Analytical characterization of academic nude paintings from the Faculty of Fine Arts of the University of Lisbon

Caracterização material das pinturas de modelo nu da coleção da Faculdade de Belas-Artes da Universidade de Lisboa

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Abstract

This study illustrates the analytical characterization of 20 academic nude paintings from the collection of the Faculty of Fine Arts of the University of Lisbon, made between 1899 and 1918. The study was performed by combining *in situ* non-invasive methods (infrared reflectography, radiography, and EDXRF) and laboratory microanalytical techniques (micro-Raman, micro-FTIR, and SEM-EDS). Infrared reflectography revealed underdrawings, underpaintings, painting style, and execution methods. Analytical techniques allowed the identification of painting materials, such as gypsum, lead white, barium white, zinc white, yellow ochre, chrome yellow, zinc yellow, red ochre, vermilion, ultramarine blue, hematite, Mars red, and lamp black. This study provides valuable information on the academic nude paintings' palette and its artistic production technique. Finally, it intends to continue a systematic analytical study of the Faculty of Fine Arts' collection, allowing the characterization of Master painters, their students, and other authors.

KEYWORDS
Nude paintings
Raman spectroscopy
EDXRF
Radiography
Infrared Reflectography
SEM-EDS

Resumo

Este estudo ilustra a caracterização analítica de 20 pinturas académicas de nu do acervo da Faculdade de Belas-Artes da Universidade de Lisboa, realizadas entre 1899 e 1918. O estudo foi realizado com métodos *in situ* (reflectografia de infravermelho, radiografia e EDXRF) e técnicas microanalíticas (micro-Raman, micro-FTIR e SEM-EDS). A reflectografia de infravermelho revelou desenhos subjacentes, pinturas subjacentes, estilo de pintura e métodos de execução. As técnicas analíticas permitiram a identificação de diversos materiais de pintura, tais como gesso, branco de chumbo, branco de bário, branco de zinco, ocre amarelo, amarelo de crómio, amarelo de zinco, ocre vermelho, vermelhão, azul ultramarino, hematite, vermelho de Marte e negro de carvão. Este estudo fornece informação relevante sobre a paleta de pinturas de nu académico e sua técnica de produção artística. Por fim, pretende-se continuar um estudo analítico sistemático deste acervo, permitindo a caracterização de mestres pintores, estudantes e outros autores.

PALAVRAS-CHAVE
Pintura de modelo nu
Espectroscopia Raman
EDXRF
Radiografia
Refletografia de Infravermelhos
SEM-EDS.

Introduction

The Faculty of Fine Arts of the University of Lisbon (FBAUL) holds more than 90 academic nude paintings dated between 1883 and 1934. These paintings represent not only the Portuguese production but also the French influence since most of its students went to study abroad at the École des Beaux-Arts de Paris, and at famous French painter's ateliers like Jean-Joseph Benjamin-Constant (1845-1902), Jules-Élie Delaunay (1828-1891) and Fernand Cormon (1845-1924) [1]. The students sent back home their paintings to be evaluated by their Professors in Lisbon, providing testimonies on both Portuguese and French production during this period.

This study discusses the analytical characterization of the pigments' palette used on 20 academic nude paintings executed in Lisbon and Paris, signed and dated between 1899 and 1918. These paintings were chosen because they were made by students of two different Professors: Master Painter Veloso Salgado, and Master Painter Columbano Bordalo Pinheiro. Analytical characterization of academic paintings made by Veloso Salgado was already published in 2016 [2] and used for comparison here.

With the aim of characterizing these student painters' palette and painting method, both imaging and analytical techniques were used on these academic nude oil paintings. The imaging approach was made with infrared reflectography

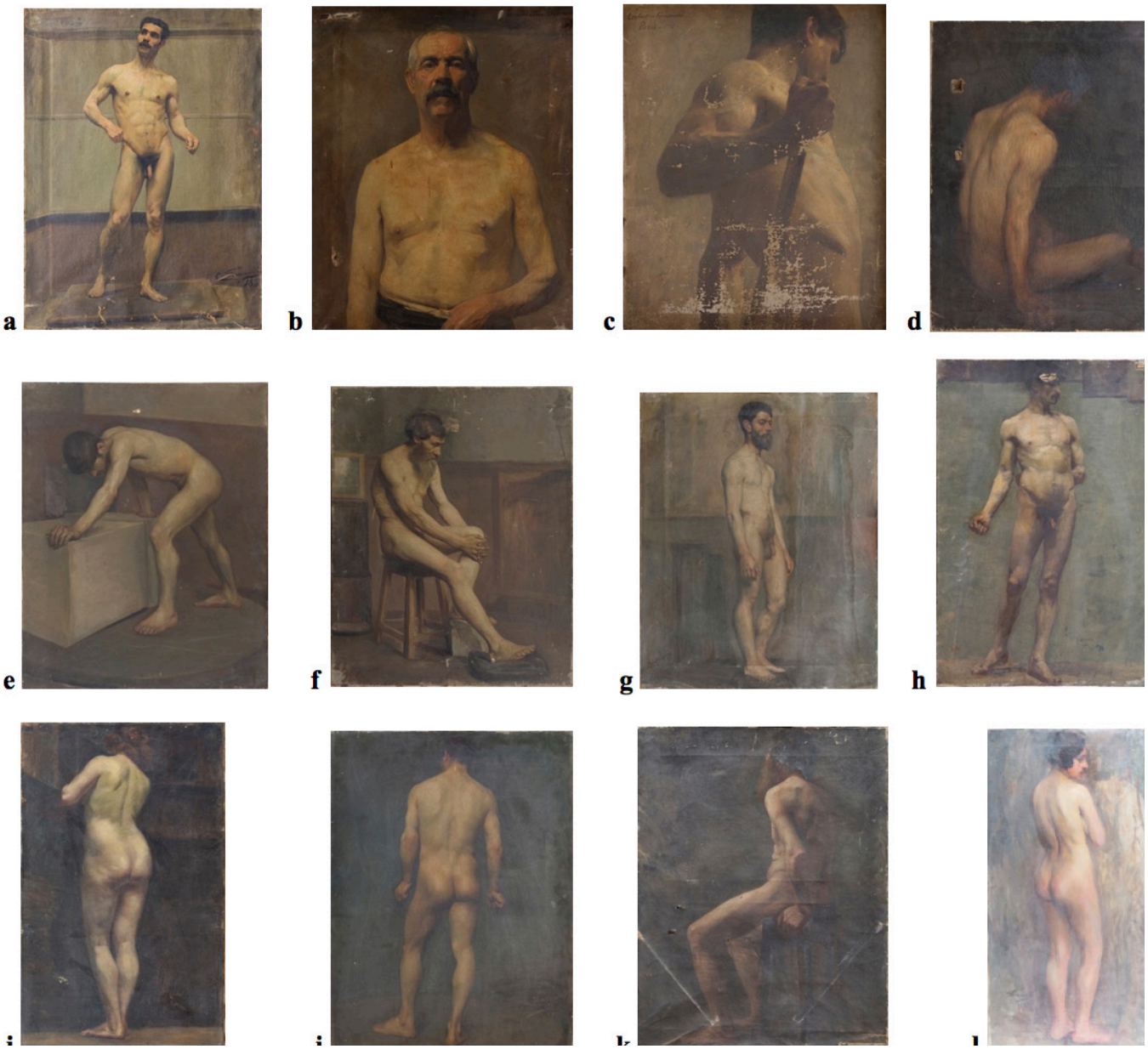

Figure 1. Veloso Salgado students' paintings: *a*) Carlos Franco (1879-1959), 1899, 80 × 60 cm, oil on canvas, Inventory No. 4102; *b*) Constantino Fernandes (1878-1920), 1899, 79 × 63.5 cm, oil on canvas, Inventory No. 3635; *c*) Constantino Fernandes (1878-1920), 1905, Paris, 59.5 × 48.5 cm, oil on canvas, Inventory No. 3601; *d*) Artur Miguel Severino (1878-?), 1901, Paris, 73 × 59.5 cm, oil on canvas, Inventory No. 4101; *e*) Artur Miguel Severino (1878-?), 1901, 80 × 64.5 cm, oil on canvas, Inventory No. 4103; *f*) Trindade Chagas (1881-1958), 18-06-1902, 81 × 64.5 cm, oil on canvas, Inventory No. 4076; *g*) Constâncio Silva (1882-1949), 1905, 81.5 × 65 cm, oil on canvas, Inventory No. 4082; *h*) José Campas (1888-1971), 1910, Paris, 80 × 54 cm, oil on canvas, Inventory No. 4090; *i*) José Campas (1888-1971), 1910, 81.5 × 50 cm, oil on canvas, Paris, Inventory No. 4095; *j*) Dórdio Gomes (1890-1976), 1909, 80 × 60 cm, oil on canvas, Inventory No. 4097; k) Henrique Tavares, no date, 83 × 62 cm, oil on canvas, Inventory No. 3679; *l*) Lacerda?, 1922, 80 × 40 cm, oil on canvas, Inventory No. 4093.

examination, which permits the reconstruction of artwork's material history by allowing non-invasive and non-destructive information from underlayers like distinctive paintbrushes of characteristic artists and schools, shadow delimitation schemes, artist's pentimenti, and underdrawings [3-8]. Furthermore, radiography allowed in some cases to provide a clear image of underpaintings and material dissipation throughout the composition.

Energy Dispersive X-Ray Fluorescence spectrometry (EDXRF) was suitable for *in situ* elemental characterization of pigments on all the 20 paintings, allowing a non-invasive and non-destructive approach for fast identification of the key elements in several pigments [7-9]. In some cases, giving the fact that there are mutual key elements in a wide range of pigments and lacking characteristic elements measurable through EDXRF, Raman and Fourier Transform Infrared (FTIR) spectroscopies were performed to enhance the data directly on micro-samples taken from areas of a different colour. Moreover, the spatial resolution and elemental analysis of Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) disclosed further information concerning the preparation and paint layers and artist's materials.

This research provides important information on academic nude painting artistic practice in the late nineteenth century and the beginning of the twentieth century at the Academy of Fine Arts of Lisbon.

Materials and methods

Sample description

The 20 paintings selected in this study (Figure 1and Figure 2) were authored by the following Veloso Salgado's students: Artur Miguel Severino (1878-?), Carlos Franco (1880-1959), Constâncio Silva (1882-1949), Constantino Fernandes (1878-1920), Dórdio Gomes (1890-1976), José Campas (1888-1917) and Trindade Chagas

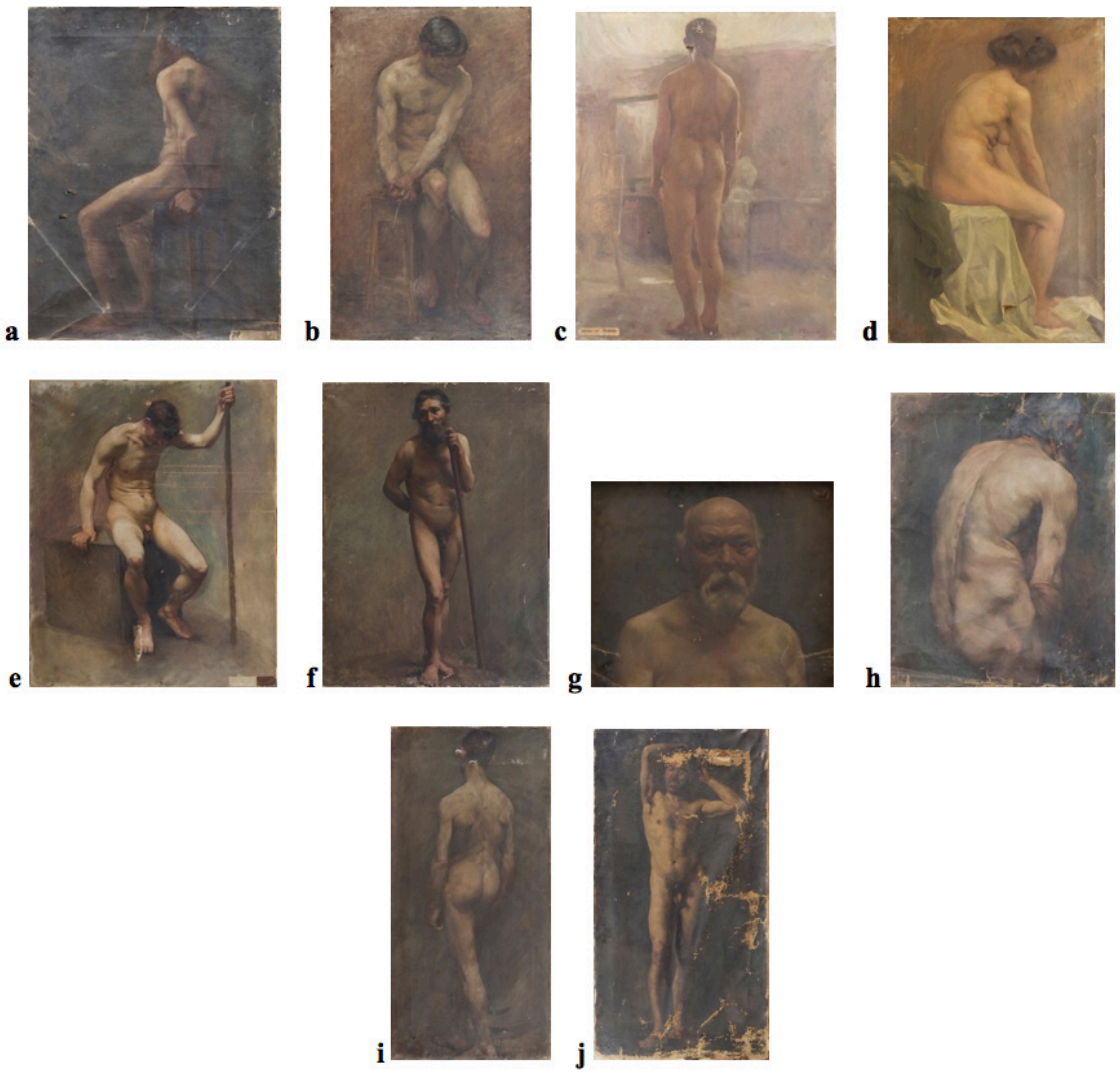

Figure 2. Columbano students' paintings: *a)* Henrique Tavares (1879-1911), Paris, 82 × 92 cm, oil on canvas, Inventory No. 3679; *b)* Henrique Franco (1883-1961), 1908, 74 × 46 cm, oil on canvas, Inventory No. 4085; *c)* Henrique Franco (1883-1961), 1910, 81 × 64.5 cm, oil on canvas, Inventory No. 4077; *d)* Henrique Franco (1883-1961), 1918, 96.5 × 65 cm, oil on canvas, Inventory No. 4099; *e)* Ricardo Ruivo Júnior (1878-1910), 12-06-1903, 81 × 65.5 cm, oil on canvas, Inventory No. 4100; *f)* Ricardo Ruivo Júnior (1878-1910), 08-04-1906(7)?, 79 × 60 cm, oil on canvas, Inventory No. 3915; *g)* Ricardo Ruivo Júnior (1878-1910), 42.5 × 51 cm, oil on canvas, Inventory No. 3612; *h)* Ricardo Ruivo Júnior (1878-1910), 73 × 55.5 cm, oil on canvas, Inventory No. 4105; *i)* Ricardo Ruivo Júnior (1878-1910), 87 × 41 cm, oil on canvas, Inventory No. 4092; *j)* Ricardo Ruivo Júnior (1878-1910)?, 107.5 ×58 cm, Inventory No. 3675.

(1881-1958); and by the following Columbano Bordalo Pinheiro's students: Henrique Franco (1883-1961), Henrique Tavares (1905-1988) and Ricardo Ruivo Júnior (1878-1910).

These paintings vary in height between 60 and 80 cm, and in width between 40 and 60 cm. They were analysed *in situ* using a portable EDXRF spectrometer. Taking into account the EDXRF results, a total of 118 micro-samples were collected from the 20 paintings (an average of six micro-samples per painting). The micro-samples were obtained *in situ* at the painting storage of the Fine Arts of Lisbon. Two scalpels were used to separate the micro-sample from the painting (one for removing and another one to assist the manoeuvring procedure), Eppendorfs were used to store the micro-samples and all the micro-samples were identified with the painting code and a number of the sampling point. All the samples were mounted in EpoFix Epoxy resin, observed under reflected light with a microscope Olympus BX41/51, using 10 ×, 50 ×, and 100 × magnification objective, and analysed by Raman, FTIR, and SEM-EDS spectroscopy.

Infrared reflectography

Infrared reflectography was performed in situ with an OSIRIS infrared camera, operating at wavelengths from 900 to 1700 nm. This camera has an InGaAs array sensor with a 0.05 mm resolution. Made by Rodenstock, the Rodagon lens consisting of six elements, has a focal length of 150 mm and an aperture range of f/5.6-f/45. Reflectograms were recorded with a working distance (front of the body camera to painting) of 170 cm, and focus (front of body camera to the lens, measured with a laser distance meter equipment) of 20 cm, an f/11 aperture, and diffused illumination at 1000 lux by reflectors with 2 × 1000 X Tungsten Halogen VC – 1000Q Quartz Light. This technique was applied to all the paintings.

Radiography

Digital X-ray radiography was performed on all the paintings with a YXLON Smart 160E/0.4 continuous emission X-ray source, with the possibility of adjusting the voltage between the range 10 and 160 kV and amperage between 2.0 to 6.0 mA. Images were obtained by flexible plates scanned with a Durr NDT-CR35SEC scanner. The high penetration of the X-rays allows collecting information about all strata, being recorded in the radiographic film the absorption of the different materials present, according to their physical and chemical composition. This examination allows to observe the state of conservation of a painting, as well as to identify the extent of restoration intervention; observe underlying layers of paint and identify and distinguish materials of different atomic weight.

Portable Energy Dispersive X-Ray Fluorescence Analysis (EDXRF)

In situ energy dispersive X-Ray Fluorescence Spectrometry (XRF) analysis was performed using a BRUKER Tracer III/IV SD handheld X-Ray Fluorescence Spectrometer. Analyses were made using a Ti/Al filter, 40 Kev voltage, 11 μA current, and 90 s acquisition time. The instrument was fixed on a tripod and positioned close to the surface of the area of interest. Spectra were analysed using the software ARTAX.

Scanning Electron Microscopy with Energy Dispersive Spectroscopy Analysis (SEM-EDS)

Scanning electron microscopy was performed on a HITACHI S3700N variable pressure scanning electron microscope equipped with a BRUKER X-Flash energy dispersive X-ray spectrometer (VP-SEM-EDS). The images were collected in backscattering mode using 20 kV and 40 mA and air pressure

Figure 3. Academic Nude Torso, Constantino Fernandes (1878-1920), 1905, 59.5 × 48.5 cm, oil on canvas, FBAUL, Inventory No. 3601: *a)* visible light and *b)* respective infrared reflectography.

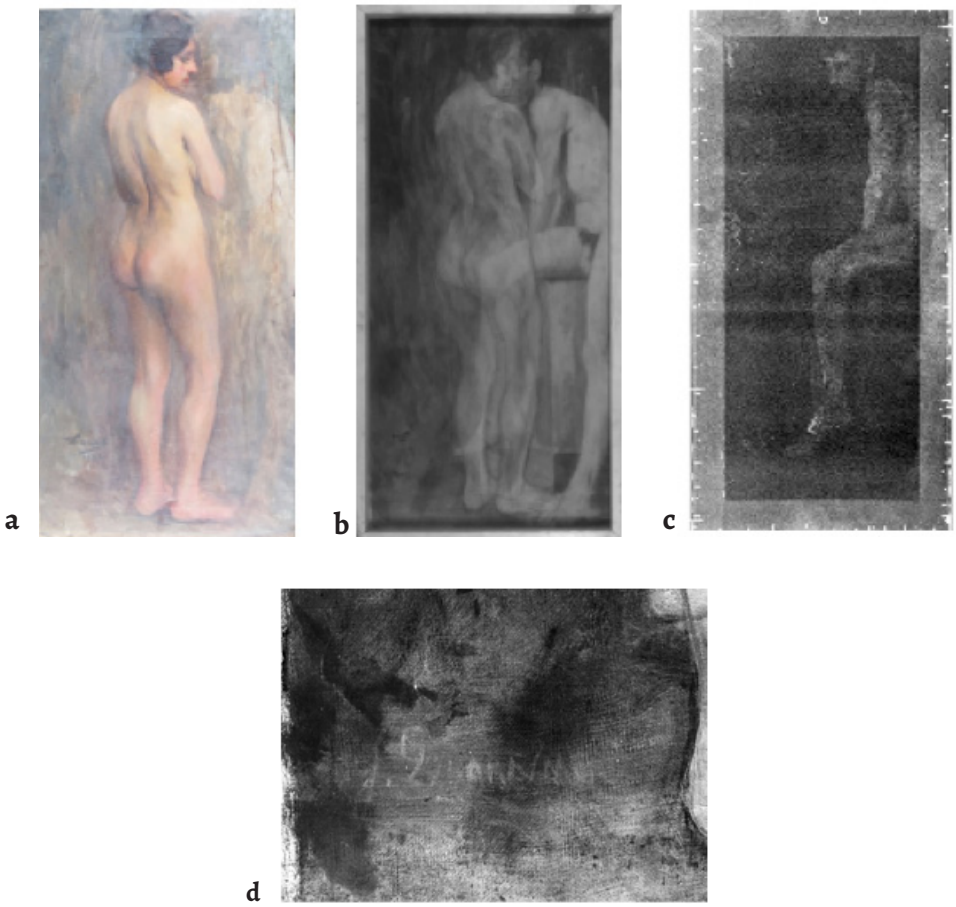

Figure 4. Academic Nude, Lacerda (?), 1922, 80 × 40 cm, oil on canvas, FBAUL, Inventory No. 4093: *a)* visible light; *b)* infrared reflectography; *c)* radiography; *d)* and with detail on the signature by Eduardo Viana on the right side.

in the chamber of 40 Pa. Single spectra and elemental maps were obtained for all layers.

Micro-Raman Analysis

Raman analyses were undertaken using a Horiba-Jobin Yvon XploRA confocal spectrometer, using a 785 nm excitation wavelength, with maximum incident power of 0.2 mW. Using a 100 × magnification objective with a pinhole of 500 µm and an entrance slit of 100 µm, the scattered light collected by the objective was dispersed onto the air-cooled CCD array of an Andor iDus detector by a 1200 lines/mm grating. Raman spectroscopy was performed using LabSpec (V5.78). The identification of pigments was made in good agreement with the literature [10-11], Spectral ID, and our own references spectra (Kremer).

Micro-Fourier Transform Infrared Analysis (µ-FTIR)

The identification of binders and pigments was performed by µ-FTIR on a Bruker Hyperion 3000 micro-spectrometer equipped with a Mercury-Cadmium-Telluride (MCT) detector and a 15 × objective in transmission mode using a compression diamond cell from ST Japan. The spectra were acquired with a 4 cm^{-1} spectral resolution and an average of 32 scans, within the IR region of 4000-600 cm^{-1}.

Results and discussion

Infrared reflectography information allowed the distinction of materials due to the differences in the reflectance detected when exposed to infrared radiation [12]. Infrared radiation can penetrate thin layers of paint, be absorbed by carbon-based elements, such as graphite and charcoal (opaque in infrared region), and reflect back to the surface through a nondesturbing medium such as the preparation layer which usually is made of chalk and gypsum (transparent in infrared region) [12].

In most paintings, reflectograms unveiled that the underdrawings were performed using carbon black. Distinct large paintbrush strokes could be observed, outlining darker shade areas, artist contour, and painters' pentimenti (Figure 1c and Figure 3).

Furthermore, the concomitant application of infrared reflectography and radiography uncovered the presence of underpaintings. The radiography technique aditionaly revealed the presence of a signature on a particular underlying painting (Figure 4), thus allowing the identification of the underlying patining's author as Eduardo Viana (1881-1967), a modern Portuguese painter. This is the only painting signed by Eduardo Viana in the collection of the Faculty of Fine Arts of Lisbon and it is hidden underneath this painting made by a student

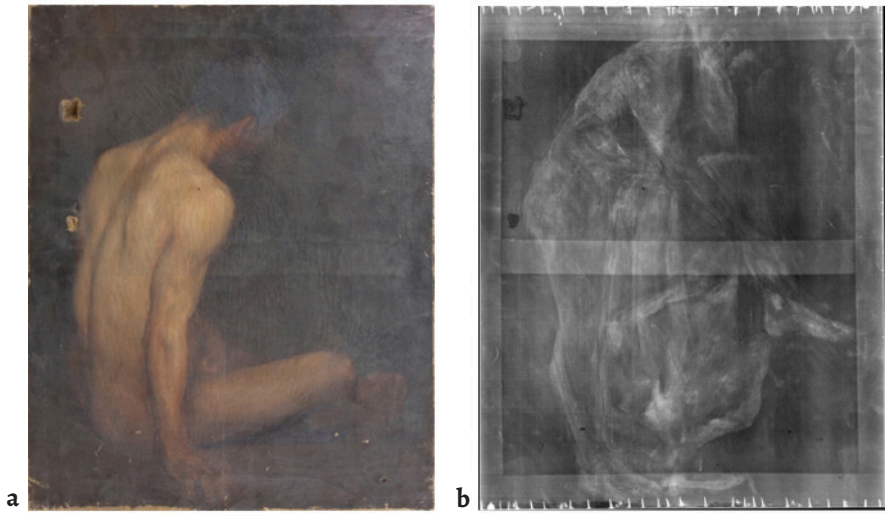

Figure 5. Academic Nude Seated, Artur Miguel Severino (1878-?) 1901, 73 × 59.5 cm, oil on canvas, FBAUL, Inventory No. 4101: *a*) visible light and *b*) related radiography .

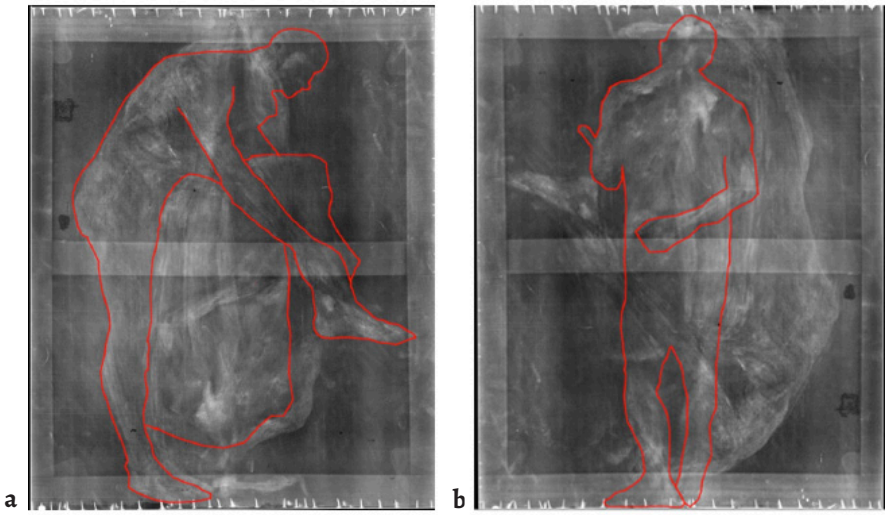

Figure 6. Radiography of Academic Nude Seated by Artur Miguel Severino (1878-?), 73 × 59.5 cm, FBAUL, Inventory No. 4101: *a*) normal position; *b*) vertical inverted image. Red outline of two different models portrayed in the same painting (possibly different layers).

(Lacerda?), in 1922. The difference between the representation of the nude model on the infrared reflectography and on the radiography (Figure 4) can be related to the fact that lead white was used in the underpainting, while on the latter painting, white pigments composed of lighter elements such as titanium (Ti), barium (Ba), or zinc (Zn) were applied, as will be discussed later on the white colouring areas section.

In the specific case of the painting executed by Severino (Figure 1d), the presence of two other different paintings/models were unveiled by radiography, which are presented in Figure 5 and outlined in Figure 6.

Nonetheless, in some paintings, the infrared reflectography technique did not reveal the presence of underdrawings. This can be correlated with non-carbon-based materials applied to define the composition rather than the absence of sketch drawing.
In all paintings' EDXRF spectra, the systematic presence of sulfur (S), calcium (Ca), and lead (Pb) elements was observed, indicating that calcium and lead-based pigments could have possibly been used as the primary preparation layer (Figure 7). The key elements of gypsum ($CaSO_4 \cdot 2H_2O$) are S and Ca, and for lead white pigment ($2PbCO_3 \cdot Pb(OH)_2$) the key element is Pb. Raman spectroscopy confirmed the presence of gypsum and lead white, due to its characteristic bands at 1087 cm^{-1} and at 1056 cm^{-1}, respectively [10-11] (Figure 13). These compounds were also confirmed using FTIR, owing to the obtained absorption bands of carbonate in calcite at 1427 cm^{-1} (C-O stretching) and 874 cm^{-1} (out-of-plane bending vibration), the absorption bands of sulphate groups in gypsum at 1114 cm^{-1} (S-O stretching), and 3400 cm^{-1} (O-H stretching vibration) [13], and characteristic lead white (hydrocerussite) bands at 681 cm^{-1} (C-O bending), 1398 cm^{-1} (C-O stretching) and 3535 cm^{-1} (O-H stretching vibration) (Figure 8) [14]. The mixture of these compounds as a preparation layer can be observed in several paintings from the nineteenth and twentieth centuries [6-8]. Moreover, as also observed in the academic paintings by

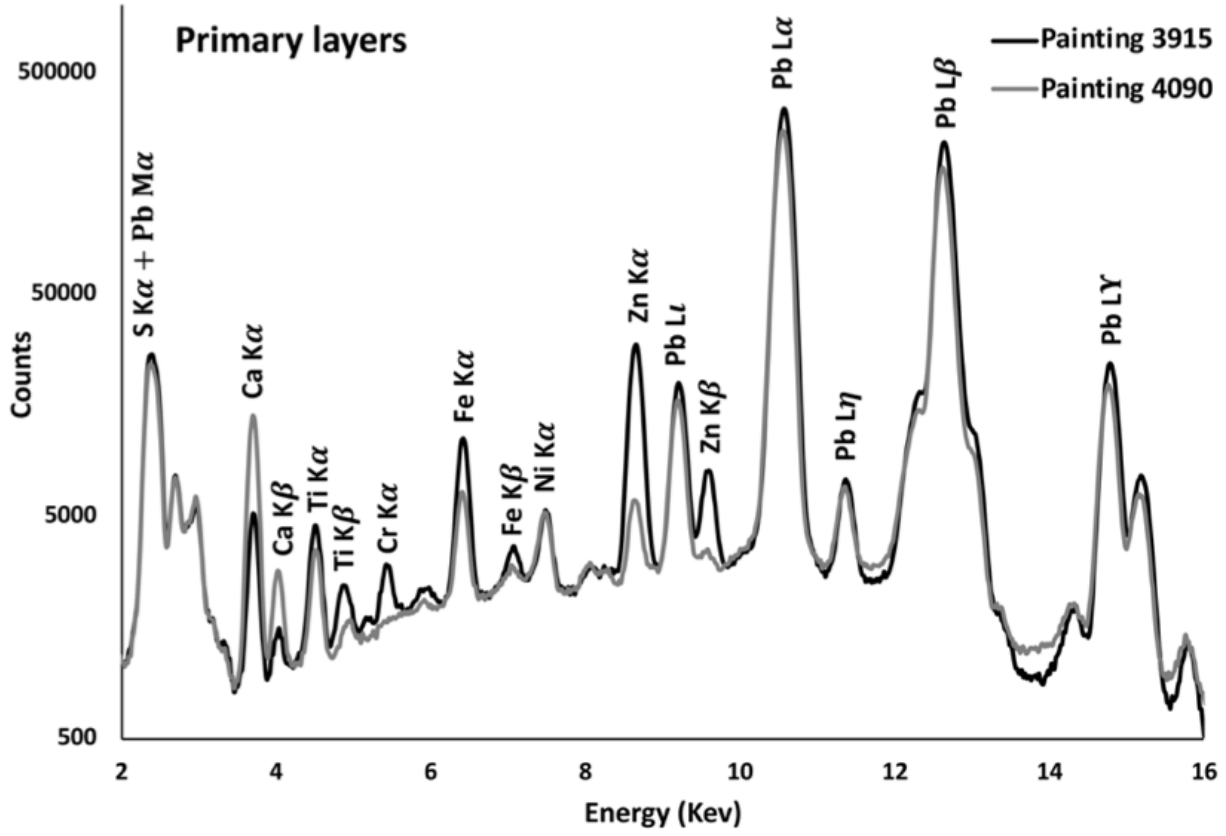

Figure 7. EDXRF spectra of primary layer of paintings Inv. Nos. 3915 (Figure 2f) and 4090 (Figure 1h).

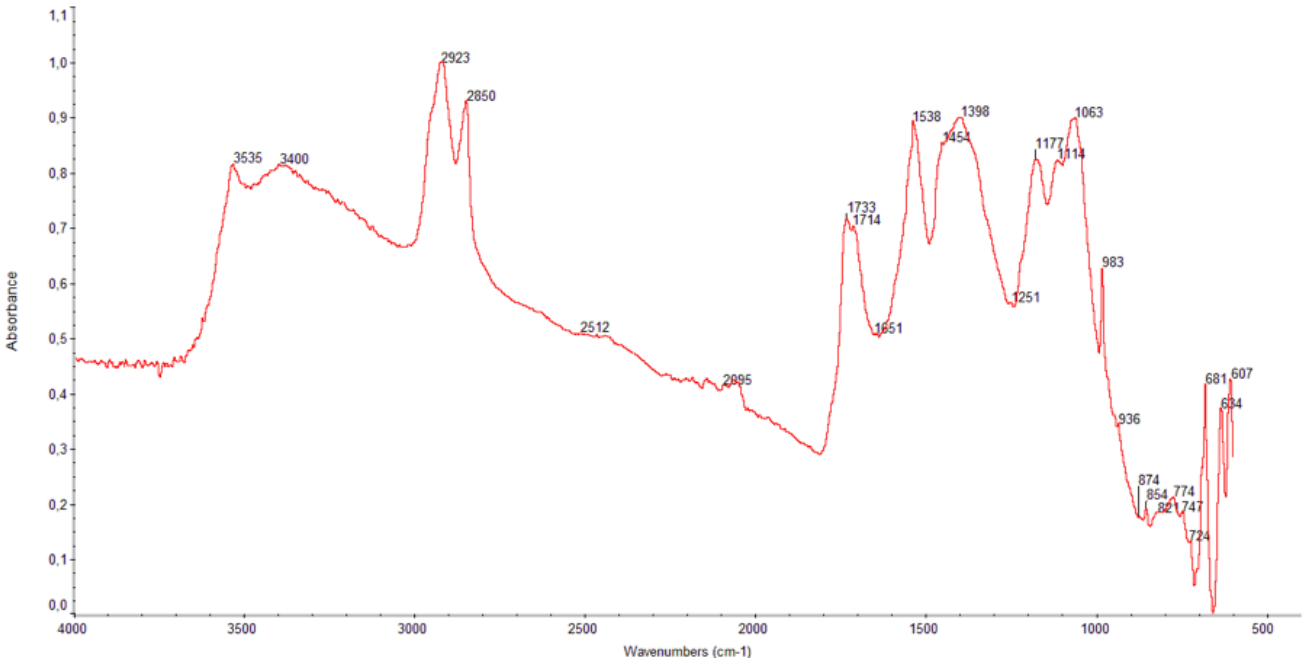

Figure 8. FTIR spectra of the primary layer of painting Inv. No. 3915 (Figure 2f).

Table 1. Summary of primary layers by painting (separated or mixed gypsum and lead white compounds).

Class	Author	Execution year	Painting	Separated layers of gypsum/ calcite and lead white	Mixed layer of gypsum/calcite and lead white
Veloso Salgado	Carlos Franco	1899	Figure 1a		×
	Constantino Fernandes	1899	Figure 1b		×
		1905	Figure 1c		×
	Artur Miguel Severino	1901	Figure 1d	×	
		1901	Figure 1e	×	
	Trindade Chagas	18-06-1902	Figure 1f	×	
	Constâncio Silva	1905	Figure 1g	×	
	José Campas	1910	Figure 1h	×	×
		1910	Figure 1i		×
	Dórdio Gomes	1909	Figure 1j	×	
Veloso or Columbano	Henrique Tavares	(?)	Figure 1k Figure 2a	×	
Columbano	Henrique Franco	1908	Figure 2b	×	
		1910	Figure 2c	×	
		1918	Figure 2d	×	
	Ricardo Ruivo	12-06-1903	Figure 2e	×	
		08-04-1906(7?)	Figure 2f		×
		(1901-1910)	Figure 2g	×	
		(1901-1910)	Figure 2h	×	
		(1901-1910)	Figure 2i	×	
	Ricardo Ruivo (?)	(?)	Figure 2j		×

the Portuguese painter Aurélia de Sousa, which can serve as a comparison in this study, overlaying both gypsum and lead white provided a more controlled drying time, which was essential due to the limited time to execute live model paintings [15].

Although titanium (Ti), zinc (Zn) and chromium (Cr) are characterized for white and yellow colouring areas as will be discussed later, these elements were not identified on the primary layer. Since the EDXRF spectrometer analyses all the paintings' layers simultaneously, the characterization of primary layers had to rely on stratigraphic micro-samples mounted on epoxy resin. These stratigraphies allowed the identification of lead white and gypsum on primary layers through Raman, and FTIR spectroscopies. Furthermore, SEM-EDS did not detect titanium, zinc or chromium elements on these primary layers.

The analysis of the primary layers' structure under SEM-EDS revealed the presence of two different types of preparations in the studied paintings: preparations made of two separate layers of gypsum or calcite and lead white; and preparations composed of a mixture of both materials applied as a single layer (Table 1 and Figure 9).

Lead white was also used in admixture with other pigments to obtain brighter colours in skin tones of the portrayed models. These tones were attained by intermixing lead white with other pigments, which were also detected in EDXRF spectra (Figure 10). This lead pigment was then progressively replaced by other less toxic white pigments such as zinc white, titanium white, barium white and other opaque white compounds [16]. In fact, the presence of Ba in five paintings as a Ba-based pigment, such as barium white, was confirmed through Raman spectroscopy due to its characteristic bands at 457 and 990 cm^{-1} [10-11] (Figure 13). Both lead white and barite were identified by FTIR analyses, with their characteristic bands at 1414 cm^{-1} (C-O stretching) and 681 cm^{-1} (C-O bending vibration), and at 606 and 637 cm^{-1} (S-O bending vibration), respectively [17] (Figure 11).

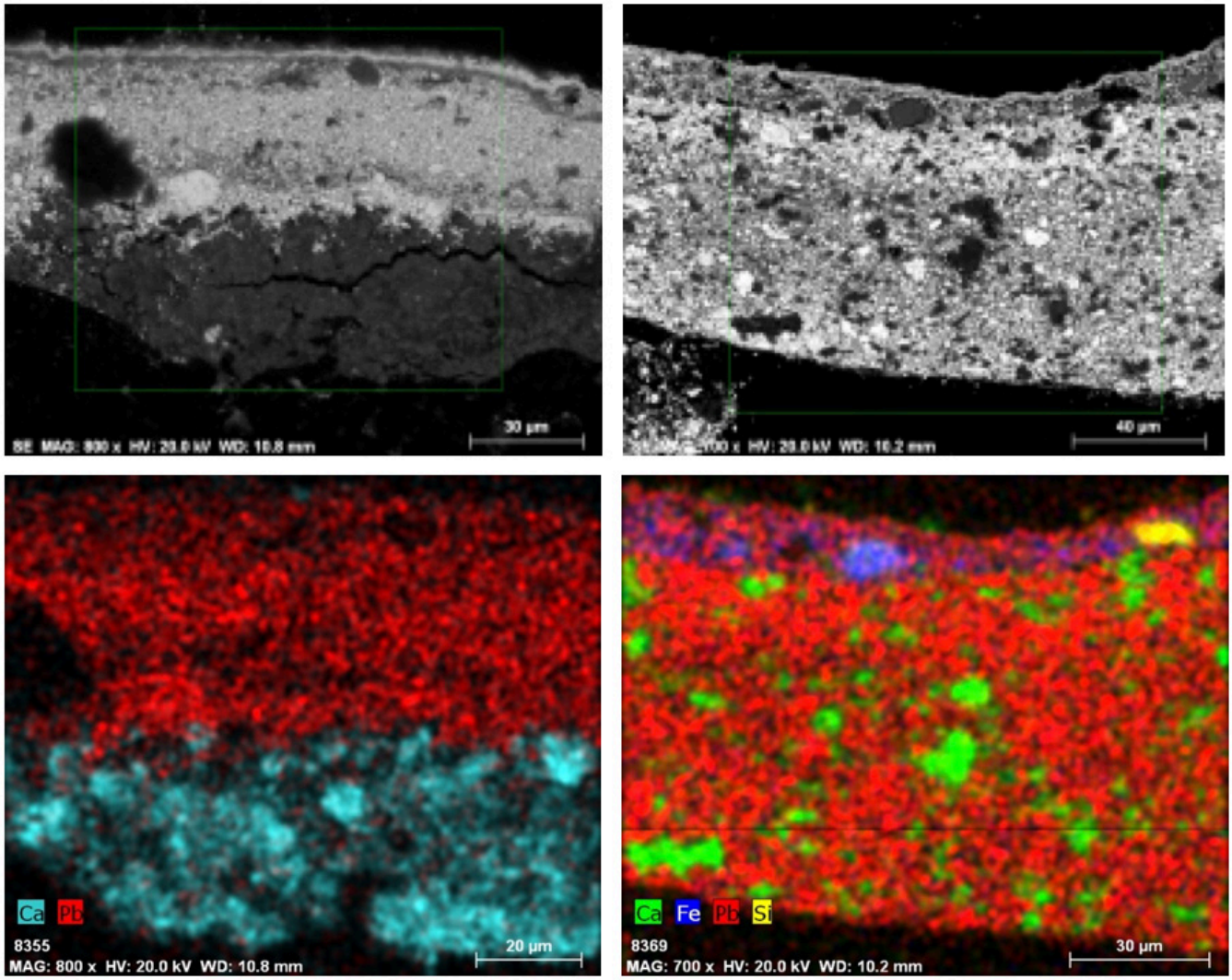

Figure 9. SEM-EDS image (*a)* and *b*)) and false colour mapping (*c*) and *d*)) of primary layers with Ca (gypsum) e Pb (lead white) of sample 4103-007 (*a*) and *c*)) and primary layers of sample 4095-004 (*b*) and *d*)) (paintings from Figure 1e and Figure 1i, respectively).

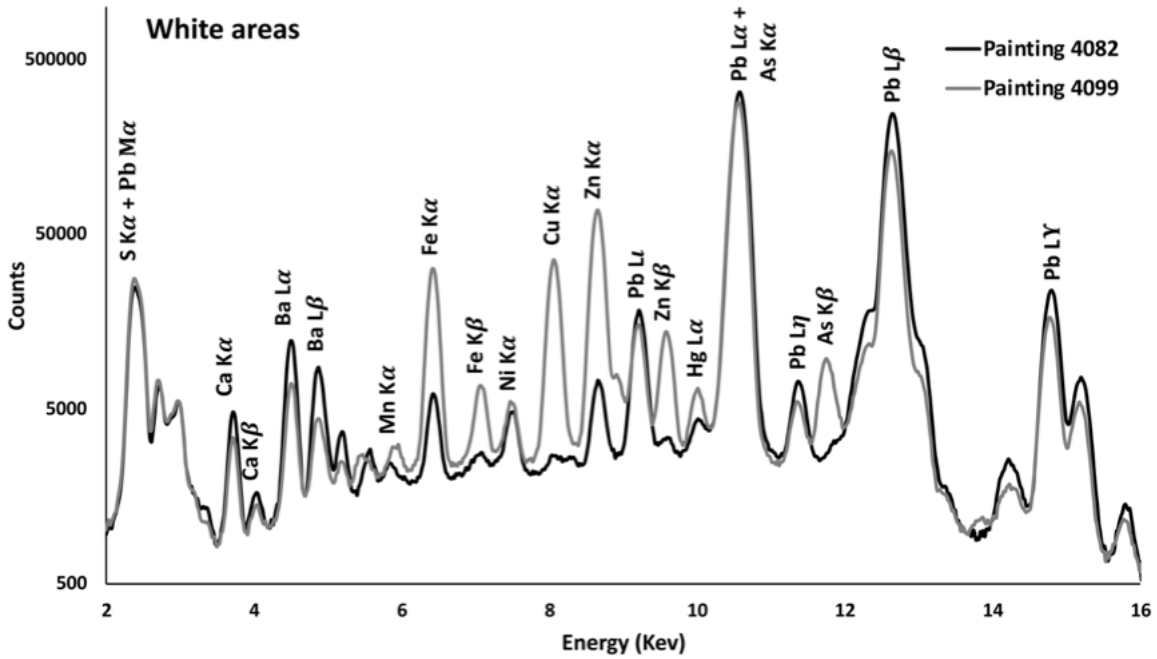

Figure 10. EDXRF spectra of white colouring areas of paintings Inv. Nos. 4082 and 4099 (Figure 1Figure 1g and Figure 2d).

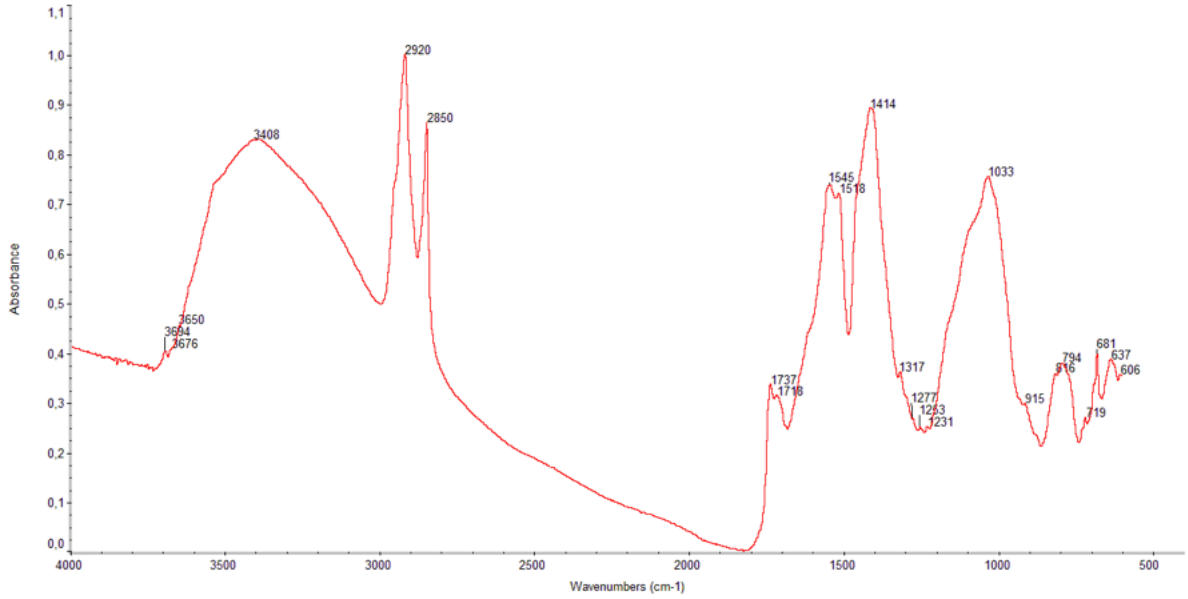

Figure 11. FTIR spectrum of white colouring areas of painting Inv. No. 3679 (Figure 1k).

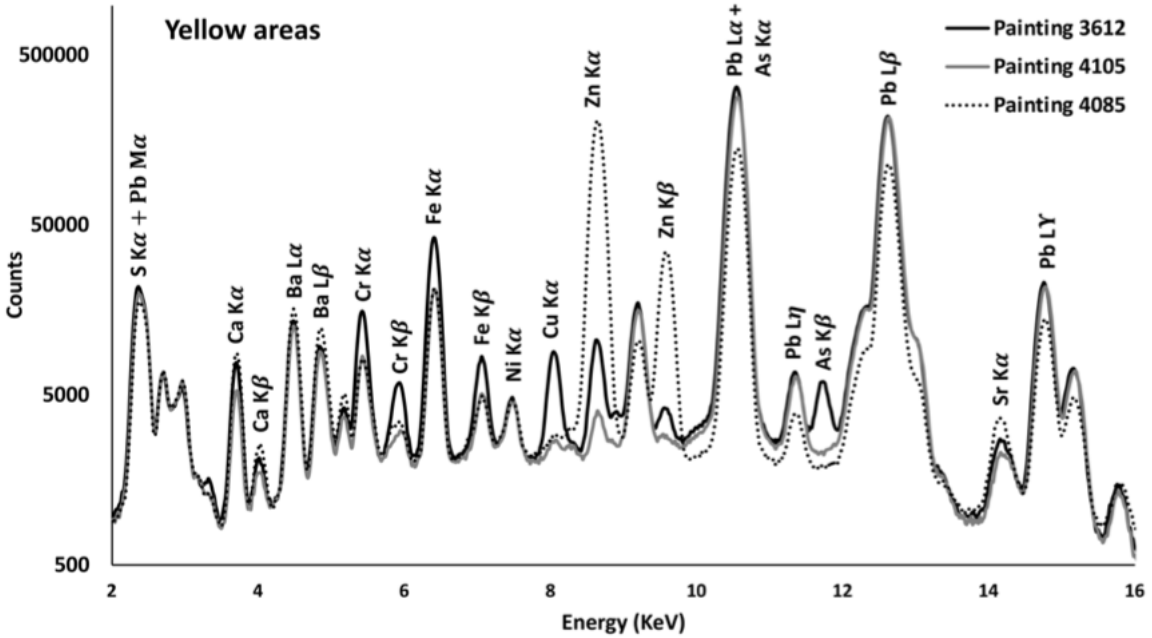

Figure 12. EDXRF spectra of yellow colouring areas of paintings Inv. Nos. 3612, 4105 and 4085 (Figure 2bg, 2h and 2b, respectively).

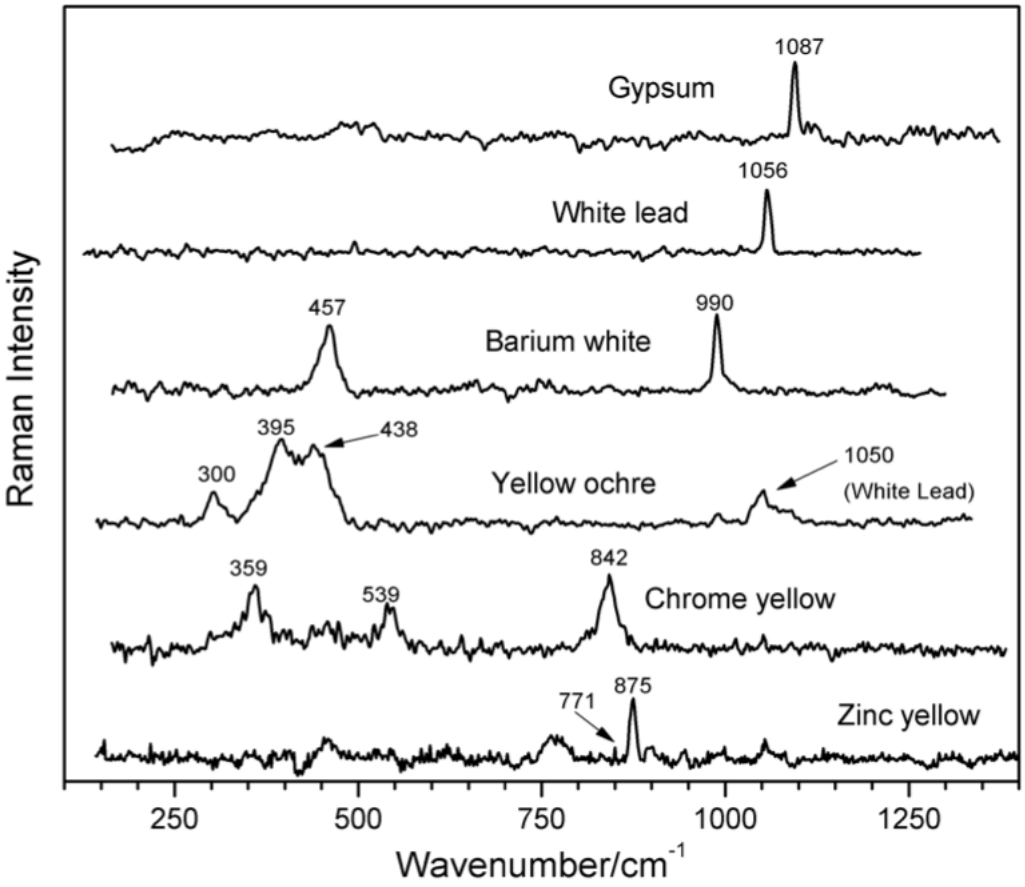

Figure 13. Raman spectra of yellow colouring areas of paintings Inv. Nos. 3612, 4105 and 4085 (Figure 2bg, 2h and 2b, respectively).

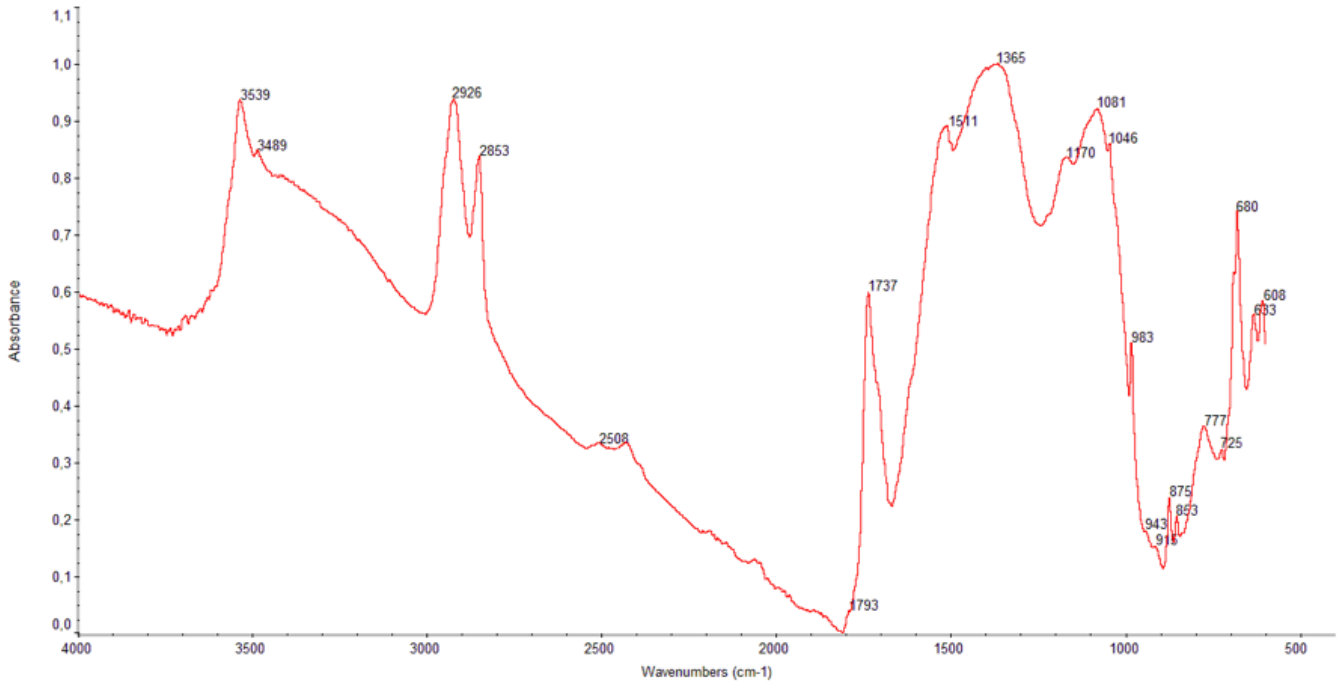

Figure 14. FTIR spectrum obtained for yellow colouring area of painting Inv. No. 4092 (Figure 2bi).

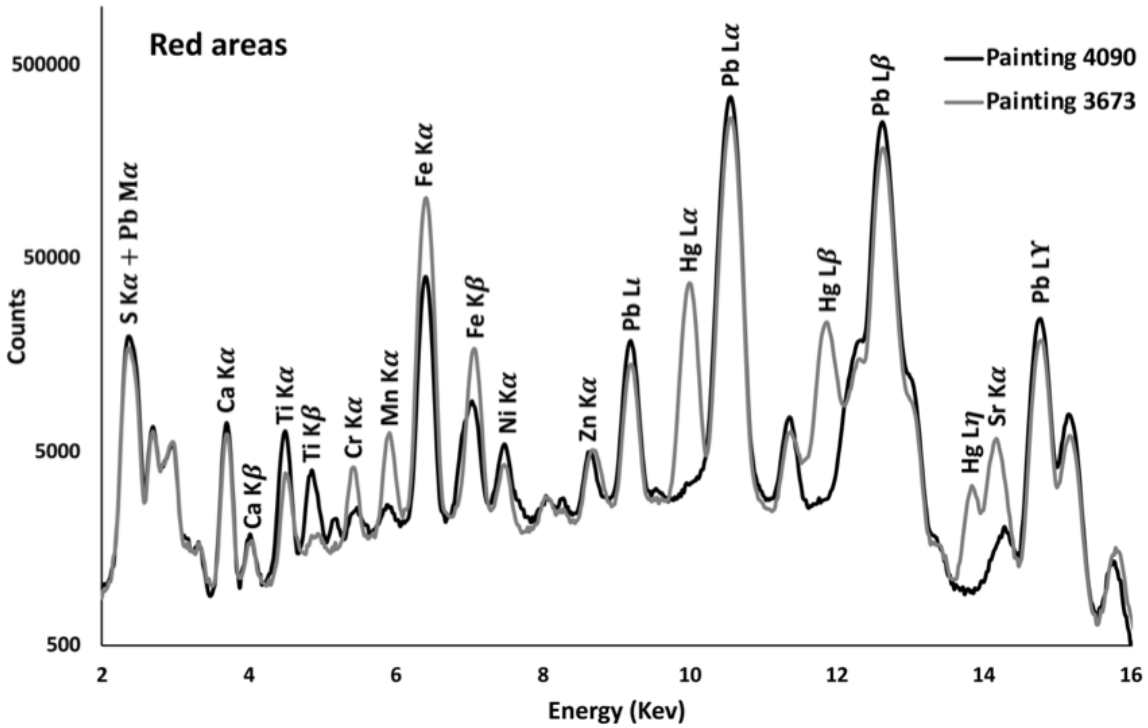

Figure 15. EDXRF spectra for red colouring areas of paintings Inv. Nos. 4090 and 3673 (Figure 1h and Figure 2bj, respectively).

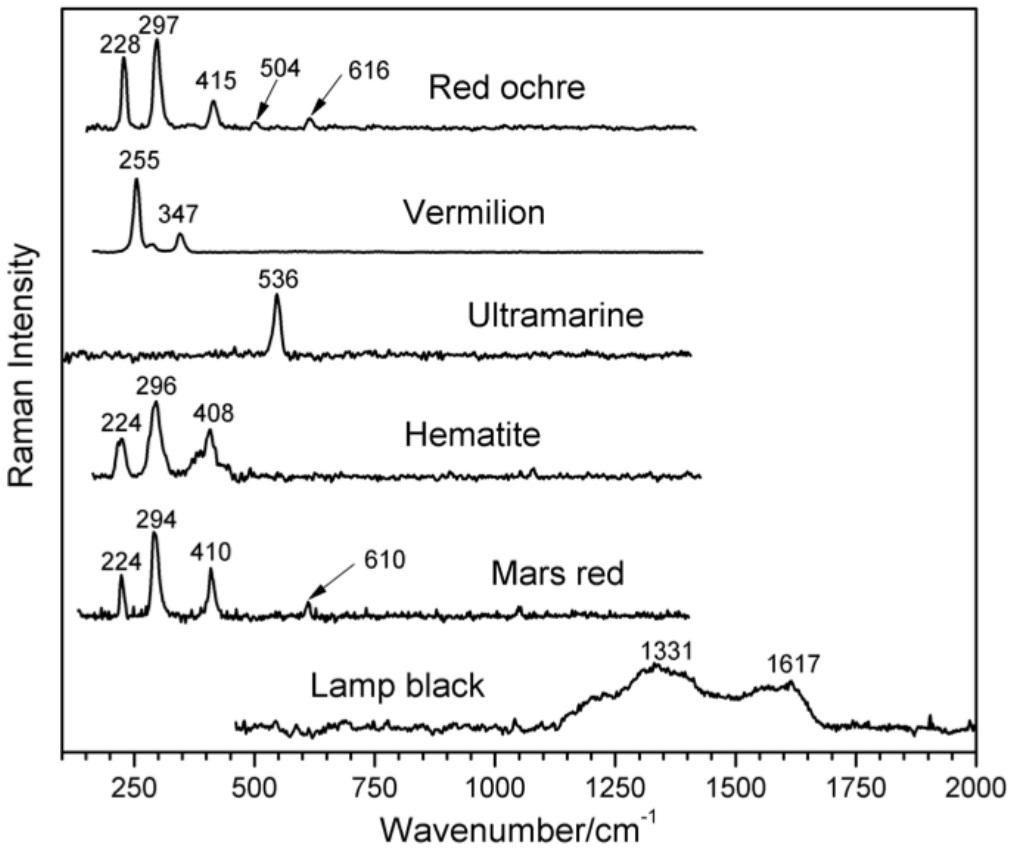

Figure 16. Raman spectra obtained for red, blue, brown and black colouring areas of paintings Inv. Nos. 3601, 3635, 3673, 3915, 4092 (Figures 1c, 1b, 2j, 2f and 2i, respectively).

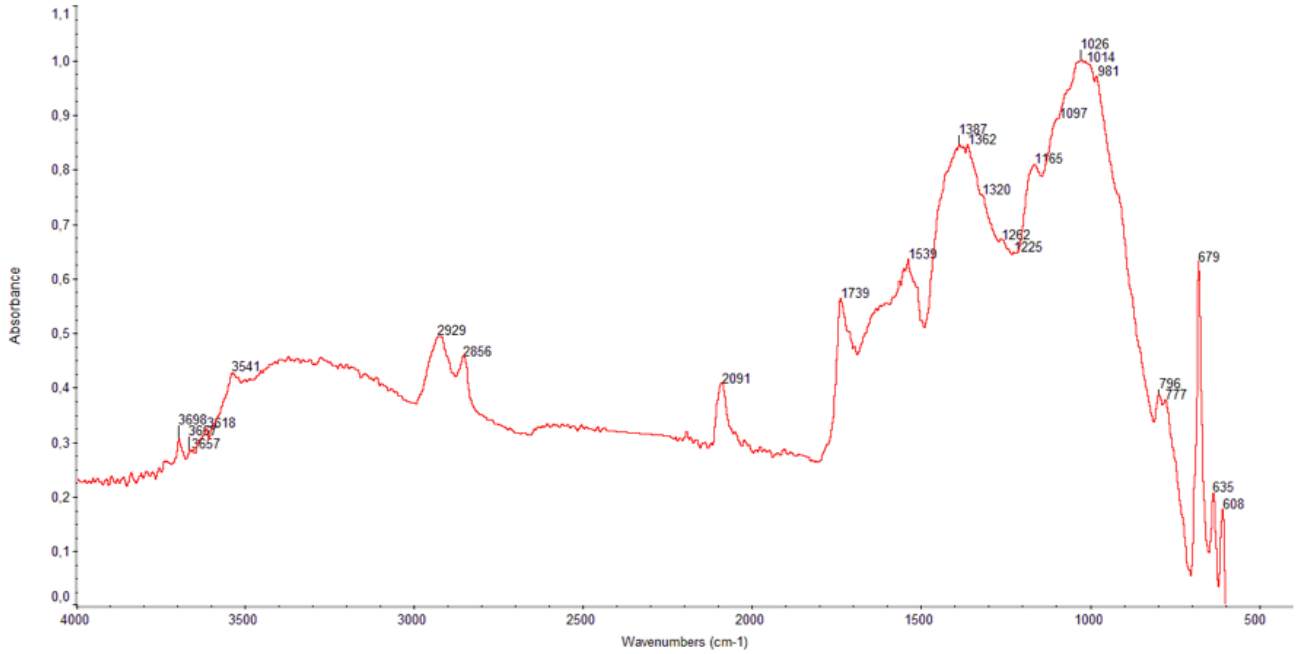

Figure 17. FTIR spectrum obtained for bluish colouring area of painting Inv. No. 4082 (Figure 1g).

In yellow areas, EDXRF spectra of the majority of the analysed paintings showed potassium (K), iron (Fe), manganese (Mn), copper (Cu) and Zn, which are regularly found in iron-based pigments such as ochres (Figure 2). Yellow ochre is a rich natural earth-based pigment, chronologically and geographically widespread, comprising aluminosilicates and iron oxides. Moreover, ochre materials are rich in potassium, which acts as a cation in the phyllosilicates mineral's arrangement. Ochre resultant sulphide ores are often enriched with minor elements such as copper, zinc, arsenic (As), and lead [16]. Concerning manganese, it features ochre as manganese oxide, which is responsible for the brownish hue of the yellow colour [18,19].

Table 2. Summary of pigments by colouring areas.

Colors	Pigments
White	Lead white; Barium white; Zinc white
Yellow	Yellow ochre; Chrome yellow; Yellow zinc
Red	Red ochre; Vermilion
Blue	Ultramarine; Prussian blue
Brown	Hematite; Mars red
Black	Lamp black

The presence of yellow ochre/goethite (FeOOH) was confirmed using Raman spectroscopy, by showing its characteristic bands at 300, 395, and 438 cm^{-1} [10] (Figure 13). The use of both EDXRF and Raman spectrometries confirm the use of a yellow ochre pigment on the majority of the paintings (Figure 1a-b, 1d, 1f-i, 1k, 2a-c, 2e-f, and 2j).

On the other six paintings (Figure 1c, 1e, 1j, and 2g-i), EDXRF spectra showed chromium (Cr) as well (Figure 12). This element indicates the presence of Cr-based pigments. Raman spectroscopy revealed the presence of chrome yellow ($PbCrO_4$), with its characteristic bands at 359, 539, and 842 cm^{-1} [11] (Figure 13). FTIR analyses confirmed the presence of chrome yellow, due to its characteristic band at 853 cm^{-1} (Figure 14).

In the particular case of painting Inventory no. 3612 (Figure 2g), the EDXRF spectrum (Figure 12) showed the concomitant presence of Zn and Cr, indicating the presence of a pigment such as zinc yellow ($ZnCrO_4$). Raman spectroscopy confirmed the presence of this pigment due to its characteristic bands at 771 and 875 cm^{-1} [11] (Figure 13). Zinc yellow was discovered by Vauquelin in 1809, but it was only developed for artists in 1847 by Murdock, and since then, this pigment has been widely used for all kinds of artistic purposes [16].

The nature of the pigment used for colouring red areas in 15 of the studied paintings (Figure 1a-h, 1k, 2a-b, 2e-h, and 2j) was determined by EDXRF to be an Fe-based pigment (Figure 10). This pigment revealed to be a red ochre (Fe_2O_3) through Raman spectroscopy, by exhibiting its characteristic bands at 228, 297, 415, 504, and 616 cm^{-1} [11] (Figure 15). Red ochre was also used by Aurélia de Sousa as a substitute for vermilion (HgS) and applied in skin tones to achieve a warmer hue. In the other five paintings (Figure 1i-j, 2c-d, and 2i), vermilion was detected using solely EDXRF, taking into account this is the only pigment known so far with Hg as a key element (Figure 15). Raman spectroscopy analyses confirmed the presence of this pigment with its characteristic bands at 255 and 347 cm^{-1} [10] (Figure 16).

For the majority of the paintings (Figure 1a-f, 1h-k, 2a-c, 2e, 2g, and 2j), on bluish hued areas, ultramarine blue ($Na_{8-10}Al_6Si_6O_{24}S_{2-4}$) could only be detected by Raman spectroscopy

due to its characteristic band at 536 cm^{-1} [10] (Figure 16). EDXRF analyses were unable to detect any specific element of this pigment. Ultramarine blue was applied in a mixture with the above identified yellow and red pigments to obtain a brownish hue, and also with white or black pigments, to achieve lighter or darker skin tones. On four of the paintings (Figure 1g, 2f, and 2h-i), FTIR analyses detected the presence of Prussian blue due to its strong C≡N absorption band at 2091 cm-1 [20] (Figure 17).

In skin shades and brown colouring areas, EDXRF spectra exhibit Fe, mercury (Hg), and Pb for most cases (Figura 15), which suggests a blend of previously identified pigments, such as red ochre, vermilion and lead white, to obtain a wide range of hues. By comparing these results with Aurélia's and Master Veloso Salgado's paintings from the same period we can conclude that they also used a mixture of green, red, yellow, and blue pigments with black or white for darker or lighter shades [2, 15].

In the three paintings depicted in Figure 1b, 1d, and 2c, Raman spectroscopy confirmed the presence of hematite (Fe_2O_3) with its characteristic bands at 224, 296, and 408 cm^{-1} [11] (Figure 16). This pigment was applied more often in the darker areas of skin tones as an approach to achieve a more natural and accurate effect on the paintings. In the paintings shown in Figure 1h, 2e, and 2h-i, on darker skin tones, Mars red (Fe_2O_3) was also identified with its characteristic bands at 224, 294, 410, and 610 cm^{-1}.

For darker skin tones, apart from the pigments previously mentioned, lamp black was used to darken the hues in all 20 paintings. This carbon-based pigment was characterized solely through Raman spectroscopy with its characteristic bands at 1331 and 1617 cm^{-1} [10-11] (Figure 16).

The results obtained lead to the conclusion that these paintings followed an artistic production methodology similar to the ones used by José Veloso Salgado (some of them were his students) and Aurélia de Sousa in academic paintings [2, 15].

White colouring areas were obtained using white lead as Salgado and Aurélia did, and yellow colouring areas with yellow ochre, chrome yellow, and zinc yellow [2, 15]. Red colouring areas were obtained mainly with red ochre instead of vermilion, which could suggest the discontinuity of the use of mercury-based pigments due to their toxicity [2]. The majority of the blue colouring areas were obtained with ultramarine blue, which is also similar to Salgado and Aurélia's techique, and the green coloured areas were obtained by intermixing yellow and blue primary hues [2, 15]. Brown colouring areas were achieved by mixing red, yellow, and blue pigments (as Salgado did), and adding darker red and black pigments, to obtain darker skin tones [2]. And finally, black colouring areas were obtained with the same pigments used by Salgado [2]. Although some students are not from Salgado's class, but from Columbano's, it is possible to determine that the selection of pigments was related to their availability rather than a master/professor's choice.

Taking into consideration that these paintings are dated from a period of great discovery and technical developments in artists' pigments and under the influence of several artistic movements from the end of the nineteenth century, a fixed or similar palette cannot be defined, even within the academic production. Moreover, some of the paintings were made in Paris, exactly where all these movements and developments were evolving. However, it is possible to observe that Columbano's students used more contemporary or modern materials such as chrome yellow or yellow zinc, while Salgado's students kept using yellow ochre. These same pigments were also observed in Columbano and Salgado's own paintings while students [2]. Table 2 summarizes all the pigments identified in the different colouring areas.

Conclusion

The results obtained in this study provided an overview of the materials and techniques used by 10 different students from two different painting classes (Veloso Salgado and Columbano Bordalo Pinheiro) from the Faculty of Fine Arts of Lisbon, during the transition of nineteenth to the twentieth century (1899-1918).

EDXRF, SEM-EDS, FTIR, and Raman spectroscopy techniques proved to be suitable to characterize the priming layers and the palettes used in the studied paintings. Imaging results provided by infrared reflectography and radiography uncovered underpaintings in three different cases, besides unveiled underdrawings and outlining.

By comparing Veloso Salgado and Columbano Bordalo Pinheiro classes, differences could be observed: the yellow pigment applied by Veloso Salgado's students was mainly yellow ochre, whereas Columbano's students preferred chrome yellow. It was also possible to infer that the palette applied by these students is similar to Veloso Salgado's when he was a student as well. This indicates that pigments used in the Academy did not change from 1883 (first year painting of Veloso Salgado) untill 1918 (last painting of Henrique Franco).

Finally, the authors intend to proceed with the research on the rest of the collection, which will provide more comprehensive information regarding the artistic training methodology in the academies by taking into consideration technical interchanges between the Portuguese and French Academies of Fine Arts.

Acknowledgments

The authors would like to thank the Faculty of Fine Arts of the University of Lisbon for lending the academic nude paintings for investigation and City University of Macao for the Sustainable Heritage Chair endowment. Ana Mafalda Cardeira acknowledges the support of Fundação para a Ciência e Tecnologia for the grant PD/BD/128382/2017. HERITAS PhD Heritage Studies Program FCT PD/00297/2013.

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RECEIVED: 2021.2.11
REVISED: 2021.9.9
ACCEPTED: 2021.9.9
ONLINE: 2021.10.14