SCIENCE APPLIED TO MODERN MURAL PAINTING STUDIES. TRADITIONAL PIGMENTS AND INNOVATIONS IN ALMADA NEGREIROS' WORKING PALETTES AT THE DN BUILDING IN LISBON (PHASE 2).

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ABSTRACT

This chapter reports the analytical study carried out on Almada Negreiros' two working palettes in the public hall of the DN Building in 1939. Both palettes were hidden behind wooden cabinets and discovered in 1991 during conservation works. The first study carried out in 2021 focused on the identification of cadmium pigments. In phase 2, the goal was to extend the research to other colour materials to ascertain the different types of pigments employed by the artist.

The analytical setup comprised in loco colorimetry and spectrophotometry in the visible range, h-OM and h-EDXRF, complemented by OM-Vis and μ-FTIR of micro samples collected from the paint layers. The data obtained were compared with the results of the analyses carried out in the pigments found in powder form at Almada's studio from the commercial brand Pigments pour la Fresque-LeFranc-Paris, as they are the most likely source of the colour materials used in the production of the working palettes.

This research highlights not only the use of traditional pigments commonly found in fresco palettes, such as earth pigments, but also the introduction of modern colourants produced in the 19th century onwards. These are the case of the Cd pigments, Cr green pigments, cobalt and ultramarine blues and, most likely, Mars colours.

KEYWORDS

Modern Art, Almada Negreiros, Mural paintings, Technical Art history, Heritage Science

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1. INTRODUCTION

In the past, it was common practice among painters to prepare and test colour materials before starting to paint. Analytical studies of pigments and working palettes of easel painters retrieved from their studios have been reported over the years, bringing valuable insights into the pigment choices and the working methods of artists (Townsend 1993, 231-254; Cove 1998, 211-216; Izzo et al. 2017, 547-567). In regards to mural paintings, material and technical recommendations are well set up in historical and modern painting treatises and manuals (e.g., Vitruvius 1874, 151-177; Cennini 2003, 88-129; Nunes 1615, 112-114; Macedo 1886: 34-38; Rochetti 1937). However, finding and being able to examine the working palettes of a mural painter is very rare as they are made on-site, and they were not meant to endure being destroyed after serving their purpose. To the best of the authors' knowledge, this is the first time that such an opportunity has presented itself and, therefore, constitutes a unique case study of valuable importance.

The two mural working palettes done by Almada Negreiros were covered by a wooden cupboard directly after the completion of the mural decoration at the former public hall of the renowned Portuguese newspaper *Diário de Notícias* (Fig. 1). The painting commission for the walls of this entire space was given to Almada Negreiros, who carried it out between 1939 and 1940 (França 198, 349). The two working palettes are located beneath the monumental mural painting known as the Planisphere (or *Mapa-mundi*), and both were most likely done to test colour materials before Almada started this painting in 1939.

Fig. 1a. Overview of DN building main public hall in 1940. Photo: a) Postcard from the first Diário de Notícias Congress, 28 November 1964. Author unknown. Made in Portugal by EXECUCÃO.

After being covered, the presence of both working palettes fell into oblivion until 1991, when the wood cabinets were removed for restoration works. From that date onwards, the palettes were left in place, uncovered, and are now the object of study within the framework of project ALMADA. The first analytical approach to the painting materials and techniques used in both working palettes was carried out in 2021 and focused on the cadmium pigments found (Gil et al. 2021, 4578-4595). In the present study, the goal was to extend the analysis to the other colours to provide a global understanding of the different types of pigments used in terms of composition and historical context, serving as a reference for future studies of the mural paintings at the DN building.

Fig. 1b. Overview of DN building and of the main public hall in 2017. The arrows indicate the location of the two working palettes A and B, respectively with 55x68 cm and 50x94 cm. Photos: M. Ribeiro 2017. All rights reserved.

2. EXPERIMENTAL CONDITIONS

The results reported in the next section are based on the spectra-colorimetric analysis and handheld X-ray fluorescence (h-EDXRF) carried out on both working palettes and on 14 pigments in powder form used as a reference from: a) Kremer manufacturer (recent purchase), b) Pigments pour la fresque - LeFranc-Paris and c) from OSAKA-Japan manufacturer. The 13 pigments from a) and b) were found in Almada's studio in rusty tins. Given the high number of tins found, these are most likely the source of the painting materials used in Almada's working palettes and his mural painting commissions from 1939 onwards. The green earth pigment from Kremer was added due to its absence in the collection retrieved from Almada's studio.

2.1. COLORIMETRY AND SPECTROPHOTOMETRY

Colorimetry and spectrophotometry analysis comprised 70 colour measurements in the paint layers of both working palettes and 14 in the pigments in powder. The goal was to carry out with a spectrophotometer a first objective colour evaluation with the trichromatic coordinates CIE L*a*b* and a first spectral characterisation of the pigments. The colorimetric data were collected with a *Datacolor CheckPlusII*, equipped with an integrating sphere, in the following conditions: diffuse illumination 8º viewing (in agreement with the CIE publication No.15.2. Colorimetry), SCE and standard illuminant/observer D65/10º. The aperture size used was USAV (Ø5mm).

The results obtained in the CIE L*a*b* colour space, defined by the International Commission on Illumination (CIE) in 1976, correspond to the average of three measurements taken on the surface of the paint layer and powdered pigments. The chromatic coordinates measured were L*, which represents lightness (0-100), a*, which stands for the red/green axes, and b*, which stands for the yellow/blue hue axes (0-100).

The diffuse reflectance spectral curve of the paint layers and pigments in powder was also measured in the visible range (360-750 nm). It was compared with spectra from literature and previous studies (Fiedler 1986; Helias et al. 2006; Barnes 1939; Gil et al. 2009; Plasters 1997; Ashok 2007; Grissom 1986; Newman 1997).

2.2. HANDHELD ENERGY DISPERSIVE X-RAY FLUORESCENCE (h-EDXRF)

h-EDXRF allowed a preliminary in situ non-invasive identification of the elemental composition of the paint layers of both working palettes and the powder pigments included in this study. A *Bruker Tracer III SD* handheld instrument, equipped with an X-ray tube with a rhodium target and a silicon drift detector, was used to analyse all samples. Spectra were recorded using a voltage and a current intensity of 40 kV and 30 μA, respectively, during 30s (real time) for the paint layers and 60s (real time) for the pigments in powder form. The instrument was controlled using the S1PXRF software (Bruker™). The spectra were later processed using the Artax (Bruker™) software to obtain semi-quantitative data.

2.2. COMPLEMENTARY TECHNIQUES

Both spectra-colorimetric data and h-EDXRF analyses were complemented by optical microscopy in the visible range carried out:

in loco on the paint layers with a handle digital microscope *Dinolite Premier*, with 430x magnification.

in the laboratory on the micro fragments of paint layers collected in 1991 and in 2017, and on cross-sections prepared for a deeper insight into the pigment's optic and physical properties and paint stratigraphy. The imaging analyses were made with a dark field optical microscope, *Leica DM2500M* and a petrographic microscope, *Leica DM2700P* in PLM mode, equipped with a *Leica DFC290HD* and *MC170HD* digital cameras, respectively. Photographic documentation was acquired in reflected and transmitted visible light mode, with 500x magnifications. For cross sections, one fraction of the paint sample was embedded in an epoxy resin (*Epofix Fix*) and polished with 1200 and 4000 sandpapers *SIC papers Grif* in a *Drehzahlregle* rotation disc.

In addition, the powder pigments retrieved from Almada's studio were also characterised by XRD diffraction to ascertain their mineralogical composition. A *Bruker D8 Discover®* diffractometer using Cu K radiation was used for this purpose. The measurements were performed over a 2 range between 3° and 75°, using a step size of 0.05°/s and step time of 1 s. Identification of crystalline phases was performed using the DIFFRAC.SUITE EVA® software and the International Centre for Diffraction Data PDF-2 database.

Table I. – Summary of the results of colorimetry in the Vis, h-EDXRF and XRD analysis carried out in the pigments in powder from LeFranc-Paris, OSAKA-Japan manufacturers. * Exact match with the cadmium selenide sulfide phases present in the PDF-2 database was not achieved suggesting a distinct S-Se proportion. ** Colorant in the pigment could not be identified by XRD indicating the potential use of a non-crystalline material.

Sample ref.	**Colour**	**Manufacturer**	**CIE chromatic coordinates**			**Elemental composition (XRF)**	**Mineralogical composition (XRD)**
			L*	a*	b*		
LF25	jaune de cadmium orangé	Le-Franc	69.72	40.85	73.37	**Cd**, Cr, Cu, Fe, S, **Se**, Ti	Otavite
LF3	jaune de cadmium citron	Le-Franc	89.71	-0.96	95.82	**Cd**, Fe, Pb, S	Otavite
LF5	jaune de mars	Le-Franc	56.92	27.26	51.65	Al, Ba, Ca, **Fe**, S, Si, Zn	Calcite; goethite; quartz (traces); clay/mica (traces)
LF6	ocre jaune	Le-Franc	81.79	16.05	50.98	Al, Ca, **Fe**, K, Mn, Pb, S, Si, Sr, Ti	Quartz; hydroxylapatite
LF19	terre de sienne naturelle	Le-Franc	60.30	18.29	48.49	Al, Ca, **Fe**, K, Mn, Se, Si, Ti	Quartz; calcite; goethite; clays/micas
LF32	terre de sienne naturelle foncé	Le-Franc	47.75	19.93	39.55	Al, As, Ca, **Fe**, K, Mn, Ti, Si	Quartz; calcite; goethite; clays/micas
LF20	terre de sienne brulée clair	Le-Franc	38.29	39.28	52.22	Al, Ca, **Fe**, K, Mn, S, Si, Ti	Quartz; calcite; ankerite; hematite; clays/micas
LF15	brun de mars	Le-Franc	37.78	19.50	27.41	Al, Ca, **Fe**, K, Mn, Pb, Si, Ti	Hematite; goethite; quartz; clays/micas

LF33	terre de sombre brulée	Le-Franc	31.32	9.83	13.84	Al, As, Ca, **Fe**, K, Mn, S, Si, Ti, Zn	Quartz; alkali feldspar; gypsum; hematite; clays/micas
LF8	rouge de cadmium clair	Le-Franc	52.77	57.08	47.86	**Cd**, Fe, S, **Se**, Ti	Cadmium selenide sulfide *
LF24	rouge de cadmium foncé	Le-Franc	47.32	56.93	38.16	**Cd**, Fe, S, **Se**, Ti	Cadmium selenide sulfide *
LF10	ocre rouge	Le-Franc	59.63	35.41	38.24	Al, Ca, **Fe**, K, Mn, Si, Ti	Quartz; hematite; clays/micas
LF13	rouge de pouzzoles	Le-Franc	57.50	29.76	29.82	Al, Ca, **Fe**, Mn, S, Si, Ti, Zn	Quartz; calcite; aragonite; hematite; clays/micas
LF12	rouge de Mars	Le-Franc	40.38	27.87	21.67	Al, Ca, **Fe**, Mn, Pb, S, Si, Ti, Zn	Gypsum; hematite
LF14	brun rouge	Le-Franc	43.28	27.35	20.28	Al, Ba, Ca, **Fe**, K, Mn, S, Si, Ti, Zn	Quartz; anhydrite; hematite; clays/micas
LF30	vert à la chaux	Le-Franc	65.61	-33.79	2.29	Ba, Ca, **Cr**, Fe, K, S, Si, Sr	Barite **
O1	viridian	OSAKA	45.69	-34.23	12.35	Ba, Ca, **Cr**, Fe, K, Pb, S, Si, Sr	Barite; quartz **
LF16	outremer	Le-Franc	31.79	30.09	-67.36	Al, Ca, Fe, K, Mn, Pb, Rb, S, Si, Sr, Ti	Quartz; calcite; clays/micas
LF29	bleu de pompei	Le-Franc	73.13	-5.54	-29.22	Al, As, Ca, **Co**, Fe, Mn, Si, Ti, Zn	Zincite; cobalt aluminum oxide

3. RESULTS AND DISCUSSION

In this section, the data obtained are represented by colours. Table I summarises the analysis results carried out by colorimetry, h-EDXRF and XRD on the powder pigments found in Almada's studio. Tables II to IV report the summary results of the analytical setup used on the 35 paint layers selected for discussion due to their representativity in both working palettes. Figures 2 to 7 give an overview of the spectral and colorimetry results, as well as optical microscopy of the surface of paint layers and the respective cross sections.

3.1. RED, YELLOW, ORANGE, AND BROWNISH HUES

Table II. – Summary of the results of colorimetry in the Vis, h-EDXRF and μ-FTIR analysis carried out on 19 red, yellow, orange, and brownish paint layers of both working palettes.

Sample ref.	**Colour**	**CIE chromatic coordinates**			**h-EDXRF** (major elements for pigments identification in bold)	**μ-FTIR**	**Pigments attribution hypothesis**
		L*	a*	b*			
A10	Light pink	72.11	7.11	11.46	Ca, Al, **Fe**, K, Mn, Rb, S, Si, Sr, Ti, Zr		Ochre/ Mars pigment
A18	Light red	57.53	33.52	17.11	Ca, **Cd**, Al, **Fe**, K, Mn, Rb, S, **Se**,Si, Sr, Ti, Zr		Ochre/Mars pigment + Cadmium red
A19	Greyish purple	53.17	6.55	6.13	Ca, Al, **Cu**, **Fe**, K, Mn, **Pb**, Rb, S, Si, Sr, Ti, Zr, Zn		Ochre/Mars pigment + Pb-based pigment?

A22	Pink	67.09	21.08	13.41	Ca, **Cd**, Al, **Fe**, K, Mn, Rb, S, **Se**, Si, Sr, Ti, Zr		Ochre/Mars pigment + Cadmium red
A24	Orange	69.26	16.90	21.61	Ca, **Cd**, Al, **Fe**, K, Mn, Rb, S, **Se**, Si, Sr, Ti, Zr		Ochre/Mars pigment + Cadmium orange/red
B4	Yellow-orange	75.34	6.22	22.89	Ca, Al, **Fe**, K, Mn, Rb, S, Si, Sr, Ti, Zr	Aluminosilicate; calcite	Ochre/Mars pigment
B5	Yellow	77.60	3.10	17.78	Ca, **Cd**, Al, **Fe**, **K**, Mn, Rb, S, Si, Sr, Ti, Zr	Otavite, calcite; sulfate	Ochre/Mars pigment? + Cadmium yellow
B6	Yellow	79.49	1.53	15.86	Ca, **Cd**, Al, **Fe**, **K**, Mn, Rb, S, Si, Sr, Ti, Zr	Inorganic compound; calcite	Ochre/Mars pigment? + Cadmium yellow
B7	Light yellow	80.55	1.19	10.40	Ca, **Cd**, Al, **Fe**, **K**, Mn, Rb, S, Si, Sr, Ti, Zr	Otavite; calcite	Cadmium yellow + Ochre/Mars pigment?
B10	Light red	71.63	17.91	12.77	Ca, **Cd**, Al, **Fe**, K, Mn, Rb, S, **Se**, Si, Sr, Ti, Zr	Calcite; gypsum	Ochre/Mars pigment + Cadmium red
B11	Light pink	76.61	9.76	9.43	Ca, **Cd**, Al, **Fe**, K, M**n**, Rb, S, **Se**, Si, Sr, Ti, Zr	Aluminosilicate; calcite; sulfate	Ochre/Mars pigment + Cadmium red
B12	Light red	59.66	29.72	16.45	Ca, **Cd**, Al, **Fe**, **K,** Mn, Rb, S, **Se**, Si, Sr, Ti, Zr	Aluminosilicate; calcite	Cadmium red + Ochre/Mars pigment?
A4	Greenish light brown	62.71	2.36	15.94	Ca, Al, Ba, **Fe**, **K**, Mn, Rb, S, Si, Sr, Ti, Zr		Fe-based pigment (ochre and green earth?)
A25	Orange-brown	71.32	10.41	20.17	Ca, **Cd**, Al, **Fe**, **K**, **Mn**, Rb, S, **Se**, Si, Sr, Ti, Zr		Ochre/Mars pigment + Cadmium pigments
A26	Brown	61.56	14.00	17.16	Ca, **Cd**, Al, **Co**, **Fe**, **K**, **Mn**, Rb, S, **Se**, Si, Sr, Ti, Zr		Ochre/Mars pigment + Cadmium red + Cobalt blue
B2	Reddish brown	60.08	10.61	11.53	Ca, Al, **Fe**, K, Mn, Rb, S, Si, Sr, Ti, Zr		Ochre/Mars pigment
B15	Reddish brown	63.12	12.79	11.05	Ca, **Cd**, Al, **Fe**, K, Mn, Rb, S, **Se**, Si, Sr, Ti, Zr	Aluminosilicate; quartz; calcite	Ochre/Mars pigment + Cadmium red
B16	Brown	69.43	7.91	15.69	Ca, Al, **Fe**, **K**, Mn, Rb, S, Si, Sr, Ti, Zr		Ochre/Mars pigment
B18	Dark brown	55.44	3.88	6.18	Ca, Al, **Fe**, **K**, **Mn**, Rb, S, Si, Sr, Ti, Zr		Ochre/Mars pigment

The combined use of h-EDXRF and spectrophotometry revealed the use of two different kinds of pigments—iron (Fe) based and cadmium (Cd) based—to produce the red, yellow, orange, and brown hues present in both working palettes (Table II and Fig.2a/b).

In the pigments in powder form that were analysed, Fe is the major element in the pigments labelled as earth pigments (ochres, umbers, and sienna), while Cd is the predominant element in the pigments labelled as cadmium yellows and reds (Table I). The difference found in the paint layers is not so obvious. As already reported in Gil et al. 2021, Cd was identified along with Fe by h-EDXRF in paint layers B5 to B7; in the orange A24; in all the reds and pinks (except for A10); in the green paint layers A2, A3, A6, A8, B33, B34 and B36, and, finally, in small to trace amounts in the brownish layers A26 and B15 (Table II). The concomitant finding of cadmium and sulphur, and of sulphur and selenide, indicate the use of yellow cadmium sulphides (CdS) and orange and red cadmium sulphoselenide [Cd (S, Se)].

The presence of iron as a major element in all the paint layers analysed could be due to mixtures of pigments. Still, it can also be related to biotite minerals (of generic formula $K(Mg,Fe)_3(AlSi_3O_{10})(F,OH)_2$) identified as aggregates in the underneath mortar substrate (Gil et al. 2021, 4582). Zinc identified in minor, or trace amounts, by h-EDXRF in both working palettes and in the cadmium powder pigments can be associated to the raw materials and by-products of the manufacturing process of Cd pigments (Fiedler 1986: 64,66,70) (Tables I and II). Zinc was often added to CdS to produce lighter hues, as well as otavite, a calcium carbonate identified by µ-FTIR in the yellow paint layers B5 and B7, and by XRD on powdered pigments LF3 and LF25 (Tables I and II).

According to Fiedler (1986), otavite was one of the raw materials originally used to produce CdS using the dry method. Nevertheless, it could also be used to attain lighter shades of yellow that, according to the same author, were chemically unstable, especially in an alkaline medium, leading to a fast fading of the colour (Fiedler 1986: 71,72). This technical concern would have been taken very seriously among artists since there was a need in the early twentieth century, to ensure the solidity of these colours when used with a fresco painting technique. Paul Baudouin expresses an example of this concern in his book *La fresque - sa Technique - ses applications*, published in 1914 in Paris, which was found among Almada Negreiros' estate. Paul Bedouin taught a course in fresco painting at the École des Beaux-Arts in Paris and was one of the principal artists responsible for reviving the fresco technique of that time in France. The following excerpt was found as a footnote in the chapter on the colours suitable for this category of paintings.

> *'1. Je donne ici une liste des couleurs pouvant encore être employées à fresque. Le chemiste de la maison LeFranc à Paris en certifie la complete solidité: jaune de cadmiam citron, jaune de cadmium orangé, ...'* (Paul Baudouin, 1914:27, footnote 1)

It should be stressed that, at the time, cadmium pigments were a relatively recent addition to artists' palettes. The yellow compound cadmium sulphide was first recommended as a pigment in 1818. However, its use on a reasonably wide scale only took place after its commercialisation, which began in the mid-1840's (Fiedler, 1986: 65). Cadmium orange and cadmium red were created in the early 20th century and, like the cadmium yellows, were popular among artists due to their increased permanence, range of bright hues, high opacity, and high tinting strength even when laid down diluted, or mixed with slaked lime, as seen in the paint layers B10 to B12 in Fig.2a; B5 to B7 and B18 in Fig.2b (Fiedler 1986: 68,71,73; Barnett e al, 2006:452).

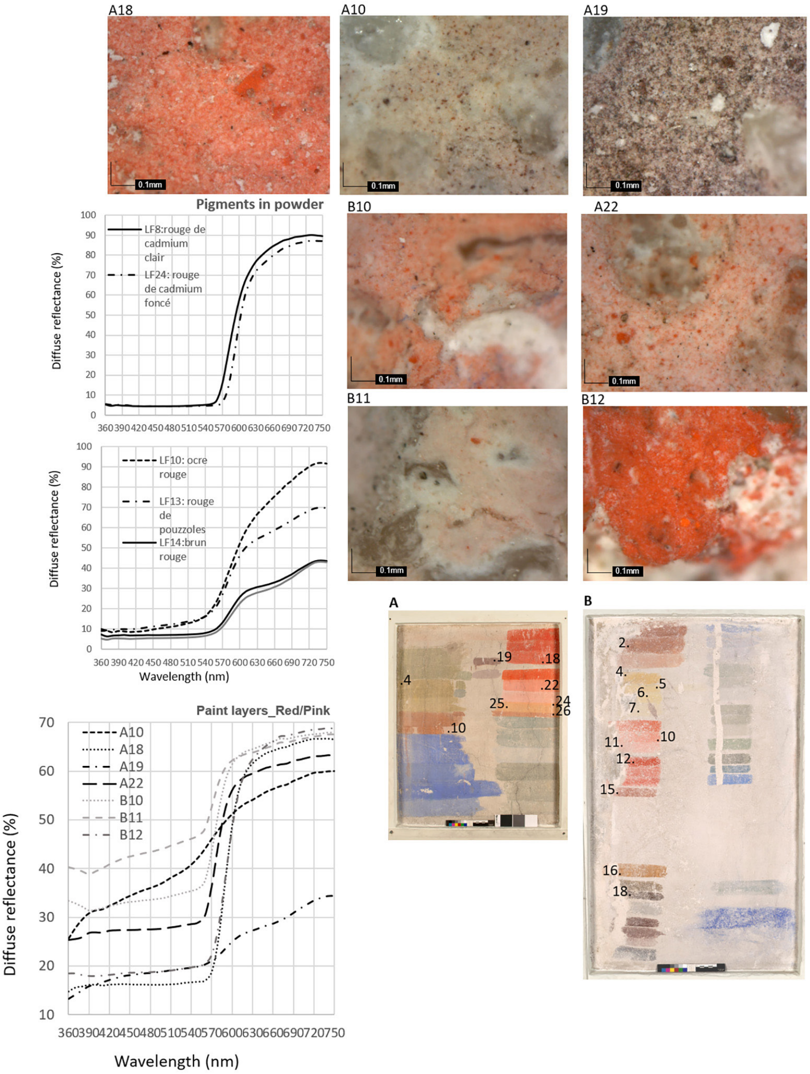

Fig. 2a. Handheld optical microscopy of red, yellow, orange, and brownish paint layers and respectively reflectance spectral curves in the visible range (360-750 nm).

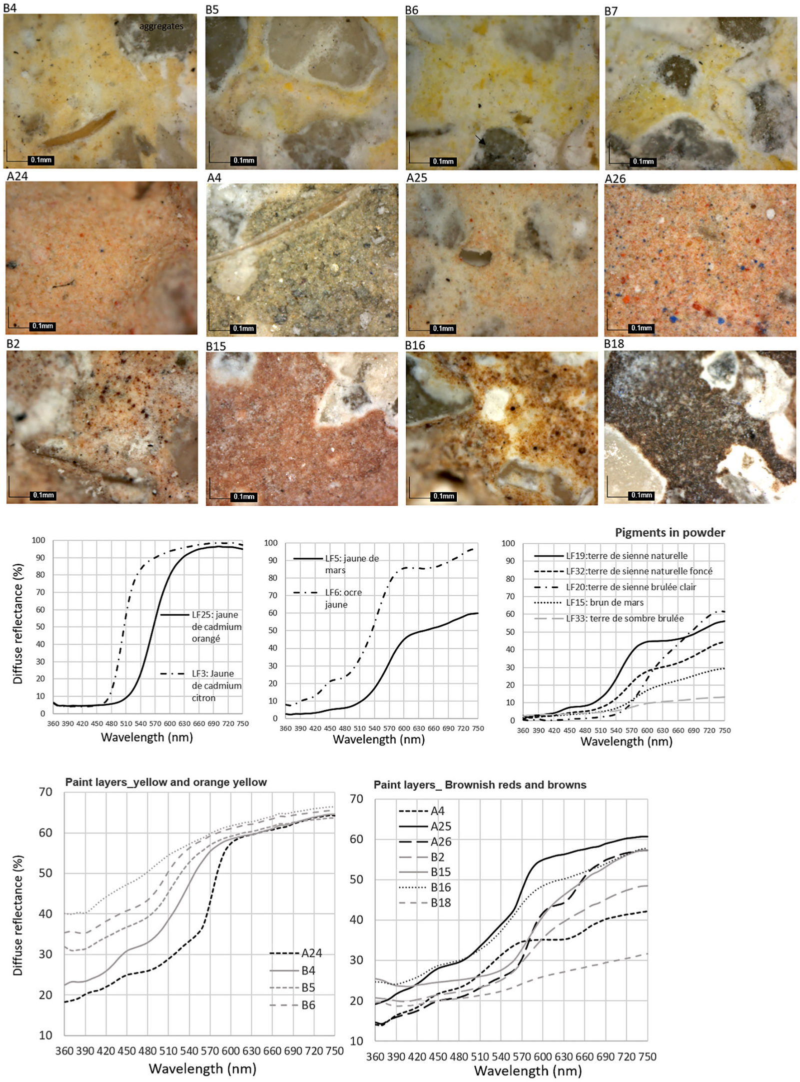

Fig. 2b. Handheld optical microscopy of red, yellow, orange, and brownish paint layers and respectively reflectance spectral curves in the visible range (360-750 nm).

The physical and optical characteristics of Cd pigments, along with its rather simple chemical composition — when compared to the more complex ones of the traditional earth pigments — explain the higher values of a* and b* chromatic coordinates in Fig.3 and the typical diffuse reflectance spectral curves in the visible range with a very sharp slope at 460 nm (yellows) and 560 nm (reds) (Fig.2a and Fig.2b). These features are clearly seen in the reference powder pigments LF3, LF25, LF8 and LF24, as reported in Table I and in Fig.2a/b, but less distinctive in paint layers B5 to B7, B10 and B11, due to the interference of lime and the presence of other earth compounds in their composition.

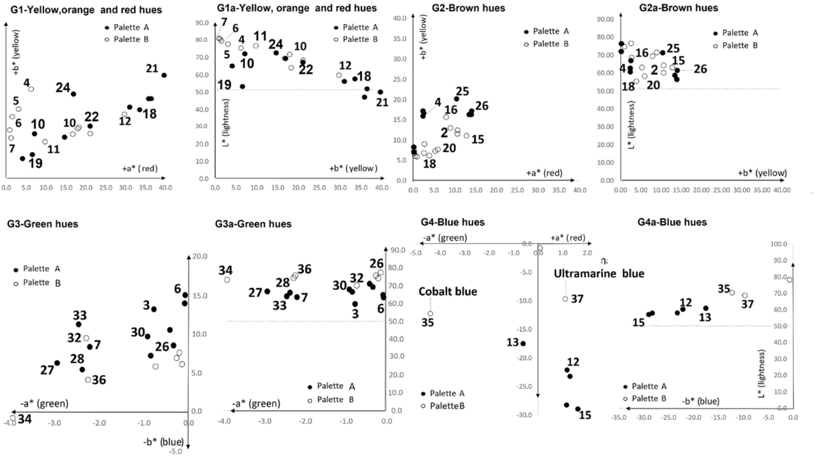

Fig. 3. Projection in the bidimensional CIEa*b* and CIEa*L* colour space of the paint layers of both working palettes by colours: G1 /G1a-yellow, orange and red hues; G2/G2a-brown hues;G3/G3a-blue hues and G4/G4a-green hues. The numbers identified the 35 paint layers discussed and illustrated in this section.

Unlike Cd pigments, Fe-based pigments include a broader array of natural, artificial, and synthetic substances, as well as compounds resulting from the mixture of substances of all types (Nicola et al. 2016, 545; Gil et al. 2007, 51-53). Iron (III) oxides are the main components of earth pigments, the largest and historically most important group of natural pigments, which includes several compounds with different chemical compositions depending on the geological source (Gil et al. 2008, 728-731). From prehistory to the present, their use has been widespread in all types of painting techniques due to their abundance in natural environments, their relatively simple preparation, and the combination of characteristics such as durability and covering power with low toxicity and low cost (Nicola et al. 2016, 545).

Moreover, earth pigments, such as ochres, sienna and umbers, were the main pigments historically used in fresco mural paintings due to their chemical stability in an alkaline environment. Almada Negreiros was, without a doubt, aware of this fact, given the variety of earth pigments in powder form retrieved from his studio (e.g., LF6, LF10, LF13, LF14, LF15, LF19, LF20, LF32, LF33). However, earth pigments were not the only Fe-based pigments in powder form found among the artist's belongings. Others, labelled as Mars pigments (e.g., LF5, LF12 and LF15), were also present and were synthetic Fe-based products developed in the eighteenth and nineteenth centuries (Barnett 2006: 451; Nicola et al. 2016, 549). As in the case of the natural earth pigments, Mars colours were available in a wide range of hues, including reds, browns, yellows, and black, and Almada Negreiros appears to have bought all of them.

Mars pigments were manufactured from iron (III) sulfide mixed with alumen (a potassium aluminium sulfate) and precipitated with alkaline substances, such as lime ($CaCO_3$), caustic soda (NaOH), or potash (K-based compounds) (Nicola et al. 2016, 549). Mars yellow was the first pigment produced by the aqueous precipitation of iron salts, which could then be further calcined to produce other hues. The final colour depended on the amount of moisture and heat used (Barnett 2006, 451).

Other iron salts, such as iron chloride, iron nitrate, and iron acetate, could also be used in the process (Nicola et al. 2016, 549-550). The resulting pigment could additionally be mixed with gypsum, barite, aluminium oxides, and, occasionally, with other pigments (inorganic and organic) (Nicola et al. 2016, 550). The advantage of Mars colours over the naturally occurring equivalents was their alleged higher chemical purity and fine-grained nature while retaining high tinting strength.

The manufacturing process of the Mars pigments found in Almada's studio is still unknown but was most likely very similar to the one reported above, thus accounting for the presence of quartz, clay/micas and gypsum found by XRD on powder pigments LF5, LF12 and LF15 (Table I).

Almada Negreiros probably used both types of Fe-based pigments in the working palettes. In both cases, the colour differences are mainly due to the type and proportion of the chromophores present. Fe-based pigments are normally made up of varying amounts of iron oxides and iron hydroxides, usually found as hematite (Fe_2O_3) and goethite (FeOOH) (Elias 2006:70). The first mineral is responsible for the red hues. In contrast, goethite is associated with shades of yellow, as evidenced by the powder pigments analysed by XRD (Table I).

In the analysis carried out in loco in the paint layers, the presence and amount of hematite and goethite (and eventually other iron-based chromophores) are reflected in the colorimetry results i.e., in the +a*(reds) and +b* (yellow) values of Fig.3G1/G2.

Hematite is usually expected to be the dominant chromophore phase (> a* values) in the reds, whereas in the yellows, goethite prevails (> b* values). The results show that both cases may occur but also a higher variability of chromophore contents across the red and yellow domains since all the paint layers show +a* and +b* contributions (Tables I and II, Fig.3G1/G2).

The diffuse reflectance spectral curves of the paint layers enabled the distinction of pigments used (Fig. 2a/b). Coloured pigments give rise to selected scattering and absorption bands that can be very characteristic, allowing for their first identification in loco. In the case of Fe-based oxides, pure hematite can be characterised by the presence of a sharp positive slope at wavelengths higher than 560 nm, whereas for goethite the first slope is around 450 nm, followed by a sharp peak at around 500 nm and secondary minimum observed around 660 nm (Gil et al. 2009, 1005). The diffuse reflectance spectral curves of both the earth and the Mars powdered pigments found in Almada's studio and of the Fe-based paint layers in Fig.2a/b exhibit the same characteristics, although more diluted due to the presence of other compounds in their composition (Tables I and II).

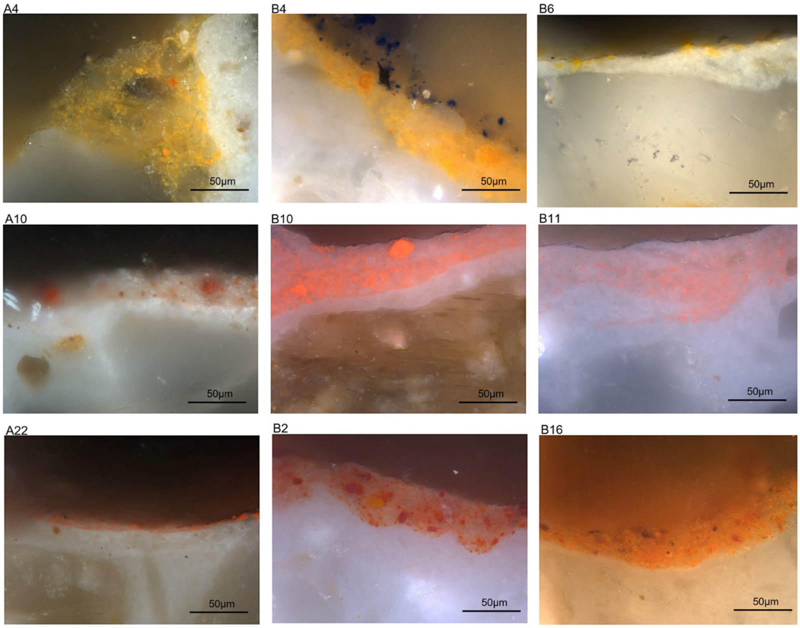

Fig. 4. Optical microscopy in the visible range of red, yellow, orange, and brownish paint layers cross sections A4, B4, B6, A10, B10, B11, A22, B2 and B16.

As expected, paint layers yellow, orange B4 and orange A24 exhibit spectral features common to both hematite and goethite. In the brown and brownish red and yellow paint layers A4, A25, A26, B2, B15, B16 and B18, the contribution of manganese (most likely in the form of oxides) identified by h-EDXRF is responsible for the visible decrease of the reflectance percentage (Fig.2b). The impact of this brownish contribution is, however, less noticeable in the lightness parameter (L*) due to the interference of the white reflective mortar substrate, which is clearly seen in most paint layer surfaces of Fig.2a/b and the cross sections of Fig.4.

All the red, yellow, orange, and brown paint layers analysed by colorimetry show L* values from 50 to 80, indicating a bright chromatic palette (Fig.3G1a and G2a). The L* parameter and the diffuse reflectance (R%) are influenced by the interference of the underneath lime mortar but also by the degree of pigment concentration and dispersion within the paint layer (Fig.4). This is the case of paint layers red B12, light red B10 and pink B11, in which Almada Negreiros played with the amount of calcium hydroxide and pigment concentrations to produce three gradations of red hues (Fig.2a, Fig.3G1/1a and Fig.4).

3.2. GREEN PAINT LAYERS

According to h-EDXRF analysis and h-OM images, the green hues in both working palettes were achieved in two different ways (Table III, Fig.5, and Fig.6).

Table III. Summary results of colorimetry in the Vis, h-EDXRF and XRD analysis carried out on 11 green paint layers analysed of both working palettes.

Sample ref.	**Colour**	**CIE chromatic coordinates**			**h-EDXRF** (major elements for pigments identification in bold)	**μ-FTIR**	**Pigments attribution hypothesis**
		L*	a*	b*			
A3	Green	59.93	-0.77	13.24	Ca, Ba, Al, **Cd, Cr**, **Fe**, K, Mn, Rb, S, Si, Sr, Ti, Zr	Aluminosilicate; gypsum; calcite	Fe-based pigment (green earth) + Cd-based pigment + Cr-based pigment
A6	Olive green	63.56	-0.07	15.06	Ca, Ba, Al, **Cd, Cr**, **Fe**, K, Mn, Rb, S, Si, Sr, Ti, Zr	Aluminosilicate; gypsum; calcite	Fe-based pigment (green earth) + Cd-based pigment + Cr-based pigment
A7	Bluish green	63.77	-2.20	8.42	Ca, Ba, **Cd**, Al, **Co**, **Fe**, K, Mn, Rb, S, Si, Sr, Ti, Zr		Cadmium yellow + Cobalt blue + Fe-based pigment?
A27	Green	66.98	-2.93	6.35	Ca, Al, **Fe**, K, Mn, Rb, S, Si, Sr, Ti, Zr		Fe-based pigment (green earth?)
A28	Green	66.28	-2.37	5.51	Ca, Al, **Fe**, K, M**n**, Rb, S, Si, Sr, Ti, Zr		Fe-based pigment (green earth?)
A30	Dark green	68.07	-0.91	9.74	Ca, Ba, Al, **Fe**, K, M**n**, Rb, S, Si, Sr, Ti, Zr		Fe-based pigment (green earth?)
A33	Green	64.20	-2.45	11.30	Ca, Ba, **Cd**, Al, **Co**, **Fe**, K, Mn, Rb, S, Si, Sr, Ti, Zr		Cadmium yellow + Cobalt blue + Fe-based pigment (Ochre/Mars pigment?)
B26	Light green	75.86	-0.26	6.99	Ca, Al, **Fe**, K, Mn, Rb, S, Si, Sr, Ti, Zr		Fe-based pigment (green earth?)
B32	Green	74.50	-2.28	9.55	Ca, Al,Cl, Cr,Cu, **Fe**, K, Mn, Rb, S,Si, Sr,Ti, Zr	Celadonite; kaolinite; calcite	Fe-based pigment (green earth?)
B34	Dark bluish green	73.52	-3.92	-0.70	Ca, **Cd**, Al, **Co**, **Fe**, K, Mn, Rb, S, Si, Sr, Ti, Zr	Aluminosilicate; quartz; gypsum; calcite	Cadmium yellow + Cobalt blue + Fe-based pigment (Ochre/Mars pigment?)
B36	Green (eroded)	75.90	-2.24	4.20	Ca, **Cd**, Al, **Co**, **Fe**, K, Mn, Rb, S, Si, Sr, Ti, Zr		Cadmium yellow + Cobalt blue + Fe-based pigment (Ochre/Mars pigment?)

The first method used a single type of pigment, as observed in the paint surfaces of A27, A28, A30, B26, and B32 in Fig. 5. In these paint layers, Fe is the main chromophore element found by h-EDXRF, along with small amounts of Mn (Table II). As previously stated, the presence of manganese is often associated with Mn oxides in earth pigments and can explain the brownish green hue of A30 (Fig. 5).

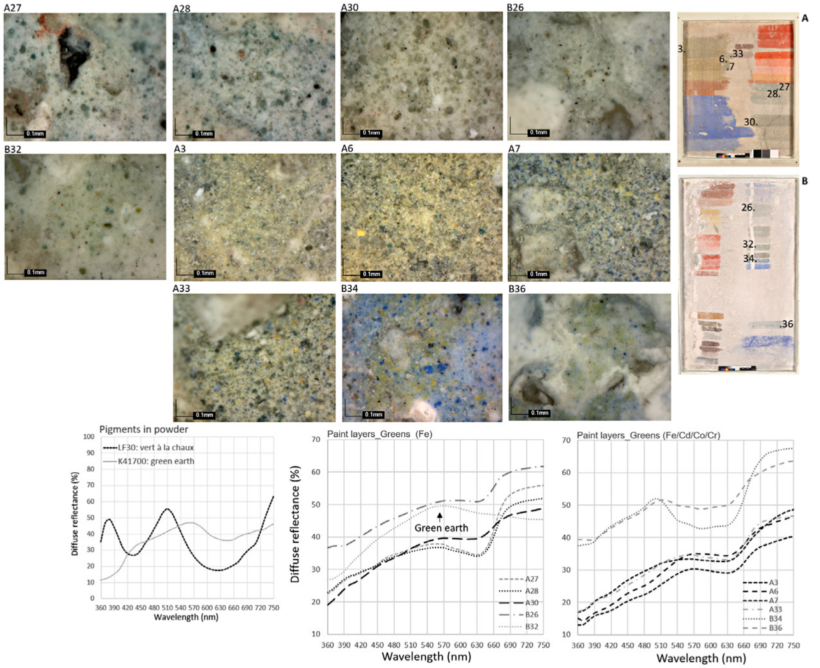

Fig. 5. On top, handheld optical microscopy of green paint layers; on the bottom, the corresponding diffuse reflectance spectral curves on the visible range.

Celedonite, a characteristic clay mineral of green earth, was identified by μ-FTIR in paint layer B32 (Table II). Green earths are mixtures of green silicates of aluminium, iron, magnesium, and potassium (Nicola et al. 2016, 549). Celedonite ($KMg_{0.8}Fe^{2+}{}_{0.2}Fe^{3+}{}_{0.9}Al_{0.1}Si_4O_{10}(OH)_2$ and glauconite $(K,Na)((Fe^{3+},Al,Mg)_2\ (Si,Al)_4O_{10}\ (OH)_2$ are the most common clay minerals found. Still, it may also be composed of other clay minerals such as montmorillonite, chlorite and kaolinite (Grissom 1986: 141). From dull greyish or brownish green to green, these green earth pigments have been widely used by artists since antiquity and were the most used ones in mediaeval times for flesh undertones in easel and mural paintings (Grissom, C.A. 1986, 141, Mora 1983, 112).

The spectral curve of green earth, as shown by the reference pigment in Fig. 5, is characterised by a broad central peak with a slight shoulder on the short wavelength side, with the percentage reflectance slightly higher at the blue end of the spectrum (400 nm) and also at the end (700 nm) (Grissom, C.A. 1986, 144). These features can be seen in paint layer B32, although slightly attenuated by the interference of lime from the paint layer and the underneath mortar, as shown by h-OM in Fig. 5 and by the cross-section in Fig. 6.

The identification of the green pigments is still uncertain in paint layers A27, A28, A30 and B26 (Fig. 5). They all exhibit green to brownish green particles on the surface, as in B32, but the spectral curves obtained are distinct and suggest the presence of more than one Fe rich chromophore due the presence of a sharp slope at 650 nm (in the red region). This last feature is accentuated in A27 and A28. It can be explained by the presence of a small amount of bright red particles on the paint surface, which are clearly seen by h-OM on the surface of A27 (Fig. 5). These green paint layers were laid down just after the red and brown A25 and A26, and thus could have been an intentional addition or just a simple brushstroke contamination (Fig. 2b and Fig. 5).

The second method used by Almada to produce vivid green hues was apparently by mixing several kinds of pigments (Table III, Fig.3G4 and Fig.5). Paint layers A7, A33, B34 and B36 are enriched in both Co and Cd, but also have variable amounts of Fe (Table III). The different yellow and blue coloured particles are visible in the paint surface in Fig. 5, in the cross-sections of A7 and B34 in Fig. 6. On the other hand, in the green and olive-green paint layers A3 and A6, the presence of Cr in small amounts also suggests the addition of a Cr based pigment to the mixture (Table III). H-EDXRF also found chromium in the powdered pigments LF30 and O1 recovered from Almada's studio and labelled as 'vert à la chaux' and viridian, respectively (Table I).

Chromium oxide (Cr_2O_3), and hydrated chromium oxide ($Cr_2O_3.2H_2O$) are, according to historical records, the only common Cr-based green pigments (Newman, 1997, 273). Both were synthesised during the first half of the nineteenth century and present a distinctive optical appearance. Chromium oxide is dull, opaque olive green, while hydrated chromium oxide is more intense, transparent, and sometimes bluish green (Newman, 1997, 273). The last optical features are visible by optical microscopy in transmitted light mode on the green pigment particles of O1 and a few bright green particles from paint layer A3 and A6, suggesting that a hydrated chromium oxide could have been used by Almada Negreiros (Fig. 6).

Hydrated chromium oxide, commercially known as viridian, was first prepared by the colour maker Pannetier and his assistant Binet in Paris around 1839 (Newman, 1997, 275). However, the pigment was so expensive at that time that it could not often be used in painting. Only after 1859, when the French chemist Charles Ernest Guignet patented a method for manufacturing the pigment, would veridian become more affordable (Newman, 1997, 275). The high price of this pigment was still an issue for artists in the early twentieth century and can explain why it was parsimoniously used in the two paint layers.

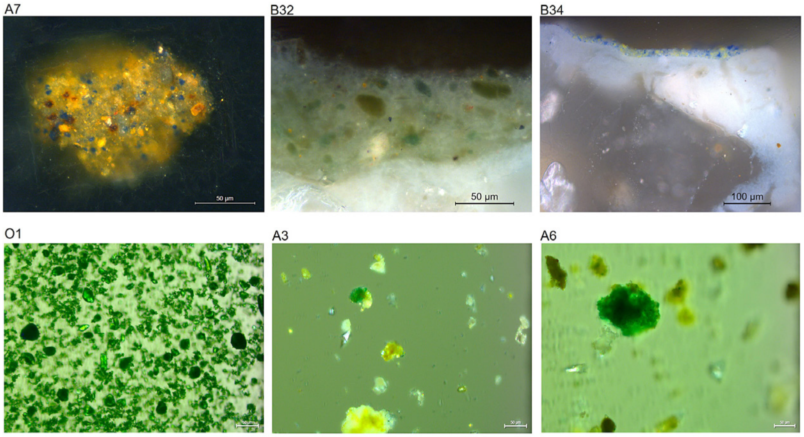

Fig. 6. On top, optical microscopy of green paint layers cross sections A7, B32 e B34. On the bottom, polarized light microscopy of pigment in powder viridian O1 and of green paint layers A3 and A6.

3.2. BLUE PAINT LAYERS

As already reported in a previous study, Almada Negreiros used two types of nineteenth-century synthetic blue pigments (Gil et al. 2021, 4588):

cobalt blue, a cobalt (II) oxide-aluminium oxide ($CoO.\ Al_2O_3$) in paint layer B35;

and ultramarine blue, a complex sulphur-containing sodium aluminium silicate of chemical formula $Na_{8-10}Al_6Si_6O_{24}S_{2-4}$ in paint layers A12 to A15 and B37.

Fig. 7 clearly distinguishes the two pigments by their diffuse reflectance spectral curves in the visible range. Ultramarine blue has a dominant wavelength around 459 nm and a characteristic rising reflectance in the red. In contrast, cobalt blue shows a broad, strong reflectance with a peak around 430-450 nm, a smaller, sharper peak centred at 495 nm, low reflectance around 520 and 650 nm, and a strong rising (red) reflectance above 660 nm.

Cobalt was also found in paint layer B35 and powdered pigment LF29 by h-EDXRF whereas ultramarine blue was confirmed by µ-FTIR in paint layer B37 (Table IV).

Given the results obtained, it is interesting that Almada has preferred ultramarine over cobalt blue for the blue paint layers while reserving the last for the mixtures with Cd and Fe-based pigments to produce the vivid green hues. It is unclear whether it was a deliberate choice of the artist, motivated by technical reasons, or a selection associated with economic motives. Compared to ultramarine blue, Cobalt blue is, still today, as it was in the past, among the most expensive pigments when supplied with genuine cobalt pigments rather than a mixture representing its hue. However, both pigments have very similar blue hues (Fig.8), although ultramarine is considered warmer than the colder cobalt blue (Roy 2007, 152). In the paint layers analysed by colorimetry, the subtle differences in blue hues are reflected in the a* chromatic values (Fig.3G4).

Table IV. – Summary of the results of colorimetry in the Vis, h-EDXRF and μ-FTIR analysis carried out on 6 blue paint layers of both working palettes.

Sample ref.	**Colour**	**CIE chromatic coordinates**			**h-EDXRF** (major elements for pigments identification in bold)	**μ-FTIR**	**Pigments attribution hypothesis**
		L*	a*	b*			
A12	Blue	58.05	1.30	-23.21	Ca, Al, **Fe**, K, Mn, Rb, S, Si, Sr, Ti, Zn		Ultramarine blue
A13	Blue	60.81	-0.61	-17.49	Ca, Al, **Fe**, K, Mn, Rb, S, Si, Sr, Ti, Zn		Ultramarine blue
A14	Blue	57.96	1.16	-28.21	Ca, Al, **Fe**, K, Mn, Rb, S, Si, Sr, Ti, Zn		Ultramarine blue
A15	Light blue	57.06	1.62	-28.91	Ca, Al, **Fe**, K, Mn, Rb, S, Si, Sr, Ti, Zn		Ultramarine blue
B35	Blue	70.33	-4.39	-12.23	Ca, Ba, Al, **Co**, **Fe**, K, Mn, Rb, S, Si, Sr, Ti, Zn	Inorganic compound; calcite	Cobalt blue
B37	Dark blue (eroded)	68.74	1.11	-9.66	Ca, Ba, Al, **Fe**, K, Mn, Rb, S, Si, Sr, Ti, Zn	Ultramarine blue; calcite; gypsum	Ultramarine blue

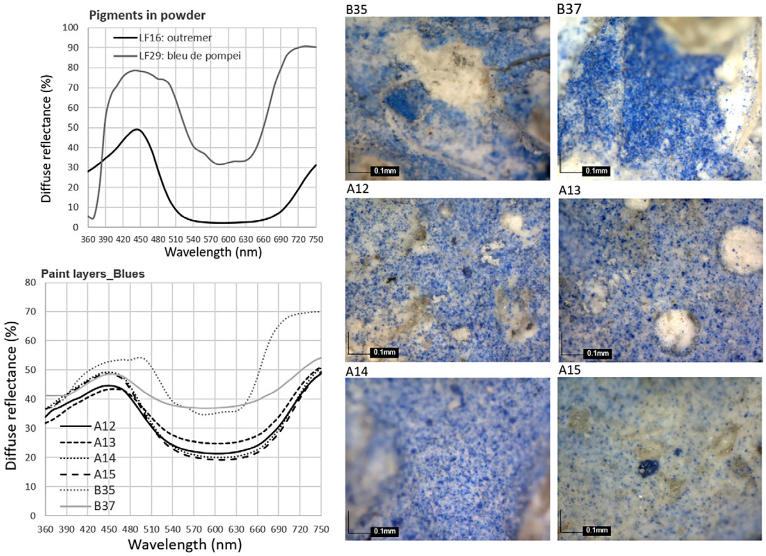

Fig. 7. On the left,handheld optical microscopy of the blue paint layers and, on the right, the corresponding diffuse reflectance spectral curve in the visible range.

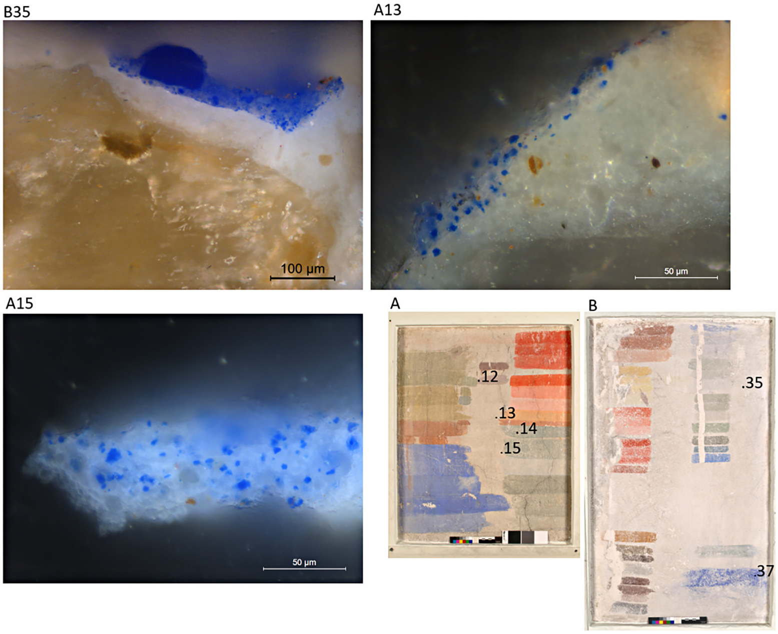

Fig. 8. Overview of the two working palettes with the indication of the blue paint layers analysed and cross sections of the blues three paint layers made with cobalt blue (B35) and with ultramarine blue pigment (A13 and A15).

FINAL NOTES

The undertaken research reveals that Almada Negreiros used traditional pigments commonly found in fresco mural paintings, such as earth pigments. However, as a twentieth-century artist, he also experimented with a range of modern synthetic pigments, including Cd pigments, Cr green pigments, cobalt blue, ultramarine blue, and most likely Mars colours.

All these pigments were found in powder form in the artist's studio, showing that Almada Negreiros was acquainted with the colour innovations of the nineteenth century available to artists. In the two working palettes, the pigments were used alone and in mixtures with lime and other pigments to broaden the range of hues, as in the greens and the pinks. The colorimetry analysis also showed that both working palettes are characterised by light colours (L* parameter >50), even in the darkest pigments, which could have been intentional or a consequence of the fresco technique used. Another important aspect highlighted by this work is the correlation and cross-linking of the scientific data with historical-artistic information, which provides context and a deeper understanding of the results and simultaneously raises new hypotheses about the use of pigments for further comparative analytical studies to be carried out at the DN building.

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