) ; Calcium oxalates (1629, 782 cm^{-1})
21	Blue (light tone)	Kaolinite (3692, 1039, 912 cm^{-1}); Gypsum (3406, 1120, 675 cm^{-1}) Calcite (2510, 1794, 1419, 874, 712 cm^{-1}); Calcium oxalates (1624, 782 cm^{-1})
25	orange	Kaolinite (3696, 3653, 3618, 1034 cm^{-1}); Barite (1087, 983, 638, 611 cm^{-1}); Gypsum (3403, 1622 cm^{-1}) ; Calcite (2510, 1795, 1416, 872, 711 cm^{-1})

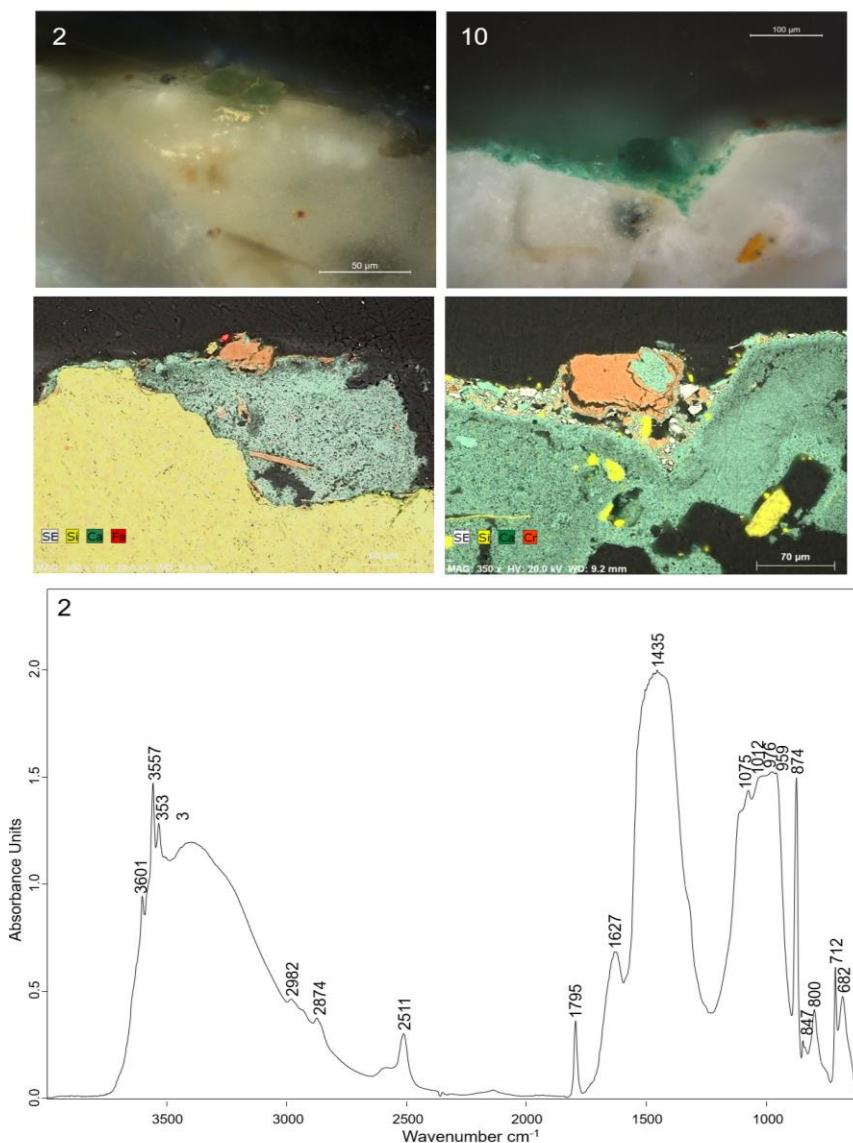


Fig. 7. Microphotographs in visible light and VP-SEM-EDS analysis of the green paint layers of micro samples 2 and 10. On the bottom: the FT-IR spectra of micro sample 2

The bands at 3601cm^{-1} (ν $\text{Al}^{3+}.\text{Mg}^{2+}\text{-OH}$), 3557cm^{-1} (ν $\text{Fe}^{3+}.\text{Mg}^{2+}\text{-OH}$), 3533cm^{-1} (ν $\text{Fe}^{3+}.\text{Fe}^{2+}\text{-OH}$), 1075 , 976 and 959cm^{-1} (ν Si-O), 840cm^{-1} (δ $\text{Al}^{3+}.\text{Mg}^{2+}\text{-OH}$) and 800 , 682cm^{-1} (δ $\text{Fe}^{3+}.\text{Mg}^{2+}\text{-OH}$, δ $\text{Fe}^{3+}.\text{Fe}^{2+}\text{-OH}$) indicate the presence of celadonite ($\text{K}(\text{Mg},\text{Fe}^{2+})(\text{Fe}^{3+},\text{Al})[\text{Si}_4\text{O}_{10}](\text{OH})_2$), one of the main components of green earth pigments. As seen in Figure 6c, the use of Cr green and green earth pigments was also confirmed by hXRF.

Brownish yellow to brownish red pigments

The high amount of a^* and $+b^*$ values at the center, displayed in Figure 4, shows a predominance of brownish yellows to brownish red and orange hues. Iron was found to be a major constituent of these paint layers by hXRF and VP-SEM-EDS, being associated with Al (Fig. 6d), Mg and Si which strongly suggests the use of earth pigments [15, 17]. Furthermore kaolinite, an aluminosilicate mineral, was identified in the powder samples 14a (red) and 25

(orange) by its main bands at 3694, 3653 and 3618 cm^{-1} (ν OH), 1034 cm^{-1} (ν Si-O) and 914 cm^{-1} (ν $\text{Al}_2\text{-OH}$) (Table 1).

Earth pigments, also known as ochres, are natural clay-based minerals with iron oxides and hydroxides as the main chromophore. The variation in hues is mainly due to the type and proportions of the chromophore present [19, 20]. Brownish hues are often associated with the presence of manganese oxides. Mn was also detected in conjunction with Fe by hXRF (Fig. 6e). However, in this case the contribution of the dirt deposits to the present hue cannot be excluded, particularly in the lighter tones. As in the case of the previously discussed pigments, earth pigments seem to have been used alone, but also mixed with Cr rich green pigments and cobalt blue (Figs. 5c and 8).

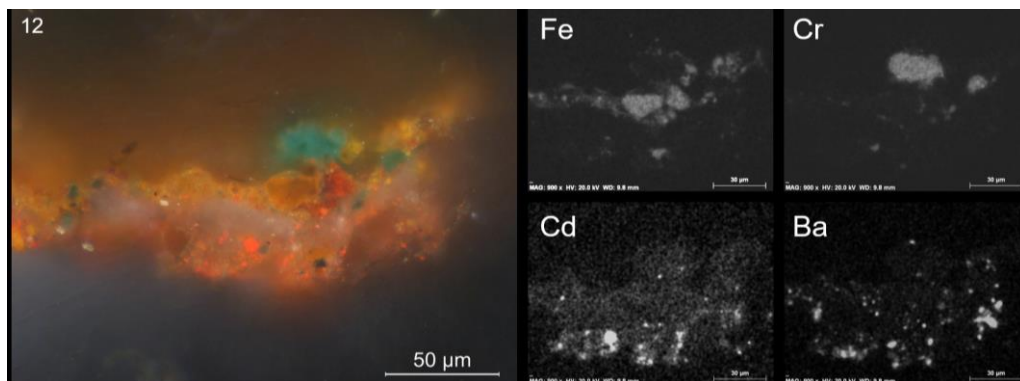


Fig. 8. Microphotographs in visible light and VP-SEM-EDS elemental map of Cd, Cr, Ba and Fe of micro sample 12

Handheld XRF also revealed the occasional use of a Cd-based pigment in the browning yellow to brownish red areas of the painting (Fig. 6f and Fig. 8). Selenium and/or sulfur were found to be associated to Cd, suggesting the use of Cadmium yellow, orange and Cadmium red pigments [20].

Binder

UV-light examination of paint layers in situ did not show any clear evidence of organic materials used as binders. Not even in the blue and green paint layers suspected to have been laid down with a painting *secco* technique due to pigments' lack of cohesion. The analysis by μ -FT-IR of eight micro samples scrapped from blue and green areas and two samples from a dark brownish red and orange areas also pointed to calcite being used as the only binder (Table 1 and Fig. 1).

OM and elemental maps obtained by VP-SEM-EDS of the paint layers in the cross-sections 8 and 18 displayed in figure 3, revealed that the pigment particles are embedded in an inorganic crystalline calcium carbonate (CaCO_3) matrix. In paint layers 2 and 12 (Figs. 7 and 8) evidences of deterioration phenomenon can be observed, which can be explained by the partial exposure of the pigment particles to environmental conditions.

In terms of painting technique, the distribution of calcium, seen in the elemental maps obtained by VP-SEM-EDS and the absence of a carbonation crust in the interface paint layer-plaster corroborate the use of a fresco technique. Julio Resende seems to have used true fresco, a technique in which pigments are only mixed with water but also lime fresco, on which the pigments are previously mixed with calcium hydroxide (most likely lime milk) before being laid down in the wet plaster surface. The higher paint layer thickness of micro sample 18 seems to point in that direction.

Conclusions

This study has unveiled for the first time the *modus operandi* and materials used in mural paintings by one of the most important Portuguese artists of the 20th century. The division of the mural into seven *giornata*, and the absence of an organic binder and of carbonation crusts in the interface paint layer-plaster in the micro samples analyzed by μ -FT-IR and VP-SEM-EDS clearly shows that Julio Resende followed the fresco tradition using conventional and modern synthetic pictorial materials. At least in this painting, his work is more in line with revivalists of the classical technique rather than experimenting with new ways of painting. The data collected are key elements for future comparisons with his other three mural painting works and with fellow contemporary artists in Portugal and abroad.

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