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On the Two Working Palettes of Almada Negreiros at DN Building in Lisbon (1939–1940): First Analytical Approach and Insight on the Use of Cd Based Pigments

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Abstract: This paper reports the first analytical approach carried out on two working palettes by Portuguese modernist master Almada Negreiros, found in 1991 behind old wood cabinets at the DN building in Lisbon. This is the only known occasion Almada left behind the color experiments done before starting to paint in the nearby walls and as such, it is a unique opportunity to analyze the materials and painting techniques that were originally used. The analytical setup comprised in loco technical photography in Vis, UVF and NIR; p-OM, spectrophotometry in Vis and h-EDXRF, complemented by OM-Vis, μ-FT-IR and VP-SEM-EDS of painting micro-samples and pigments in powder form. Preliminary results suggested the use of fresco painting technique and revealed some technical details, such as the use of a coarse lime sand finishing mortar mixed with natural vegetable fibers, and the extensive use of cadmium-based pigments that were not commonly used (or even recommended) in an alkaline environment. The Cd pigments were used alone or in mixtures with Fe based pigments in the warm hues and with cobalt and ultramarine blue pigments in some green paint layers. No clear evidence of organic materials that could have been used as binders was detected.

Keywords: Almada Negreiros; mural paintings; TP; p-OM; h-EDXRF; SEM-EDS

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1. Introduction

Almada Negreiros (1893–1970) is a key figure of the first generation of Portuguese Modernists. Since his first appearance in 1911, he marked the artistic panorama through a multifaceted career of almost sixty years. As a muralist, he created several works of art in Portugal, most of them integrated in architectural projects of Pardal Monteiro, a renowned architect from the Estado Novo Regime (1933 to 1974) [1]. The mural paintings of Almada Negreiros, executed between 1939–1940 at the DN building located in the heart of Lisbon, are the second public commission made by the artist and they are recognized today for their value in modern art historiography [2]. These monumental mural paintings, classified as his first fresco achievement, have been widely discussed regarding their plastic and iconographic attributes [2]. Yet hardly anything is known about the modus-operandi of Almada Negreiros.

Almada was knowledgeable in the art of fresco painting but was also an experimentalist. Over the years, the flaking and lack of cohesion of some of the paint layers at the DN Building raised suspicion, among conservators-restorers, that Almada may have used dry techniques and pigments beyond the fresco palette. In 1991 two working palettes of the

artist were discovered during conservation-restoration works, behind the old wood cabinets standing beneath the painting depicting the mapa-mundi in the main hall (Figure 1). This is the only known occasion where Almada left behind the experiments carried out on the wall before starting to paint. Both working palettes are visually strikingly bright and consist of 70 paint layers in total ranging from warm to cold hues and light/dark values. Both palettes were protected from light and untouched for 50 years, thus providing a unique opportunity to analyze the original materials, the pictorial technique and some technical details employed by Almada Negreiros.

Figure 1. Main view of the hall at the DN Building in 2017 with the location of the two working palettes. They are 1 m from the ground and measure 55 × 68 cm (palette A) and 50 × 94 cm (palette B).

This paper discusses the first results of the analytical approach to cadmium-based pigments (alone or mixed with other pigments) that were found in both working palettes. The data obtained lead to a comprehensive understanding of Almada's innovative character and provided reference materials for further studies of the DN mural paintings and other sets within the framework of the research project ALMADA: Unveiling the mural painting art of Almada Negreiros (1938 to 1956).

2. Experimental

The research was carried out in loco on paint layers of both palettes and in the laboratory on microsamples of paint layers collected by conservators-restorers in 1991 and by the authors in 2017 (Figure 1). Additionally, three pigments in powder retrieved from Almada's studio in 2017 were also used as reference for comparison purposes. They are identified as LF25 (jaune de cadmium orangé), LF8 (rouge de cadmium clair) and LF24 (rouge de cadmium foncé). All are from the commercial brand Pigments Pour la Fresque of LeFranc-Paris.

2.1. In Loco Research

2.1.1. Technical Photography in the Visible Light Range (Vis and Vis-Racking), Ultraviolet Induced Visible Fluorescence (UVF) and Near Infrared at 1000 nm (NIR1000)

Records in Vis and UVF on both palettes were acquired in loco with a Nikon D3200 24 Mpx digital single lens reflex and objective Nikkor 18–55mm f:3.5–5.6 GII. NIR images were carried out with a Nikon D3100 14 MpX camera modified for full spectrum with high pass filters X-nite 780, 850 and 1000 nm. Photographs in visible racking light (Vis-Racking)

were obtained under the angle of 15–20° from the painting surface. Halogen lamps 1000 W-230 V D58525 were used for Vis and NIR photography whereas for UVF, Labino® MPXL UV PS135 light (35 W PS135 UV Midlight 230 V) with UV filter included (310,400 mm and a peak at 365 mm), a midlight distribution angle of 20° and a start-up time full power after 5–15 s. Raw image output was used with target QpCard101 v3 and AIC PhD target for white balance calibration. The fluorescence emission of the red swatch of the AIC PhD target was also used for calibration of the UVF photos.

Figure 2 gives a global view of the two-color palettes in Vis, UVF and NIR (1000 nm) with the indication of the paint layers discussed and illustrated in subsequent sections.

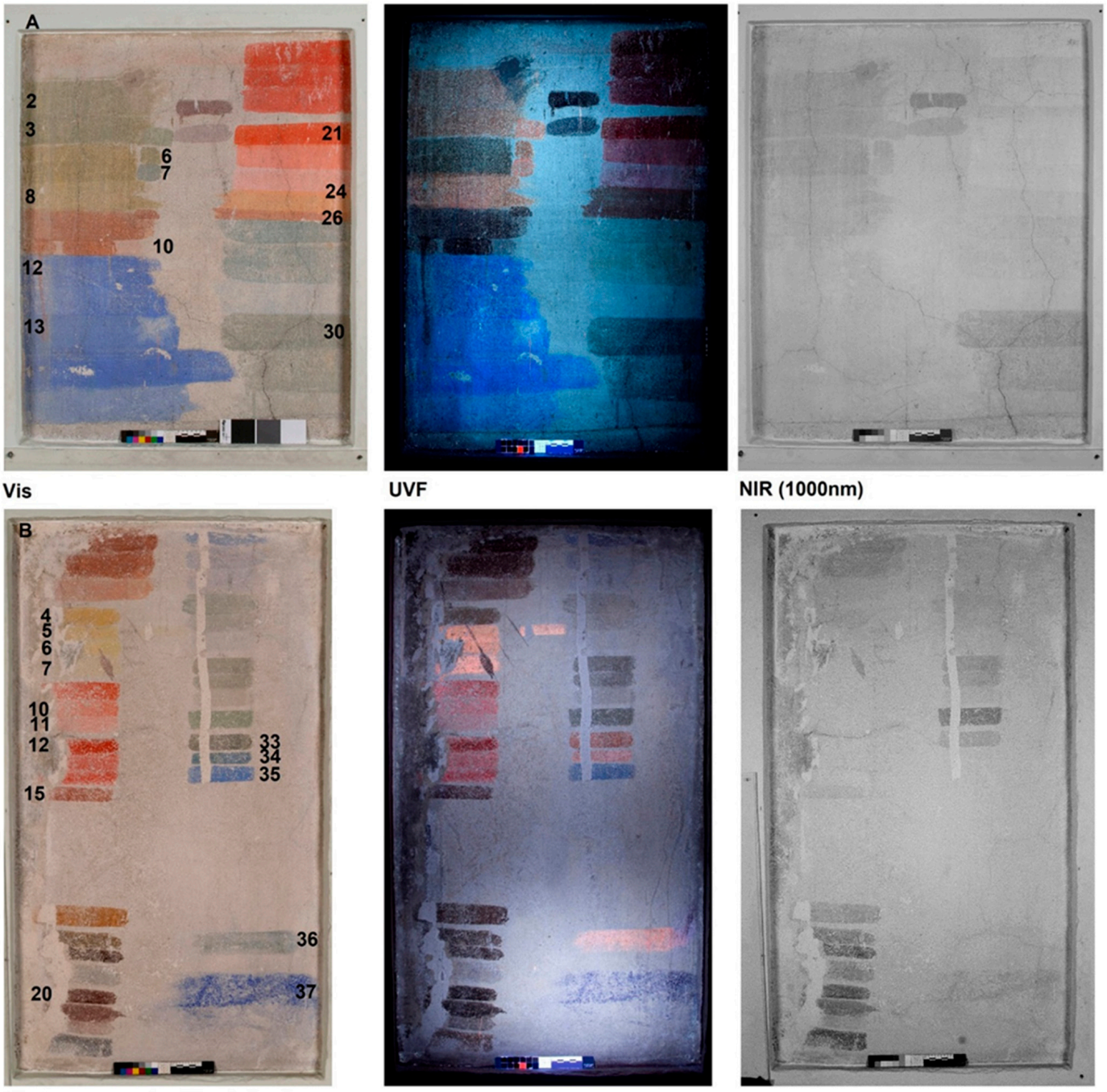

Figure 2. Technical photography in the Visible, UVF and NIR (1000 nm) of the working palettes (**A**) (on top) and (**B**) (on the bottom).

2.1.2. Portable Optical Microscopy (p-OM)

Portable optical microscopy was carried out with two hand-held optical digital microscopes, Dinolite PROAM13T-FVW and DinoLite Premier AD3713TB with 20 and 435× magnifications to record details of the paint layers such as pigments particles, textures and brushstrokes.

2.1.3. Spectrophotometry in the Visible Range

The diffuse reflectance spectral curves of paint layers in the visible range (380–750 nm) were measured in loco with a dataColor CheckPlusII, equipped with an integrating sphere, in the following conditions: diffuse illumination 8° viewing (in agreement with the CIE publication No. 15.2 Colorimetry), SCE and standard Illuminant/Observer D65/10°. The aperture size used was USAV (Ø5 mm) and punctually (Ø2.5 mm). The data obtained are the average of three measurements taken on each paint layers. All paint layers were analyzed but this paper presents only the results which enabled the distinction of the two blue chromophores found in the paint layers.

2.1.4. Handled X-ray Fluorescence Spectrometry (h-EDXRF)

Handheld X-ray fluorescence spectrometry allowed a preliminary in situ and non-invasive identification of the elemental composition of the paint layers of both working palettes. A handheld X-ray fluorescence analyzer Bruker Tracer III SD was used, equipped with an X-ray tube with rhodium target and a silicon drift detector. A total of 83 measurements covering the entire palette's color range were analyzed. Spectra were recorded using a voltage and a current intensity of 40 kV and 30 μA, respectively, during a 30 s real-time count. The instrument was controlled using the S1PXRF software (Bruker™, Billeric, MA, USA). The spectra were later processed using the Artax (Bruker™) software to obtain semi-quantitative data. Each sample was analyzed in one or two locations (a and b; Appendix A). The generated net areas of the fluorescence lines were normalized to the counts of the Rh Kα lines [3,4].

2.2. Laboratory Research

2.2.1. Optical Microscopy (OM-Vis-UV)

Optical microscopy record of micro fragments collected from the paint layers was initially performed to ensure further material and technical characterization. The samples were analyzed as micro fragments and as cross sections. Paint layers selected for cross sections were embedded in epoxy fix resin (Epofix, Struers A/S) and polished with different MicroMesh sanding sheets. Optical microscopy was performed with reflective visible light and ultraviolet radiation at 200 and 500× magnification, using a dark field microscope Leica DM2500M. For UV mode a high-pressure burner 103W/2 UV lamp and an excitation Pass Band filter 340–380 nm, a dichromatic mirror 400 nm and a suppression filter Lp425, size K coupled, were used. Photographic documentation was obtained with a Leica DFC290HD digital camera.

2.2.2. X-ray Diffraction (μ-XRD)

A Bruker D8 Discover® diffractometer using Cu Kα radiation was employed to identify the main mineralogical phases of the pictorial support. This analysis was carried out in one mortar sample collected right below the paint layers from palette B during the restoration works in 1991. The sample was mounted as powder on a zero-background specimen holder. An angular range of 3–75° 2θ, step size of 0.05° per second and step time of 2 s was used for collecting the diffractograms. Identification of crystalline phases was performed using the DIFFRAC.SUITE EVA® software and the ICDD PDF-2 database.

2.2.3. Variable Pressure Scanning Electron Microscopy (SEM-EDS)

Variable pressure scanning electron microscope (SEM) coupled with an energy dispersive spectrometer (EDS) enabled high resolution images of the cross sections and to map

the elemental composition of the mortar and paint layers to complement h-EDXRF results. The analysis was carried out with a variable pressure SEM HITACHI S-3700N operator with an accelerating voltage of 20 kV and at 40 Pa. SEM was coupled with Bruker XFlash 5010 Silicon Drift Detector (SDD) with resolution of 129 eV at Mn Kα.

2.2.4. Micro-Fourier Transform Infrared Spectroscopy (μ-FT-IR)

Micro-Fourier transform infrared spectroscopy was carried out for the chemical identification of compounds within the paint layers, in particular organic materials. Samples were collected in loco by gently scratching the paint surface. Analyses were made with a Bruker Tensor 27 Mid-IR (MIR) spectrometer, coupled with HYPERION 3000 microscope, and controlled by OPUS 7.2 software with corresponding OPUS library (copyright© 2012 Bruker Optics and Microanalysis GmbH, Berlin, Germany). A MCT (Mercury Cadmium Telluride) detector was used, cooled with liquid nitrogen. Analyses were done in transmission mode using a 15× objective and an EX'Press 1.6 mm diamond compression microcell, STJ-0169. Spectra were acquired in the region of 4000–600 cm^{-1}, with 64 scans and a resolution of 4 cm^{-1}. The bands attribution was made by comparison with bibliographic references on the subject [5–11].

3. Results and Discussion

This section gives a first overview of the composition of the pictorial support; of the yellow and red painting materials used and highlights some technical details. Data characterization resulting from different analytical techniques are also compared with three powder pigments from the LeFranc-Paris manufacturer retrieved from Almada's studio in 2017. The goal was to ascertain if Almada could have used these pigments in 1939 in the two working color palettes at DN building.

3.1. Pictorial Support (Mortar)

Figure 3 shows the results of XRD, OM and SEM-EDS carried out for the mortar characterization. The main phases identified by XRD in a mortar sample collected from palette B were calcite ($CaCO_3$), quartz (SiO_2), plagioclase ($(Na,Ca)Al(Si,Al)_3O_8$), potassium (K-) feldspars and accessory biotite from the mineral group of micas, with chemical formula $K(Mg,Fe)_3(F,OH)_2(Al,Fe)Si_3O_{10}$.

In turn OM and SEM-EDS analyses of a paint layer cross section (B10) indicate that calcite corresponds mainly to the binder phase whereas the silicate phases described above are present as aggregates (Figure 3b,c).

Most of the aggregate's particles are coarse and can been seen on the paint surface conferring a rough and uneven texture to the paint (Figure 3d). Another interesting technical feature found by OM on the samples collected is the presence of natural vegetable fibers within the mortar and at the paint surface. Two examples observed are shown in Figure 3d,e. These organic materials, being natural moisture holders, were likely used to strengthen the lime-based mortar by preventing the appearance of cracks upon drying.

3.2. Paint Layers (Pigments)

3.2.1. Cadmium Based Pigments

The UVF and NIR images of both working palettes in Figure 2 reveal differences in the paint layers' response to the different wavelengths. Particularly interesting are the UVF images of the yellow and green paint layers A2, A3, A7, A8, A33, B5, B6, B7, B33, B34 and B36 that stand out due to their intense orange fluorescence (Figure 2). A closer look with p-OM at 430× magnification of the yellow paint layers B5, B6, B7 show clusters of bright yellow particles on the surface. In the green hues of A7, B34 and B36, they are also found mixed with blue pigments (Figure 4a,b). No evidence of these bright yellow pigments was found however in the yellow paint layer B4 and in the green A30, which lacked fluorescence under UV radiation (Figures 2 and 4).

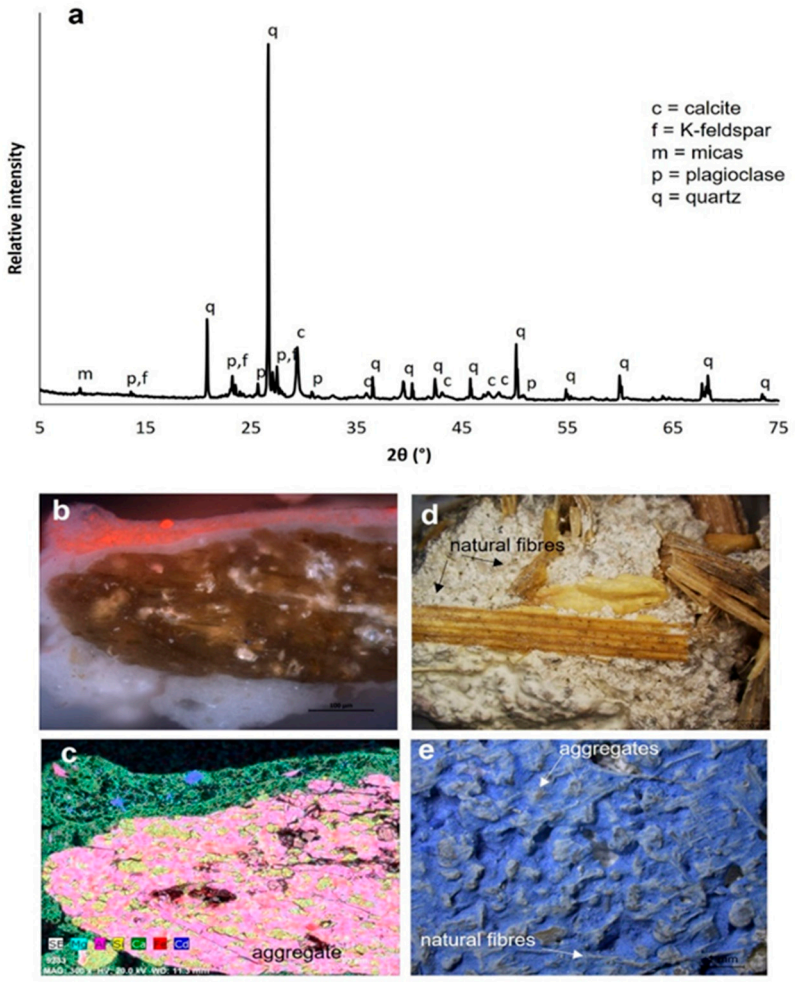

Figure 3. (**a**) Diffratogram of the mortar collected below the paint layer in palette B; (**b**,**c**) OM at 200× magnification and SEM-EDS of B10 paint layer cross section showing the presence of an Al-Si coarse aggregate particle in a Ca matrix. In the elemental distribution map Si is in yellow, Al in pink and Ca in green; (**d**,**e**) OM at 20× magnification of the mortar sample and paint layer B35, unveiling the presence of natural vegetable fibers within the mortar and at the surface.

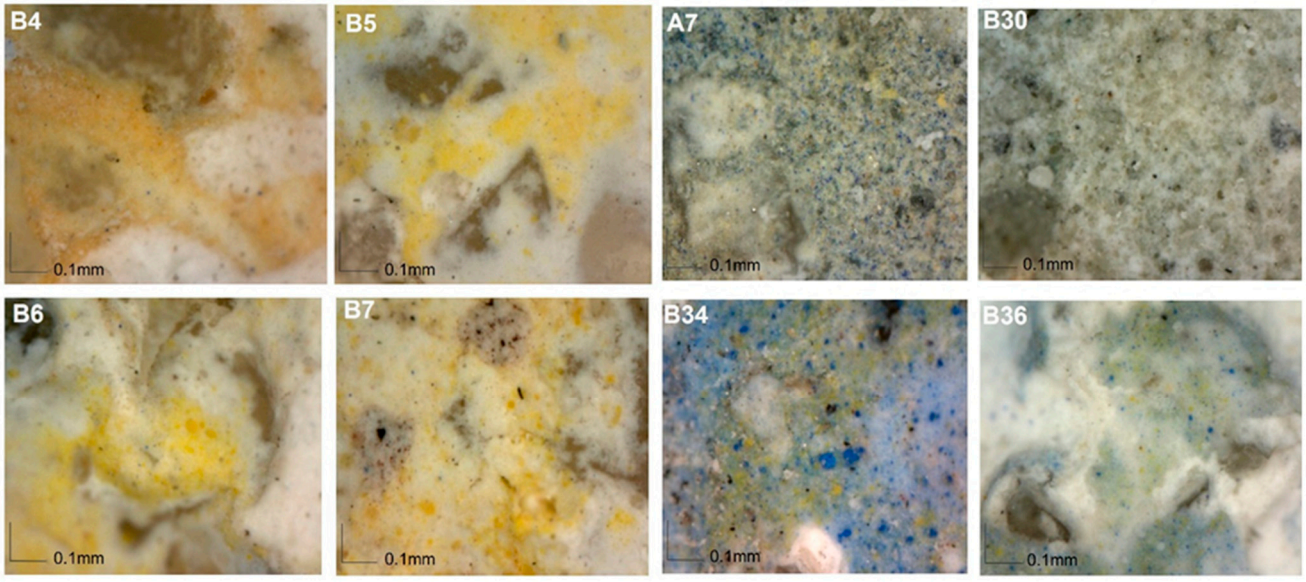

Figure 4. p-OM images at 435× magnification of yellow paint layers B4 to B7 and green paint layers A7, B34, B36 and A30.

The emission induced in the visible range can depend on many factors such as the wavelength and bandwidth of the UV source, the painting materials used originally, or in later interventions, how these materials interact with each other and, additionally, how they have aged [12,13]. The pigments and the binders originally used were the focus of the current research to explain this phenomenon since there is no record of past consolidation and retouching in both working palettes.

Among the yellow pigments available for artists in Portugal since the 19th century stand earth pigments, Naples yellow, Lead tin yellow (I and II), Orpiment, Massicot, Mars yellow, Chrome yellow and Cadmium yellow [14–16]. Most of them were historically used by Portuguese painters in easel paintings, sculptures and manuscripts from the 15th Century onwards [14,17–24]. The exception being Mars colors, and the synthetic chrome and cadmium pigments discovered only in the 19th century with the advance of chemical industries [14,25].

In mural paintings, earth pigments were the main painting materials used for frescoes due to their chemical stability in an alkaline environment [26–30]. With mural secco techniques, the color palette could be extended and the use of brighter artificial yellow pigments such as Naples yellow and Lead tin yellow (I and II) were reported in Portuguese mural paintings made in the 16th and 17th centuries [31,32]. However, for the first half of the 20th century no analytical data was found except for one mural painted in 1955 by Julio Resende, a renowned artist from the second generation of Portuguese Modern Art [33]. In his mural painted at fresco in a small a church in Évora countryside (southeast Portugal), Julio Resende used mainly earth pigments but there is evidence that he may have resorted to small amounts of cadmium pigments to achieve more orange saturated hues [33].

In what concerns Almada Negreiros, there are not yet scientific studies published on his painting materials. It can be deduced by the artworks left that he was acquainted with both easel and mural painting techniques and therefore it is not surprising to find all kinds of natural and synthetic pigments among the materials left in his studio. Besides earth pigments such as ochres, umbers, and siennas, Mars pigments, Naples yellow and Cd based pigments were also found in his studio. The Cd based pigments ranging from lemon yellow to dark red were selected for comparison as they not only show bright colors like the paint layers under study, but this kind of pigment may also show fluorescence in UVF due to irregularities in the crystal structure, such as vacancies and impurities [34,35].

Table A1 in Appendix A reports the elements found by h-EDXRF in the paint layers of both palettes and in the powder pigments from Almada's studio labelled as jaune de cadmium orangé (LF25), rouge de cadmium clair (LF8) and rouge the cadmium foncé (LF24).

The presence of cadmium (Cd) was confirmed in the yellow paint layers B5 to B7, in the orange A24 and in the green paint layers A2, A3, A6, A7, A8, B33, B33, B34 and B36 (Table 1). This heavy element was also detected by h-EDXRF in all the red and pinkish paint layers (except for A10) and in small to trace amounts in the brownish layers A26 and B15 (Table 1, Figure 5a).

Cadmium pigments have varying hues ranging from the yellows and light oranges of cadmium sulfides (CdS), to the deep orange and red colors characteristic of Cd sulfoselenides Cd(S,Se) [11,35,36]. As seen in Figure 5b, both Cd and Se were detected in all the pinks (except A10), reds, oranges and in the brown paint layers A26 and B15 cited above, indicating that Cd(S,Se) was used to produce these hues in both color palettes. In Figure 5c, the presence of iron (Fe) in the Cd-Fe plot can be associated to earth pigments but also to biotite identified previously as a mortar aggregate by XRD (Figure 3).

In Figure 6a,b, the comparison between the h-EDXRF spectra of the yellow and light red paint layers B5 and B10 and the three powder pigments LF25, LF8 and LF24 reveals a common elemental identity in the main chromophores (CdS and Cd(S,Se)) and in other minor elements such as Fe, Ti, Cu and Zn (Figure 6a,b) that might be attributed to the same manufacturing process.

Table 1. Summary of the μ-FTIR results of 21 paint layers from palette A and B.

Sample Ref.	Compounds Identified (Characteristic Absorption Bands (cm^{-1}))
A2	Aluminosilicate (3696, 3616, 1031, 1010, 782, 764, 692, 646) Gypsum (3404, 1620, 611) Calcite (2512, 1795, 1424, 874, 713)
A3	Aluminosilicate (3693, 3621, 1113, 1028, 1009, 778, 761, 693, 646) Gypsum (3407, 1619, 670, 612) Calcite (2512, 1795, 1419, 874, 713)
A6	Aluminosilicate (3691, 1112, 1029, 1006, 648) Gypsum (3555, 3406, 1620, 669) Calcite (2514, 1795, 1418, 875, 714)
A7	Aluminosilicate (3696, 3651, 3619, 1110, 1026, 1011, 781, 693, 646) Quartz (798, 780, 694) Gypsum (3408, 1620, 669) Calcite (2511, 1794, 1409, 873, 712)
A8	Aluminosilicate (3697, 3618, 1033, 1009, 781, 695) Gypsum (3545, 3401, 1620, 1148, 1118, 671) Calcite (2511, 1795, 1416, 875, 713)
B4	Aluminosilicate (3698, 3668, 3647, 3618, 1107, 1031, 1007, 914) Calcite (2509, 1794, 1408, 873, 712)
B5	Otavite (1414, 861, 835, 723) Calcite (2512, 1795, 1419, 874, 713) Sulfate (1155, 1008)
B6	Inorganic compound (1144, 669, 628) Calcite (2512, 1795, 1418, 874, 713)
B7	Otavite (114, 859, 721) Calcite (2512, 1794, 1415, 873, 713)
B9	Aluminosilicate (1040, 1009) Calcite (2513, 1795, 1419, 874, 713)
B10	Calcite (2511, 1795, 1427, 875, 713) Gypsum (1138, 671, 606)
B11	Sulfate (1156, 1137) Aluminosilicate (3692, 1043) Calcite (2511, 1794, 1419, 874, 712)
B12	Aluminosilicate (1034, 1009, 914) Calcite (2512, 1795, 1405, 874, 712)
B15	Aluminosilicate (3697, 3669, 3651, 3620, 1113, 1033, 937, 914) Quartz (1164, 799, 778, 694) Calcite (2511, 1794, 1419, 874, 713)
B15 (Fiber)	Natural fiber-vegetable (2897, 1594, 1376, 1324, 1265, 1233, 1203, 1158, 1107, 1057, 898, 666, 618) Calcite (2517, 1794, 1421, 874, 712)
B33	Aluminosilicate (1032, 1010, 779, 694) Calcite (2512, 1795, 1428, 874, 713)
B34	Aluminosilicate (3692, 3677, 3651) Calcite (2511, 1794, 1410, 873, 713) Gypsum (3409, 1130, 671, 607)
B35	Inorganic compound (1645, 1115, 1047, 690) Calcite (2516, 1798, 1455, 873, 712)
B37	Ultramarine blue (1005, 694, 667) Calcite (2515, 1795, 1451, 874, 711) Gypsum (3536, 3405, 3244, 1682, 1622, 1131, 1005, 667)

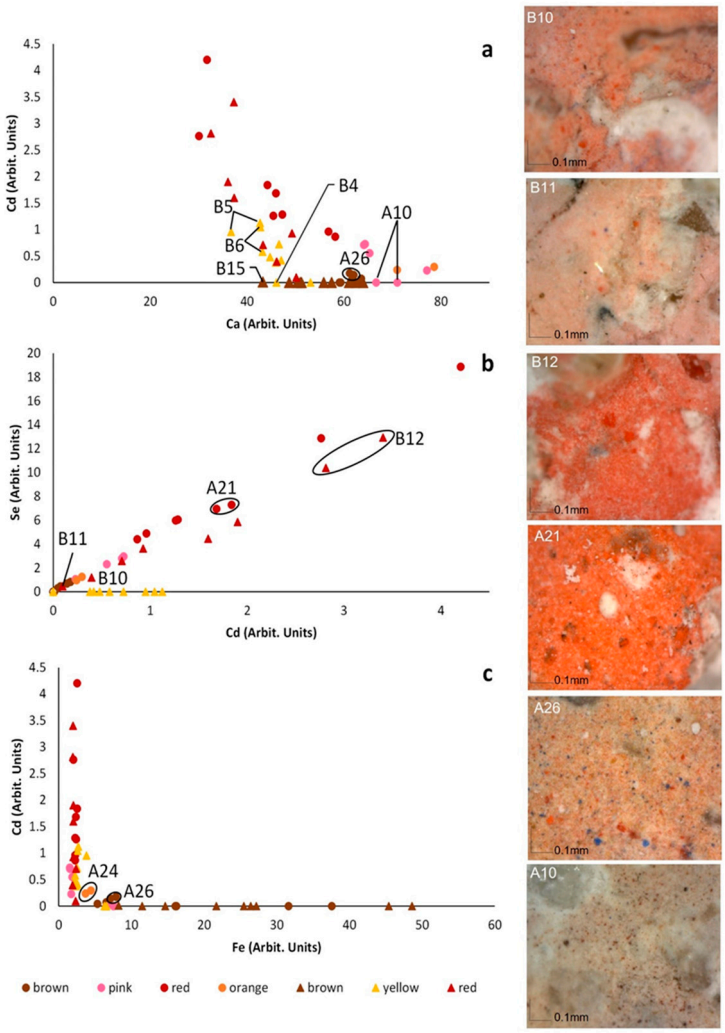

Figure 5. (**a**) h-EDXRF Cd-Ca plot showing the presence of Cd pigments mixed or over Ca based materials; (**b**) h-EDXRF Cd-Se revealing the use of Cd(S,Se) in the pink (except A10) and red paint layers; (**c**) h-EDXRF Cd-Fe plot showing the presence of Cd and Fe based pigments. On the left, from top to bottom, p-OM at 435× magnification of red/pink paint layers B10 to B12, A21; of brownish layer B26 and the pinkish layer A10. The dots refer to paint layers from palette A and the triangles from palette B.

Similar chemical composition of the yellow paint layer B5 and powder pigment LF25 is also ascertained by μ-FT-IR spectra in Figure 6c. Cadmium carbonate (otavite) was identified based on the characteristic bands at 1414, 861, 835, 723 cm^{-1}, while bands at 1155 and 1008 cm^{-1} can be attributed to sulfates.

To find otavite in paint layer B5 and in the powder pigment LF25 was not surprising since this material has been detected in studies of modern and historical Cd yellow pigments [11,37]. According to Fiedler (1986), otavite was one of the raw materials that were originally used in the dry method to produce CdS, by mixing it with sulfur in anoxic conditions at 300–500 °C. In addition, otavite could also be added to CdS to produce lighter yellow shades, which according to historical records were unstable [11]. So far there is no information on the methodology used by LeFranc manufacturer in the early 20th century but most likely it would have been similar to the one described above.

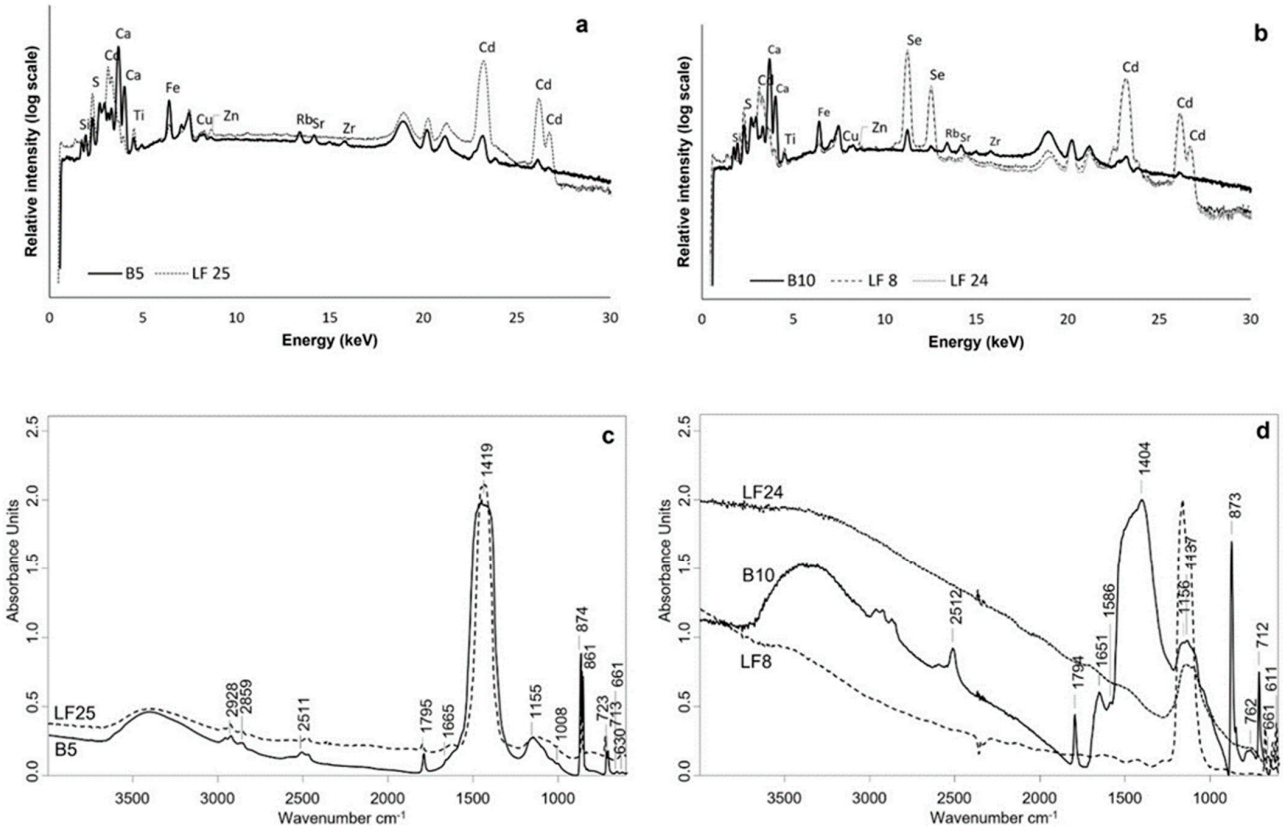

Figure 6. (**a**) h-EDXRF spectra of yellow paint layer B5 and of powder pigment LF25 latablebelled as jaune de cadmium orangé; (**b**) h-EDXRF spectra of pink paint layer B10 and of powder pigment LF8 and LF24 labelled as rouge de cadmium clair and foncé; (**c**,**d**) μ-FT-IR of paint layers B5 and B10 and the powder pigments LF25, LF8, LF24.

The comparison between the red paint layer B10 and the two Cd based pigments LF8 and LF24 in Figure 6d, on the other hand, was not straightforward as the main absorption bands assigned to CdS are in the far-IR region [11]. In the mid-IR, the bands seen in Figure 6d can be assigned to sulfates at 1155, 1156, 1008 and 1137 cm^{-1} that might be related to fillers added to the pigments. Calcite identified by FT-IR in both paint layers B10 and B5 based on the characteristic bands at 2511, 1795, 1419, 874 and 713 cm^{-1} is most likely associated to the painting technique used.

Considered to be among the most stable pigments, capable of producing bright shades with good hiding power and being compatible with most materials, cadmium pigments were rapidly adopted by artists worldwide following their widespread commercialization in the second half of the 19th century [11,38]. However, their use was not recommended in a fresco alkaline environment due to the known instances of fading and bleaching caused by the presence of cadmium oxalate and carbonate and free sulfur in the composition of Cd sulfides [9]. The presence of free sulfur and iron can also cause noticeable hue darkening due to the formation of iron sulfide [11], but this was not the case in both palettes at the DN building which do not show evidence of color alteration.

3.2.2. Other Hues Obtained with Cadmium Pigments

As stated above, Cd element was also detected by h-EDXRF in the pinkish paint layers (except for A10) and in small to trace amounts in the brownish layers A26 and B15 (Table A1, Figure 5a). Cadmium pigments are also known to mix well with blue pigments to produce green hues [9] and Almada Negreiros most likely knew that. Handheld-EDXRF results revealed that the green paint layers A7, B34 and B36 are enriched in both Co and Cd, but also have variable amounts of iron, suggesting mixtures of cobalt blue, cadmium pigments and Fe-rich pigments to produce the different hues (Figure 7a,b). The occurrence

of other chromophores is also evidenced by h-EDXRF. The presence of manganese is often associated to Mn oxides in earth pigments and could explain the brownish green hues in both palettes (Figure 7c). On the other hand, the composition of a Cr green pigment in paint layers A2, A3 and A6 is still not understood and must be further analyzed (Figure 7d).

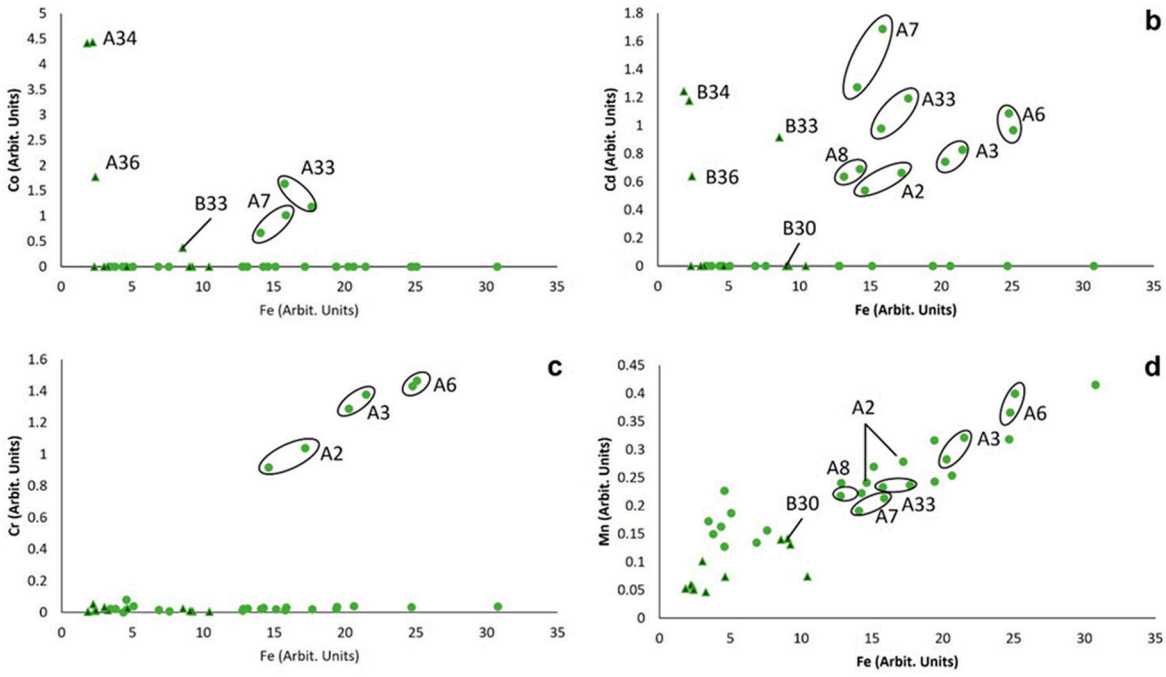

Figure 7. (**a**,**b**) h-EDXRF Co-Fe and Cd-Fe plots revealing mixtures with blue and Cd pigments; (**c**,**d**) h-EDXRF Cr-Fe and Mn-Fe plots suggesting the use of Cr green pigment and green earth pigments. The green dots refer to paint layers from palette A and the green color circles to palette B.

In what concerns the blue pigments, the h-EDXRF results and the Vis-reflectance curves of A12-A14, B35 and B37 reveal that cobalt blue ($CoO{\cdot}Al_2O_3$) was not the only, or even, the main pigment used to produce blue hues (Table A1, Figure 8a,b). Ultramarine blue, a complex sulfur-containing sodium aluminum silicate of chemical formula $Na_{8–10}Al_6Si_6O_{24}S_{2–4}$, seems to be responsible for most of the dark to light blue colors displayed in both palettes. Ultramarine blue and cobalt blue are distinguished by their spectral curves in the visible range. As Figure 8a shows, ultramarine blue has a dominant wavelength around 459 nm and a characteristic rising reflectance in the red whereas cobalt blue shows a broad strong reflectance with a peak around 430-450 nm, a smaller sharper peak centering on 495 nm, low reflectance around 520 and 650 nm, and a strong rising (red) reflectance above 660 nm [39,40].

The presence of ultramarine blue was also confirmed by μ-FTIR in paint layer B37 due to the presence of a very strong absorption band between 950 and 1200 cm^{-1} and a weaker absorption band around 698 and 663 cm^{-1} (Figure 8c) [8]. In the eroded paint layer B37, the interference of calcite from the underneath support is responsible for the attenuation of the spectral curve and higher reflectance values (R%).

Portable OM images of B35 and B37 in 430× magnification revealed, in both cases, rounded and fine blue particles below 1 μm in size hindering their distinction based on particles morphology (Figure 9). Both ultramarine and cobalt blue found in the palettes are synthetic pigments discovered in the 19th century and rapidly adopted by painters due to their pure deep blue color and stability in different media [32,33]. Both pigments were a common component of the impressionist and post-impressionist palette in Europe; in Portugal, they were the main blue pigments used by the renowned Amadeu de Sousa Cardoso (especially cobalt blue), one of the closest friends of Almada Negreiros [23,24,38,40].

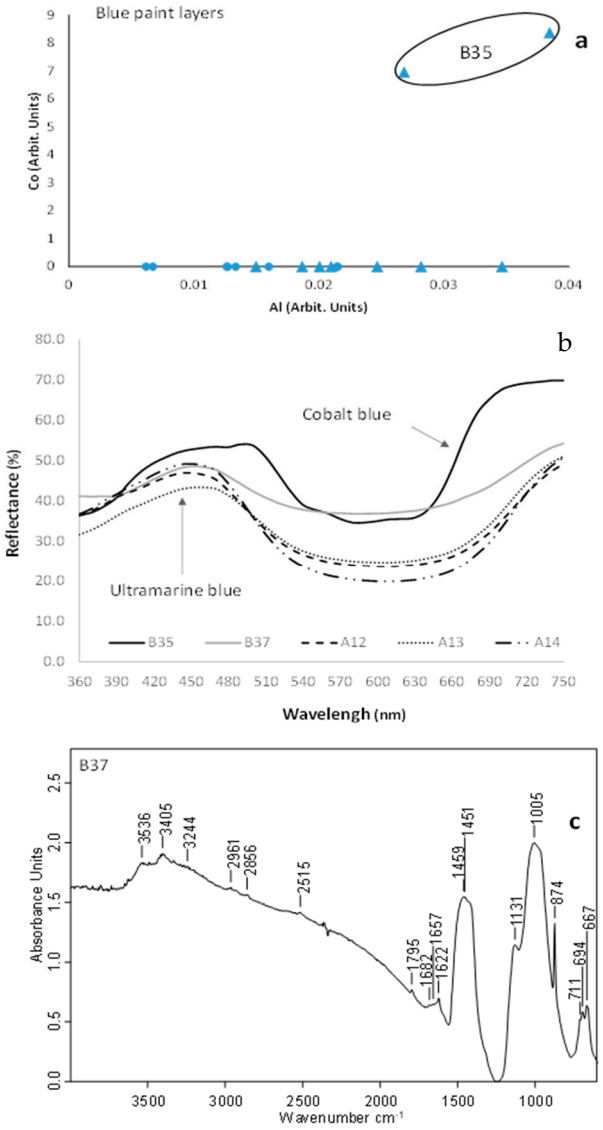

Figure 8. (**a**) h-EDXRF Ca-Al plot; (**b**) Vis-reflectance curves of blue paint layers A12 to A14, B37 and B35; (**c**) μ-FTIR spectra of the blue paint layer B37. The blue dots refer to paint layers from palette A and the blue color triangles from palette B.

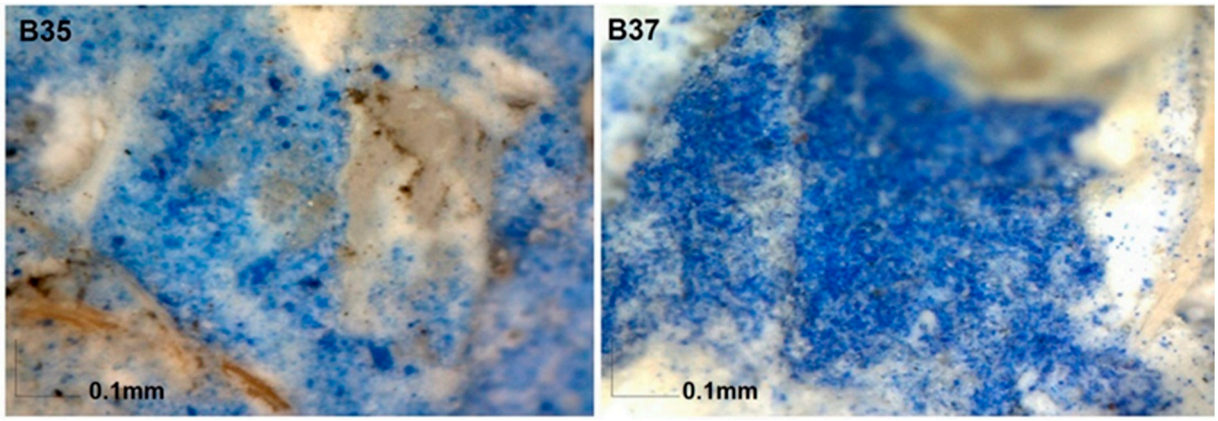

Figure 9. p-OM of the blue paint layers B35 (cobalt blue) and B37 (ultramarine blue) at 435× magnification.

3.3. Paint Layers (Binders and Pictorial Technique)

Table 1 reports the results of μ-FTIR performed in 21 paint layers from palette A and B. FTIR analysis revealed the presence of calcite in all spectra, reporting typical vibrational assignments of CO_3^{2-} and O-C-O stretching and bending groups, respectively [5,6].

Only paint layers B5 and B10 of Figure 6c,d) reports traces of an organic material by the presence of CH/ NH bands around 2928 and 2859 cm^{-1}. According to Silva et al. [9] and Gettens et al. [10] the absence of vibrational group C=O and also CO and NH bands in the fingerprint region, commonly assigned to an organic binder [7,41] can be related to the presence of traces of organic matter that can be found in $CaCO_3$ sedimentary rocks. In fact, no evidence of organic materials was found in the paint layers that have shown fluorescence in UVF photography (Figure 2). Therefore, results obtained so far suggest that lime carbonation was the binding mechanism of pigment particles. The same hypothesis is corroborated by SEM-EDS analysis.

In Figure 10, EDS elemental map distribution of calcium shows the pigments particles embedded in a Ca-rich matrices. The cross section of paint layers B10 in Figure 2 and paint layers B4, B35 and B36 in Figure 10 also show that the pigments were laid down in a single layer into the mortar surface while it was fresh but maybe also in a later stage. The use of a fresco technique is suggested in paint layers B5, B10 and B36 by the absence of a Ca-rich crust in the interface mortar-paint layer [42]. However, the Ca-rich crust is clearly identified in B35, which may indicate that Almada laid down the blue pigment in a more advanced stage of the carbonation process (Figure 10).

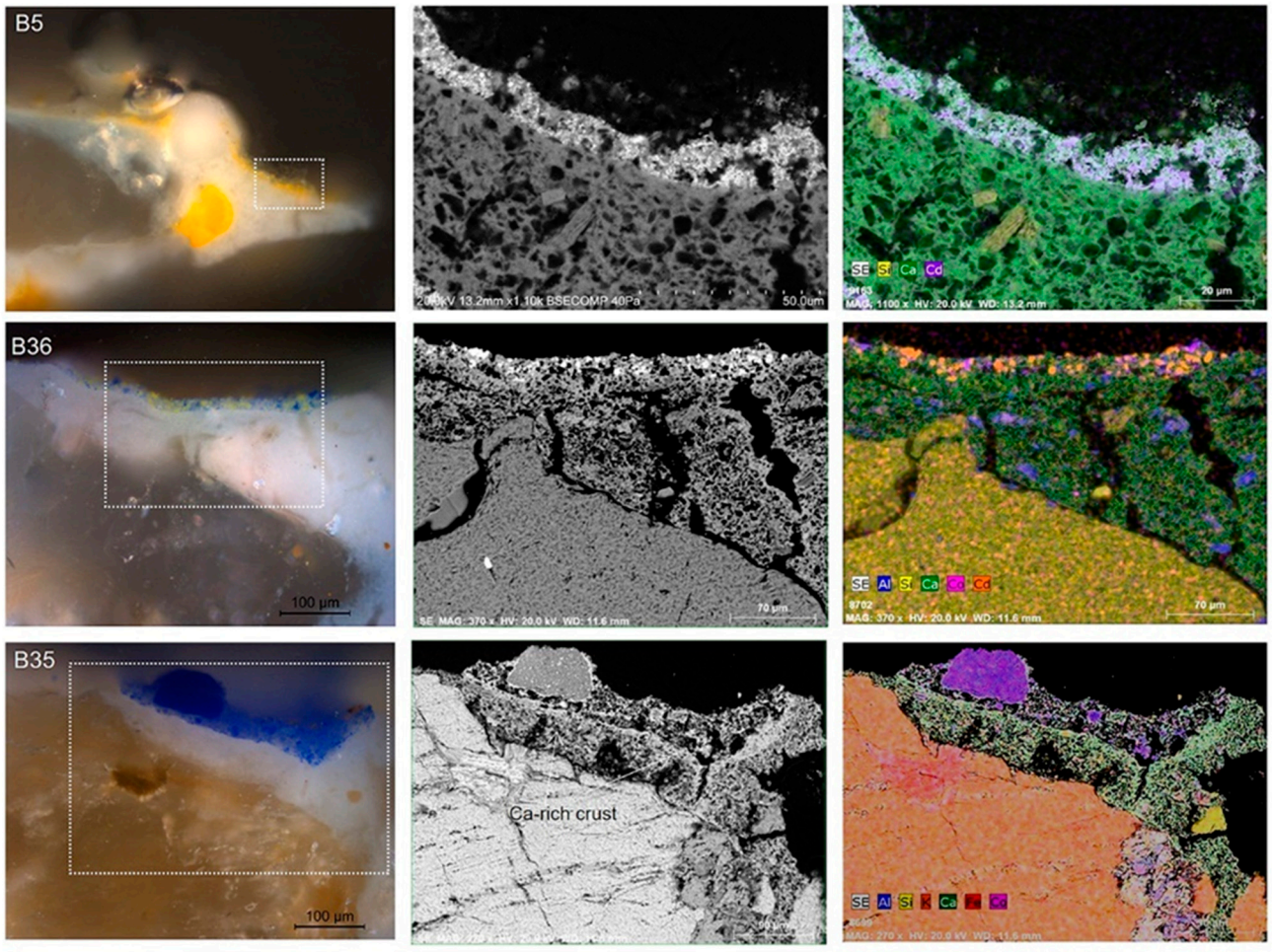

Figure 10. OM; SEM images and EDS elemental mapping of paint layers cross sections B5, B36 and B35. The calcium elemental distribution map is identified in green in all paint layers.

The origin of gypsum in the paint layers B5, B10, B24, B34 and B37 is still uncertain. It may be the result of neo-formation due to water infiltration from old leaking pipes or it may have been added as a filler. According to Plaster (1997), anhydrous sodium sulfate and/or carbonate are also among the raw materials reported for the manufacture of ultramarine blue [37]. Finally, the presence of Si-O stretching band around 1030 cm^{-1} and OH stretching bands in the region of 3700–3620 cm^{-1} characteristic of aluminosilicate compounds are present in almost all paint layers (see Table 1). These compounds are most likely related to iron-based earth pigments and/or Al-Si mortar aggregates, also identified by XRD (Figure 3).

4. Conclusions

This paper unveils for the first time the pigments used by Almada Negreiros in two working palettes left on the wall of the DN building and uncovered in 1991 during restoration works. Preliminary results revealed, for the first time, that while Almada followed the traditional way of making fresco paintings, he introduced new painting materials. This confirms the hypothesis raised by conservator-restorers. The use of Cd pigments goes beyond the traditional fresco palette and Almada seems to have extensively used them to produce most hues in both working palettes. Yellow and red cadmium pigments were used alone but also in conjunction with other pigments such as cobalt blue, ultramarine blue, and earth pigments to extend the variety of hues produced. Surprisingly, the Cd pigments analyzed are in a good condition. Could their stability be explained by their extremely limited exposure to light having been preserved behind wood cabinets for 50 years? Are they well preserved since only 83 years have passed since the painting's execution? Or can these pigments against all odds remain stable in an alkaline environment? Future research will give more answers by extending the analytical research to all paint layers and by comparing the two working palettes with the surrounding mural paint layers exposed since 1939–1940.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Table A1. h-EDXRF results (net areas normalized to the counts of the Rh Kα lines; arbitrary units) of the 27 paint layers discussed in the results discussion and of the three powder pigments.

Colors	Sample	Al	Ba	Ca	Cd	Cl	Co	Cr	Cu	Fe	K	Mn	Pb	Rb	S	Se	Si	Sr	Ti	Zn	Zr
yellow	B4_a	0.020	-	46.049	-	0.076	-	0.034	0.203	6.302	0.769	0.051	-	0.394	1.001	-	0.285	0.267	0.235	0.083	0.106
	B4_b	0.012	-	53.089	-	0.090	-	0.037	0.102	6.580	0.983	0.104	-	0.447	0.758	-	0.257	0.261	0.218	0.082	0.133
	B5_a	0.011	-	42.687	1.125	0.018	-	0.029	0.123	2.690	0.750	0.057	-	0.423	0.927	-	0.248	0.305	0.233	0.111	0.146
	B5_b	0.015	-	36.693	0.953	0.059	-	0.019	0.193	3.817	1.120	0.054	-	0.509	0.739	-	0.228	0.341	0.284	0.097	0.109
	B6_a	0.009	-	43.187	0.581	0.030	-	0.047	0.129	2.270	1.061	0.044	-	0.415	0.901	-	0.284	0.286	0.208	0.059	0.103
	B6_b	0.015	-	42.742	1.045	-	-	0.038	0.135	2.593	0.963	0.079	-	0.481	1.115	-	0.198	0.319	0.200	0.055	0.129
	B7_a	0.015	-	44.732	0.479	0.052	-	0.020	0.138	2.210	1.104	0.041	-	0.450	1.083	-	0.308	0.276	0.243	0.065	0.113
	B7_b	0.012	-	45.913	0.378	0.037	-	0.007	0.138	2.392	0.794	0.067	-	0.473	1.093	-	0.288	0.312	0.221	0.087	0.121
orange	A24_a	0.019	-	78.594	0.296	0.186	-	0.014	0.099	4.431	0.243	0.079	-	0.349	0.645	1.253	0.093	0.314	0.137	0.095	0.261
	A24_b	0.015	-	70.952	0.240	0.141	-	0.007	0.106	3.677	0.241	0.145	-	0.315	0.674	0.977	0.101	0.258	0.129	0.089	0.203
	LF-25	-	-	-	29.625	-	-	0.028	0.082	0.388	-	-	0.091	-	1.993	-	-	-	0.352	0.167	-
red	A21_a	0.013	-	44.191	1.840	0.025	-	0.016	0.153	2.544	0.476	0.149	-	0.345	0.895	7.288	0.072	0.264	0.151	0.109	0.100
	A21_b	0.011	-	45.952	1.685	0.019	-	0.014	0.103	2.357	0.412	0.128	-	0.302	1.013	6.947	0.095	0.264	0.145	0.107	0.096
	B10_a	0.025	-	46.138	0.396	0.005	-	0.031	0.118	1.914	0.717	0.062	-	0.396	1.088	1.203	0.301	0.321	0.158	0.055	0.128
	B11_a	0.017	-	50.137	0.097	0.037	-	0.029	0.135	2.331	0.778	0.079	-	0.455	1.058	0.462	0.257	0.401	0.156	0.089	0.247
	B12_a	0.016	-	37.260	3.404	0.009	-	0.003	0.115	1.972	0.889	0.084	-	0.377	1.417	12.928	0.227	0.274	0.149	0.152	0.104
	B12_b	0.026	-	32.541	2.814	-	-	0.006	0.131	1.956	1.106	0.074	-	0.423	1.040	10.384	0.280	0.278	0.155	0.082	0.099
	LF-8	-	-	-	36.844	-	-	0.020	0.111	0.306	-	-	-	-	2.836	76.925	-	-	0.255	0.239	-
	LF-24	-	-	-	38.259	-	-	0.025	0.124	0.442	-	-	-	-	2.038	97.999	-	-	0.263	0.113	-
pink	A10_a	0.007	-	71.000	-	0.187	-	0.012	0.117	7.542	0.325	0.167	-	0.372	0.673	-	0.089	0.253	0.189	0.087	0.202
	A10_b	0.003	-	66.638	-	0.175	-	0.021	0.169	6.521	0.423	0.158	-	0.410	0.526	-	0.074	0.255	0.277	0.109	0.136
brown	A26_a	0.022	-	62.028	0.142	0.176	0.742	0.005	0.132	7.107	0.639	0.160	-	0.437	0.554	0.690	0.125	0.258	0.209	0.092	0.120
	A26_b	0.015	-	61.164	0.177	0.179	0.791	0.008	0.144	7.877	0.628	0.117	-	0.385	0.599	0.833	0.158	0.266	0.201	0.103	0.142
	B15_a	0.017	-	43.263	0.011	0.072	-	0.013	0.231	8.243	0.633	0.038	-	0.441	1.459	0.019	0.259	0.320	0.252	0.069	0.107
	B20_a	0.017	-	57.464	-	0.147	-	0.024	0.681	48.618	0.432	0.243	0.850	0.399	1.467	-	0.206	0.249	0.234	2.342	0.124

Table A1. *Cont.*

Colors	Sample	Al	Ba	Ca	Cd	Cl	Co	Cr	Cu	Fe	K	Mn	Pb	Rb	S	Se	Si	Sr	Ti	Zn	Zr
green	A2_a	0.019	0.008	33.424	0.664	0.135	-	1.038	0.204	17.204	0.939	0.278	-	0.433	0.335	-	0.318	0.412	0.346	0.108	0.151
	A2_b	0.027	0.006	37.299	0.537	0.143	-	0.916	0.171	14.612	0.927	0.241	-	0.380	0.380	-	0.307	0.351	0.308	0.075	0.139
	A3_a	0.018	0.005	30.670	0.826	0.149	-	1.377	0.116	21.496	0.883	0.321	-	0.432	0.431	-	0.354	0.413	0.300	0.137	0.163
	A3_b	0.021	0.009	28.901	0.741	0.149	-	1.286	0.180	20.270	0.900	0.282	-	0.430	0.402	-	0.385	0.424	0.415	0.114	0.154
	A6_a	0.032	0.009	30.384	1.086	0.130	-	1.429	0.150	24.763	0.950	0.366	-	0.446	0.489	-	0.377	0.530	0.447	0.143	0.158
	A6_b	0.031	0.015	27.503	0.966	0.098	-	1.464	0.201	25.082	0.901	0.400	-	0.386	0.408	-	0.348	0.476	0.477	0.121	0.141
	A7_a	0.022	0.009	32.474	1.687	0.113	1.016	0.029	0.147	15.857	0.870	0.213	-	0.391	0.569	-	0.306	0.428	0.329	0.143	0.142
	A7_b	0.021	0.010	34.117	1.273	0.093	0.668	0.021	0.176	14.078	0.948	0.191	-	0.423	0.515	-	0.293	0.342	0.342	0.183	0.131
	A8_a	0.015	0.012	38.217	0.636	0.147	-	0.023	0.133	13.132	0.976	0.221	-	0.493	0.423	-	0.301	0.336	0.288	0.172	0.115
	A8_b	0.015	0.005	34.409	0.689	0.136	-	0.027	0.125	14.258	0.766	0.222	-	0.407	0.388	-	0.295	0.324	0.286	0.088	0.148
	A30_a	0.022	0.011	44.440	-	0.200	-	0.022	0.154	19.395	0.623	0.316	-	0.397	0.323	-	0.258	0.510	0.236	0.137	0.131
	A30_b	0.019	0.015	49.661	-	0.185	-	0.020	0.141	15.130	0.499	0.270	-	0.329	0.370	-	0.259	0.438	0.345	0.126	0.113
	A33_a	0.020	0.006	34.633	1.193	0.092	1.184	0.018	0.106	17.683	0.820	0.237	-	0.406	0.430	-	0.308	0.456	0.360	0.131	0.129
	A33_b	0.025	0.004	36.969	0.980	0.072	1.634	0.014	0.094	15.772	0.779	0.233	-	0.409	0.424	-	0.285	0.429	0.352	0.125	0.119
	B33_a	0.017	0.009	43.014	0.916	0.038	0.375	0.024	0.109	8.575	0.663	0.140	-	0.389	1.199	-	0.269	0.386	0.388	0.099	0.099
	B34_a	0.021	-	45.915	1.177	0.055	4.436	0.052	0.109	2.227	0.688	0.059	-	0.393	1.335	-	0.248	0.300	0.313	0.166	0.120
	B34_b	0.022	-	49.320	1.243	0.060	4.413	0.005	0.109	1.842	0.443	0.053	-	0.353	1.408	-	0.162	0.301	0.751	0.156	0.096
	B36_a	0.019	-	56.828	0.640	0.085	1.768	0.014	0.112	2.415	0.422	0.051	-	0.397	1.924	-	0.131	0.308	0.176	0.116	0.146
blue	A12_a	0.021	-	59.507	-	0.160	-	0.004	0.120	2.689	0.630	0.139	-	0.361	0.961	-	0.183	0.242	0.198	0.125	0.167
	A12_b	0.013	-	61.535	-	0.143	-	0.035	0.113	2.536	0.497	0.137	-	0.360	0.979	-	0.152	0.279	0.239	0.094	0.136
	A13_a	0.006	-	56.762	-	0.151	-	0.056	0.152	2.785	0.467	0.117	-	0.429	0.514	-	0.130	0.231	0.234	0.069	0.092
	A13_b	0.016	-	57.685	-	0.146	-	0.006	0.156	2.537	0.371	0.083	-	0.375	0.537	-	0.089	0.294	0.212	0.080	0.083
	B35_a	0.038	-	54.411	-	0.123	8.364	0.027	0.098	2.192	0.602	0.046	0.132	0.389	1.297	-	0.186	0.309	0.451	0.159	0.090
	B35_b	0.027	-	56.309	-	0.090	6.954	-	0.122	1.945	0.437	0.044	0.114	0.392	1.527	-	0.125	0.298	0.323	0.110	0.083
	B37_a	0.035	-	47.581	-	0.062	-	0.014	0.105	2.545	0.736	0.042	-	0.430	1.240	-	0.312	0.316	0.236	0.094	0.146
	B37_b	0.028	-	46.604	-	0.071	-	0.014	0.117	2.239	0.741	0.032	-	0.396	1.197	-	0.273	0.265	0.245	0.070	0.101

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