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Calcium sulfate fillers and binders in Portuguese 15th and 16th centuries: Ground layers from a family painting workshop — Study by multianalytical spectroscopic techniques☆

Vanessa Antunes [a,b,*], António Candeias [c,d], Maria José Oliveira [c], Mercês Lorena [c], Ana Isabel Seruya [b], Maria Luísa Carvalho [b], Milene Gil [d], José Mirão [d], João Coroado [e], Virgínia Gomes [f], Vitor Serrão [a]

[a] Instituto História da Arte da Faculdade de Letras da Universidade de Lisboa (IHA-FLUL), Alameda da Universidade, 1600-214 Lisboa, Portugal
[b] LIBPhys-UNL: Laboratory for Instrumentation, Biomedical Engineering and Radiation Physics, Departamento Física, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
[c] Laboratório José de Figueiredo da Direcção-Geral do Património Cultural (LCRJF-DGPC), Rua das Janelas Verdes 37, 1249-018 Lisboa, Portugal
[d] Laboratório HERCULES, Universidade de Évora, Rua Romão Ramalho 59, 7000-676 Évora, Portugal
[e] Instituto Politécnico de Tomar (IPT), Quinta do Contador-Estrada da Serra, 2300-313 Tomar, Portugal
[f] Museu Nacional de Machado de Castro, Largo Doutor José Rodrigues, 3000-236 Coimbra, Portugal

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ABSTRACT

This study presents results on a developed methodology to characterize ground layers in Portuguese workshops. In this work a set of altarpieces of the 15th and 16th centuries, assigned to Coimbra painting workshop was studied, overall the masters Vicente Gil (doc. Coimbra 1498–1525), Manuel Vicente (doc. Coimbra 1521–1530) and Bernardo Manuel (act. c. 1559–94), father, son and grandson, encompassing from late gothic to mannerist periods. The aim of the study is to compare ground layers, fillers and binders of Coimbra workshop, and to correlate their characteristics to understand the technical evolution of this family of painters, using complementary microscopic techniques.

The cross-sections from the groups of paintings were examined by optical microscopy and the results were integrated through the analysis obtained by μ-X–ray diffraction, scanning electron microscopy with energy dispersive X–ray Spectrometry, μ-confocal Raman and occasionally with μ-Fourier transform infrared spectroscopy imaging. Ground layers are of calcium sulfate, present as *gesso grosso* (mainly anhydrite with small amounts of gypsum) in the first and last phases of the workshop and *gesso mate* (mainly gypsum with small amounts of anhydrite) in an intermediate period. Binders have protein and oleic characteristics.

1. Introduction — pictorial corpus under study

Formerly known as the workshop of the Master of Sardoal [1,2] it is known nowadays by historical documentation on the artists, as being Coimbra workshop, led by Vicente Gil (doc. Coimbra 1498–1525) and his collaborators, Manuel Vicente (doc. Coimbra 1521–1530) and Bernardo Manuel (act. c. 1559–94), father, son and grandson, with activity from the late 15th to late 16th centuries [3–5]. This family workshop is of crucial importance to understand the continuity practices of Portuguese painting and its influences of national and international context.

The pictorial corpus under study is composed by a set of panel paintings usually associated to Coimbra workshop, overall to the referred masters, encompassing from late gothic to mannerist periods (Table 1):

– Christ on the Cross, with no authorship defined, it has been lately linked to earlier works of Coimbra workshop, namely to *Santa Clara-a-Velha* altarpiece [6,7].
– *Santa Clara-a-Velha* altarpiece has no defined authorship, being previously associated to the work of Vicente Gil and Manuel Vicente, father and son. Formerly studied in a first multianalytical study published in 2010 on *Santa Clara-a-Velha* altarpiece, allowed to identify ground layers as calcium sulfate [6,8]. *Santa Clara-a-Velha* altarpiece is nowadays connected to Italian and Spanish gothic–renaissance influences [9] and consists of four paintings: Saint Clara and the miracle of Assisi, Agony in the Garden (file 20-08C), Lamentation of Christ (file 20-08A) and the predela Christ and the Apostles (file 20-08D). The analytical results of the three last paintings are presented here.

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* Corresponding author at: LIBPhys-UNL: Laboratory for Instrumentation, Biomedical Engineering and Radiation Physics, Departamento Física, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal.
E-mail address: vanessahantunes@gmail.com (V. Antunes).

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Table 1
Set of studied paintings.

Title	Dating	Assignment	Location	File sample numbers	Inventory number
Christ on the Cross	Late 15th century	Anonymous, Coimbra workshop	Church of São Silvestre de Unhos, Sacavém	16–81	–
Santa Clara-a-Velha altarpiece	Late 15th century	Anonymous, Coimbra workshop (?)	Museu Nacional de Machado de Castro (MNMC)	20-08 (A to D)	inv. MNMC2521 to MNMC2524; P8
S. Simão triptych	early 16th century	Anonymous, Coimbra workshop	Museu de Aveiro (MA)	113-11	MA4/A; MA4-1/A; MA4-2/A
Assumption of the Virgin	1510–1520	Vicente Gil	MNMC	32-13	MNMC2520;P50
S. Bartholomew	1515–1520	Vicente Gil and Manuel Vicente	MNMC	11-10E	MNMC2608;P42
Montemor-o-Velho polyptych	1515–1520	Manuel Vicente	Holy House of Mercy of *Montemor-o-Velho*	12-75 and 33-76	–
Celas polyptych	1515–1520	Manuel Vicente	MNMC	31-13 (A to F)	MNMC 2543 to MNMC2548; P1 to P6
polyptych assigned to Bernardo Manuel	1570–1580	Bernardo Manuel	MNMC	119-12 A and B	MNMC2526; P26

- *S. Simão* triptych, assigned to the same workshop, integrates paintings of different manufacture, which are distinguished from the support, to the preparatory layer and pictorial technique. *S. Simão* triptych consists of five paintings: the Central Panel, The Savior (PC), right front leaf the Apostle St. Simon (DF) and in the verso the Coat of arms of Noronha (DV), left front leaf St. James the Lesser (EF), and verso Coat of arms of Almeida and Silva (EV). We integrate in this study the analytical results of the five paintings.
- The painting Assumption of the Virgin, assigned to Vicente Gil, is a work of circa 1510–1520. Being transferred from Santa Clara-a-Velha monastery this painting is part of an original altarpiece donated by Queen D. Leonor to this monastery. Its support is made on Baltic oak (Fig. 1a).
- S. Bartholomew, painted circa 1515–1520, also assigned to Vicente Gil and Manuel Vicente's work, was also transferred from *Santa Clara-a-Velha* monastery and is associated by some authors to the previous altarpiece [10]. Nevertheless, material and technical evidences show different patterns when compared to the previous painting being the support made of chestnut wood and the ground layer of a different type [11,12].
- *Montemor-o-Velho* polyptych, of circa 1515–1520, belongs to a second phase of Coimbra workshop and is usually assigned to Manuel Vicente work [4,13]. Possibly from the private chapel of Montemor-o-Velho hospital, the polyptych is nowadays in the Holy House of Mercy. The polyptych of *Montemor-o-Velho,* or of the Life of Christ, consists on the following paintings: Nativity, Adoration of the Magi, Lamentation over the Dead Christ, St. Peter (Annunciation in verso leaf), St. John the Baptist (Angel Gabriel in verso leaf) and the predela, with sixteen busts of saints.
- *Celas* polyptych, of about 1515–1520, is assigned to Manuel Vicente work to the Monastery of Santa Maria de Celas, Coimbra. Is a polyptych of six paintings: Ascension of Christ, Assumption of St. Mary Magdalene, Incredulity of St Thomas, St. Catherine of Alexandria, Pentecost (file 31-13A) and Adoration of the Magi (file 31-13B) (Fig. 1b). We present the integrated data of these two last paintings.
- The paintings Lamentation and Apparition of Christ to the Virgin (files 119-12 A and B) (Fig. 1c) are part of a polyptych assigned to Bernardo Manuel painted circa 1570–1580. This group was crucial to understand the technical evolution of this family workshop of painters. Integrated in mannerist period this work belongs to a set of four remaining paintings. The other paintings of the set have the thematic of the Annunciation and the Holy Trinity.

The studied paintings of Coimbra Workshop were analyzed through different techniques with the purpose of identifying ground layer specificities. By comparing ground layers of Coimbra workshop it was possible to recognize technical evolution of this family workshop of painters, using complementary microscopic techniques.

2. Material and methods

2.1. Sample collection and preparation

An interdisciplinary approach was followed on the methodology for analysis of the paintings ground layers. The collection of samples was carried out after an exhaustive inspection of the paintings by the naked eye and other techniques, such as infrared photography, to analyze the state of conservation of the paintings and choose the best place to collect them. After collection, the samples were assembled on specific supports and polished. For the selection of the samples, some

a) b) c)

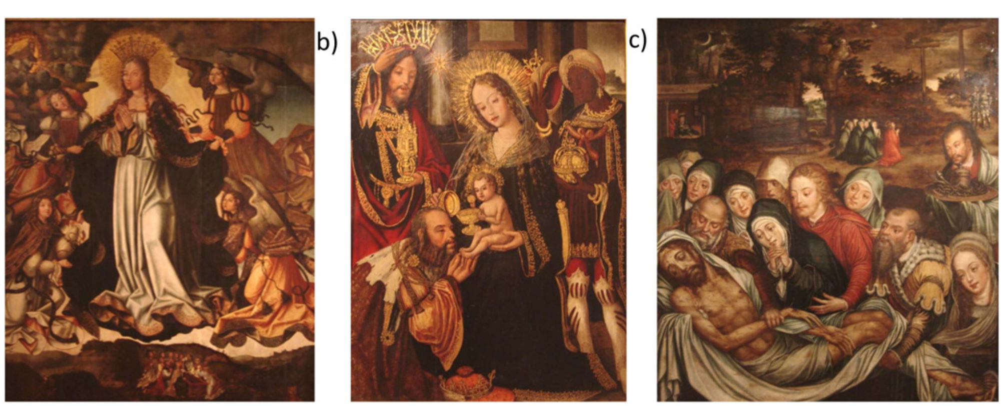

Fig. 1. a) Assumption of the Virgin (file 32-13, MNMC) assigned to Vicente Gil, c. 1510–1520 (photo Vanessa Antunes, 2013); b) Adoration of the Magi, *Celas* polyptych (file 31-13, MNMC) assigned to Manuel Vicente, c. 1515–1520 (photo Vanessa Antunes, 2013); c) Lamentation (file 119-12 A, MNMC) assigned to Bernardo Manuel, c. 1570–1580 (photo Vanessa Antunes, 2013).

aspects have been taken into account: spatial location in the painting, ground layer thickness, the existence of more than one ground layer (as stated in treatises) and samples of the original painting, without repaints. Part of the chosen samples were mounted as cross-sections in epoxy polymeric resin and polished with silicon carbide. Some samples were kept without any further treatment, to be analyzed by micro-X-ray diffraction (μ-XRD) and micro-confocal Raman spectroscopy (μ-Raman).

2.2. Description of the analytical techniques

2.2.1. Optical microscopy (OM)

Samples were studied primarily by optical microscopy using a Leitz Wetzlar optical dark field and bright field microscope. This microscope is coupled with digital camera Leica DC 500.

2.2.2. Scanning electron microscopy with energy dispersive X-ray spectrometry (SEM–EDS)

Scanning electron microscopy imaging (Backscattering mode) and analysis was achieved with a Hitachi S-3700 N scanning electron microscope with a coupled Bruker XFlash 5010 SDD energy dispersive detector. The elemental composition was obtained analyzing the cross-sections of the samples by SEM–EDS, operating at 20 kV. Some cross-sections were coated with a conductive film of carbon. Some of the samples were analyzed in variable pressure to preserve them in order to be analyzed by other analytical methods.

2.2.3. Micro-X-ray diffraction (μ-XRD)

Micro-X-ray Diffraction was performed using a Bruker general area detection diffraction system (GADDS) microdiffractometer (Bruker AXS, D8 Discover). The microdiffractometer is equipped with a two-dimensional HiStar gas filled area detector, a Goebel mirror, a laser-video sample alignment system and a motorized XYZ stage. Diffraction data were registered using Cu Kα radiation, tube running at 40 kV, 40 mA and the incident beam collimated to 1 mm diameter. The XRD patterns were measured with a recording time of 1800 s for each step in the range 8° to 70° 2θ and a step size of 0.02°. Identification of crystalline phases was carried out using the International Centre for Diffraction Data Powder Diffraction Files (ICDD PDF).

The samples were analyzed in different spots in the upper (P1, P2) and bottom (E1, E2) sides of the ground layer and unmounted.

2.2.4. Micro-confocal Raman spectroscopy (μ-Raman)

Raman spectra were performed using an Xplora (Horiba) spectrometer. The spectrometer is equipped with a 785 nm Laser diode, a 100× objective and a 1200 l/mm optical grating with a spectral resolution of about 4 cm^{-1}. The incident laser power on the samples was 3–5 mW. In order to identify the detected compounds literature and databases (Spectral ID, Crystal Sleuth, RRUFF) were used [14].

2.2.5. Micro-Fourier transform infrared spectroscopy

To perform infrared analysis the samples were mounted in an epoxy polymeric resin and cross-sectioned with a Leica microtome in a thickness of 20 μm in order to remove micro–samples of the upper and lower

Table 2
Analytical results of μ-XRD identifying chemical composition in ground layers of paintings. Samples of paintings were analyzed in different spots in the upper (P1, P2) and bottom (E1, E2) sides of the ground layer.

Samples	Analyzed points	Composition					
		Anhydrite	Gypsum	Bassanite	Calcite	Quartz	Dolomite
16-81-31	E1 + E2	x	x	x		x	x
	P1 + P2	x		x	x	x	x
16-81-33	E1 + E2 + P1 + P2	x		x		x	x
20-08-A6	E1 + E2	x	x			x	
	P1 + P2	x	x				
20-08-A9	E1 + E2 + P1 + P2	x	x		x	x	
20-08-A16	E1 + E2 + P1 + P2	x	x			x	
20-08-A24	E2 + P2	x	x			x	
20-08-C12	E1 + E2 + P1 + P2	x	x		x	x	
20-08-C14	E1 + E2 + P1 + P2	x	x		x	x	
20-08-D14	E1 + E2 + P1 + P2	x	x			x	
20-08-D18	E1 + E2 + P1 + P2	x	x			x	
20-08-D11	E1 + E2 + P1 + P2	x	x				
113-11-5 DF	E1 + E2 + P1 + P2	x	x			x	
113-11-7 DF	E2 + P2	x	x			x	
113-11-8 DV	E1 + E2 + P1 + P2	x	x			x	
113-11-9 DV	P1 + P2	x	x				
113-11-10 DV	E2 + P2	x	x				
113-11-15 EF	E1 + E2 + P1 + P2	x	x				
113-11-19 EF	P1 + P2	x	x			x	
113-11-23 PC	E1 + E2 + P1 + P2	x	x			x	
113-11-27 PC	E2	x	x			x	
113-11-30 PC	P2	x	x			x	
32-13-1	E1 + E2 + P1 + P2	x	x			x	
32-13-2	E1 + E2 + P1 + P2	x	x			x	
11-10-E7	E1 + E2 + P1 + P2		x				
11-10-E9	E1 + E2 + P1 + P2		x				
12-75-14	E1 + E2 + P1 + P2	x	x	x		x	
12-75-20	E1 + E2 + P1 + P2	x	x			x	
31-13-A1	E1 + E2 + P1 + P2	x	x			x	
31-13-A2	E1 + E2 + P1 + P2	x	x			x	
31-13-B1	E1 + E2 + P1 + P2	x	x			x	
31-13-B2	E1 + E2 + P1 + P2	x	x			x	
119-12-A3	E1 + E2 + P1 + P2	x	x			x	
119-12-A4	E1 + E2 + P1 + P2	x	x			x	
119-12-B3	E1 + E2 + P1 + P2	x	x			x	
119-12-B4	E1 + E2 + P1 + P2	x	x			x	

areas of each ground layer. This material was analyzed in transmission mode after being compressed in a Spectra–Tech (Sample Plan micro–compression diamond cell). For each spectrum 256 scans were recorded with a spectral resolution of 4 cm^{-1} using a Thermo Nicolet Nexus spectrometer coupled to a Nicolet Continuum microscope, equipped with a Nicolet mercury–cadmium–telluride (MCT-A) detector (working range: 4000–650 cm^{-1}).

2.2.6. Micro-Fourier transform infrared spectroscopy imaging

FTIR imaging made in one of the samples, 32-13-1, allowed us to confirm the location of each binder in the ground layer. The analysis was made in a Bruker (HYPERION 3000) equipped with an FPA detector. The analysis area was 160 × 32 μm and the mapping image is the result of 20,480 overlapped spectra.

3. Data treatment

The identification of the different phases of ground layers materials was performed using a Bruker EVA software (Version 3.0) and the PDF-ICDD Powder Diffraction Database (International Centre for Diffraction Data). The quantitative calculation of the percentage of gypsum and anhydrite of historical samples was based on different formulations of reference samples prepared to the specific study of ground layers with 10% variation between both materials, from 0% to 90% of anhydrite. Semi-quantitative analysis were based on the reference-intensity-ratio (RIR) allowing the identification of the material patterns to the observed peaks in the powder pattern, by scaling the maximum intensities of the International Center for Diffraction Data base (ICDD PDF) which has been provided by EVA software.

The determination of the percentage of gypsum in each historical sample from the calculated percentages obtained by the EVA code was made by comparing these results to a calibration curve. This curve allowed creating a conversion coefficient of the gypsum amounts calculated for the reference samples plotted against the theoretical gypsum (weighted) and then compared to the calculated percentages of historical samples [15–17].

4. Results and discussion

4.1. Fillers — calcium sulfate ground layers

We can find two main types of calcium sulfate in ground layers of Coimbra painting workshop: anhydrite and gypsum. These materials are combined to form *gesso grosso*, with higher amount of anhydrite than gypsum, and *gesso mate*, with bigger quantity of gypsum than anhydrite.

- Christ on the Cross (samples 16–81) presented *gesso grosso* in the ground layers. The results obtained by μ-XRD showed the presence of the compounds gypsum, anhydrite, bassanite, calcite, dolomite and quartz (Table 2); the presence of bassanite, rarely found in ground layers of the ancient Portuguese studied paintings [11,18, 19], may suggest that the initial mixture of calcium sulfate might have been anhydrite and a small amount of bassanite. Part of this last one might have been transformed into gypsum during the hydration process of mixing water or glue, before extending the ground layer. Semi quantitative results performed to the analyzed areas by μ-XRD showed 4 to 18% of gypsum and 82 to 96% of anhydrite, disregarding the hardly measurable percentage of bassanite (Table 3). SEM–EDS allowed identifying the following elements: Mg, Al, Si, S, Ca and Fe. Calcium has the strongest peak and can be found both with C and O, probably as calcite, or in a mixture with S and O as calcium sulfate. The presence of the remaining elements is most probably due to aluminosilicates.
- Agony in the Garden (samples 20-08C) of Santa Clara-a-Velha altarpiece has been previously studied by SEM, presenting a *gesso grosso* ground layer beneath a *gesso mate* layer [8]. In addition, in the present study, we could confirm with complementary techniques, SEM–EDS and μ-XRD, that the paintings were composed only by *gesso grosso* but with different granullometry of calcium sulfate. Micro-XRD results showed the presence of the compounds gypsum, anhydrite, calcite and quartz (Table 2) in paintings 20-08A and C. Semi quantitative results performed by μ-XRD to gypsum and anhydrite peaks showed 14 to 26% of gypsum and 74 to 86% of anhydrite (Table 3). Micro-Raman data confirmed the presence of anhydrite identified by further analysis (Table 4). SEM–EDS showed that the predominant elements in the paintings were Ca and S probably due to calcium sulfate as main compound. The simultaneous presence of Ca and Mg identify the position of dolomite.
- *S. Simão* triptych (samples 113-11) is a singular case in what concerns to panel painting techniques. Each one of the three panels presents distinct materials and techniques. The central panel is made of Baltic oak (Quercus) and is flanked by two smaller lateral panels made of fruit tree wood [20]. Micro-XRD results showed the presence of the compounds gypsum, anhydrite and quartz (Table 2). Semi quantitative μ-XRD results showed that while the central panel ground layer is formed mainly by *gesso grosso* (anhydrite (76 to 83%), with some gypsum (17 to24%) (Table 3, samples 23 and 27 PC)); the two lateral panels, on the side representing the Saints, the ground layers are mainly *gesso mate* (gypsum (55 to 89%), with some anhydrite (17 to 45%) (Table 3, samples 5, 7 DF and 15, 19 EF)). On the sides of the coats of arms the composition of the ground layer is formed by anhydrite and gypsum in identical proportions (42 to 52% gypsum and 48% to 58% anhydrite (Table 3, samples 8, 9, 10 DV), (Fig. 2)); micro-Raman confirmed the presence of anhydrite and gypsum (Table 4); SEM–EDS showed the major occurrence for both S and Ca, due to calcium sulfate; even though, we can find Ca grains isolated, indicating the presence of calcite. We can also find Ca combined with Mg, suggesting the occurrence of dolomite. Na, Al, Si and Fe are also found,

Table 3
Semi quantitative results for the areas of the μ-XRD gypsum peak at 3.06 Å and anhydrite peak at 3.50 Å for samples of paintings analyzed in different spots in the upper (P) and bottom (E) sides of the ground layer.

Samples	Gypsum %	Anhydrite %
16-81-31_E/P	4/6	96/94
16-81-33_E/P	18/7	82/93
20-08-A6_E/P	18/21	82/79
20-08-A9_E/P	25/23	75/77
20-08-A16_E/P	14/14	86/86
20-08-A24_E/P	29/28	71/72
20-08-C12_E/P	14/15	86/85
20-08-C14_E/P	26/18	74/82
20-08-D14_E/P	40/48	60/52
20-08-D18_E/P	22/21	78/79
113-11-5DF_E/P	55/68	45/32
113-11-7DF_E	83	17
113-11-8DV_E	52	48
113-11-9DV_P	42	58
113-11-10DV_E/P	42/44	58/56
113-11-15EF_E/P	65/68	35/32
113-11-19EF_E/P	89/88	11/12
113-11-23PC_E/P	24/24	76/76
113-11-27PC_E	17	83
113-11-30_P	15	85
11-10-E4_E/P	93/94	7/6
11-10-E7_E/P	90/91	10/9
12-75-14_E/P	78/80	22/20
12-75-20_E/P	91/86	9/14
31-13-A1_E/P	54/67	46/33
31-13-A2_E/P	37/37	63/63
32-13_E/P	12/13	87/88
119-12-A3_E/P	16/21	84/79
119-12-A4_E/P	16/16	84/84
119-12-B3_E/P	14/15	86/85
119-12-B4_E/P	10/17	90/83

Table 4
Analytical results of μ-Raman analysis identifying elemental composition obtained for different grains in ground layers of some studied paintings.

Samples/ analyzed points	Peaks/cm^{-1}	Compounds
20-08-c12-02	418/ 675/ 1017	Anhydrite
20-08-c12-03	417/ 495/ 1009/ 10018	Gypsum,Anhydrite
20-08-c12-03	175/ 300/ 725/ 1099	Dolomite
11-10E-9_02	417 / 1009	Gypsum
11-10E-9_03	417 /673/ 1010	Gypsum
12-75-14-02	1008	Gypsum
33-76-1-02	1009	Gypsum
31-13-A2 2D	417 /1008/1018 /1087	Gypsum , Anhydrite, Calcite
32-13-2-01_8/10/ 13	1018	Anhydrite
113-11-15-01_2	1009	Gypsum
113-11-1-01	418 /1008/ 1018	Gypsum , Anhydrite
113-11-1-01_1	416/ 1018	Anhydrite
113-11-1-02_1	1008/ 1018	Gypsum,Anhydrite
119-12-1-01	1017	Anhydrite
119-12-B3-01	415/674/1016/1128	Anhydrite
119-12-B3-02	413/494/1007/1016	Anhydrite, Gypsum
119-12-B4-01	1009/1017	Anhydrite, Gypsum

probably due to the presence of aluminosilicates. Lead was also observed, most likely due to a small addition of lead white to lighten the ground layer or due to painting layers contamination.

– Assumption of the Virgin (samples 32-13) is made of *gesso grosso*. Micro-XRD results showed the presence of compounds gypsum, anhydrite and quartz (Table 2); the semi quantitative calculations performed for gypsum and anhydrite showed 12 to 13% of gypsum and 87 to 88% of anhydrite (Table 3); micro-Raman data confirmed the presence of anhydrite identified by further analysis (Table 4). SEM–EDS allowed identifying several associated elements which might give us some idea about the used compounds. Sulfur appears associated to Ca probably due to calcium sulfate. The simultaneous presence of Mg, Al, S, Si, P, K, Ca, Fe and Ti, suggests the use of a mixture including calcium sulfate, dolomite and aluminosilicates. Lead was also identified, for the reason hitherto explained; Finally, the presence of Sr, is most likely celestite, often found in Portuguese painting ground layers [21]. Furthermore, in Fig. 3a it is also possible to observe in images obtained by SEM (BSE) the irregular grains of big dimensions in the bottom of the ground layer, such as the grain showed in Fig. 3b bigger than 100 μm, as in other Portuguese paintings of the same period [11].
– S. Bartholomew painting (samples 11-10E) presents a *gesso mate* ground layer and its support is made of chestnut, differently from Assumption of the Virgin. Micro-XRD results showed only gypsum as the main compound (Table 2); Semi quantitative results showed 90 to 94% of gypsum and 6 to 10% of anhydrite (Table 3); micro-Raman data confirmed the presence of gypsum identified in the previous analysis (Table 4). SEM–EDS, besides S and Ca constituents of gypsum, allowed identifying other elements such as Si, Mg, Al possibly due to aluminosilicates; other elements such as Fe, Ca, S, Si, Na, Mg and Al, probably iron oxides (ochre) with iron sulfates and silicates and calcium sulfate contaminations, such as Sr probably due to celestite.
– St. Peter (samples 12-75) of *Montemor-o-Velho* polyptych is mainly composed by *gesso mate*. Micro-XRD results showed the presence of gypsum, anhydrite, bassanite and quartz (Table 2); Semi quantitative results showed 78 to 91% of gypsum and 9 to 22% of anhydrite (Table 3); μ-Raman data recognized the occurrence of gypsum made by the prior analysis (Table 4). The results obtained by SEM–EDS

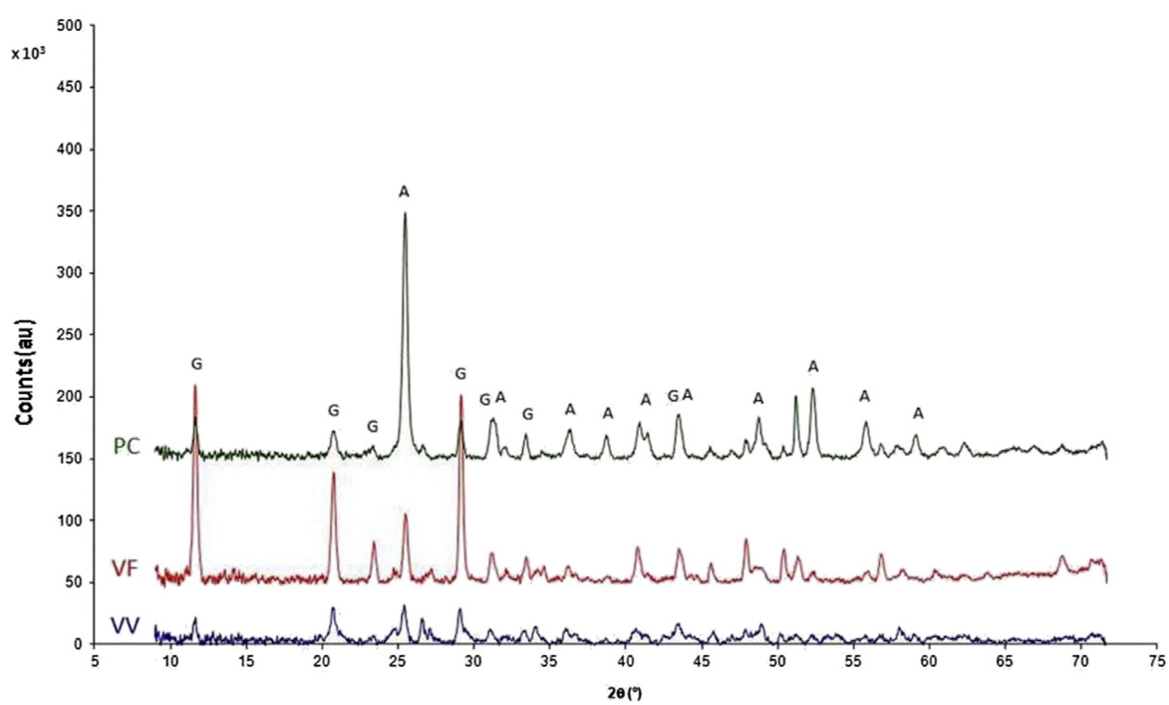

Fig. 2. Diffractograms corresponding to ground layers of *S. Simão* triptych: A — Anhydrite; G — gypsum; PC — Central Panel; VF — Front paintings (Saints); VV — Verse paintings (Coats of arms). These diffractograms show central panel ground layer formed mainly by anhydrite; the two lateral panels in front paintings (Saints) ground layers mainly composed of gypsum, while verse paintings (Coats of arms) ground layers are formed by anhydrite and gypsum in identical proportions.

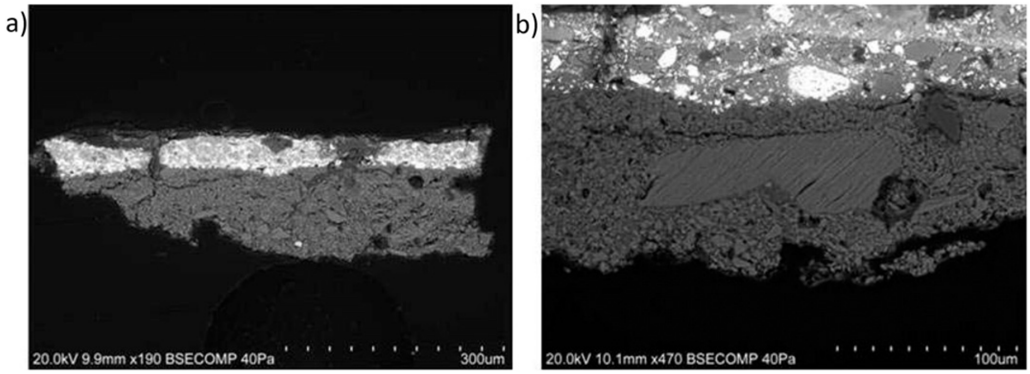

Fig. 3. a) SEM (BSE) image of the sample 32-13-3 from the painting Assumption of the Virgin, assigned to Vicente Gil, showing irregular grains of big dimensions in the bottom of the ground layer; b) SEM (BSE) image of the sample 32-13-2 from the painting Assumption of the Virgin (MNMC) showing the big dimensions of a grain (bigger than 100 μm) in the ground layer.

allowed identifying similar elements to the ones found in S. Bartholomew painting, with exception to Sr, not found in the studied samples.

– Pentecost (samples 31-13A) of *Celas* polyptych has *gesso mate* as ground layer. Micro-XRD results verified the occurrence of gypsum, anhydrite and quartz (Table 2); Semi quantitative results showed 37% to 67% of gypsum and 33 to 63% of anhydrite (Table 3). These percentages are similar to those obtained for the wheels of *S. Simão* triptych and the predela of *Santa Clara-a-Velha* altarpiece (samples 20-08D, Table 3), probably executed also in the epoch of Manuel Vicente, the son; μ-Raman data confirmed the previous analysis by the identification of gypsum, anhydrite and also calcite (Table 4). Analysis performed by SEM–EDS allowed identifying the elements present on S. Bartholomew painting. Iron, already present in SEM (BSE) images, gives an ocher tone to ground layer, as evidenced by the grains of this element (Fig. 4a and b) (Table 4). Contrarily to what happens in Assumption of the Virgin, smaller dimension grains are observed.
– Lamentation of Christ (samples 119-12A) and Apparition of Christ to the Virgin (samples 119-12B), the altarpiece from the end of the 16th century (1570–1580), assigned to the painter Bernardo Manuel, grandson of Vicente Gil and son of Manuel Vicente present *gesso grosso* in the ground layers. Micro-XRD results showed the presence of gypsum, anhydrite and quartz (Table 2); Semi quantitative results showed 10% to 21% of gypsum and 84% to 90% of anhydrite (Table 3); μ-Raman data confirmed the presence of anhydrite and gypsum identified in previous analysis (Table 4); SEM–EDS allowed to identify elements indicating the presence of calcium sulfate as main component, dolomite and calcite. Furthermore, other elements are indicative of the presence of aluminosilicates. Black grains observed in the ground layer by optical microscopy were confirmed by SEM–EDS, indicating the presence of the element P, suggesting the occurrence of bone black (Fig. 5a and b). Likewise, the confirmation of yellow grains by SEM–EDS established the presence of Fe, probable iron oxy-hydroxides, integrating the technology of adding pigments to ground layer of the previous period of this workshop. In SEM images (BSE) it is possible to observe smaller dimensions of the grains in the two layers of the ground (being the lower one less compact) (Fig. 6a) when compared to the paintings assigned to the beginning of the 16th century, such as *Santa Clara* altarpiece paintings (Fig. 6b).

4.2. Binding materials

Previously studied by μ-FTIR, the binder materials that compose the ground layers of Coimbra workshop, specifically addressing to the referred paintings, were identified as proteins, probably animal glue, and oil [22]. The oil might come from impregnation of the upper painting layers or being in the ground layer formulation. This aspect was particularly studied in the painting Assumption of the Virgin (samples 32-13) with the technique of FTIR imaging. This technique applied in the sample 32-13-1 allowed confirming the location of each binder, both

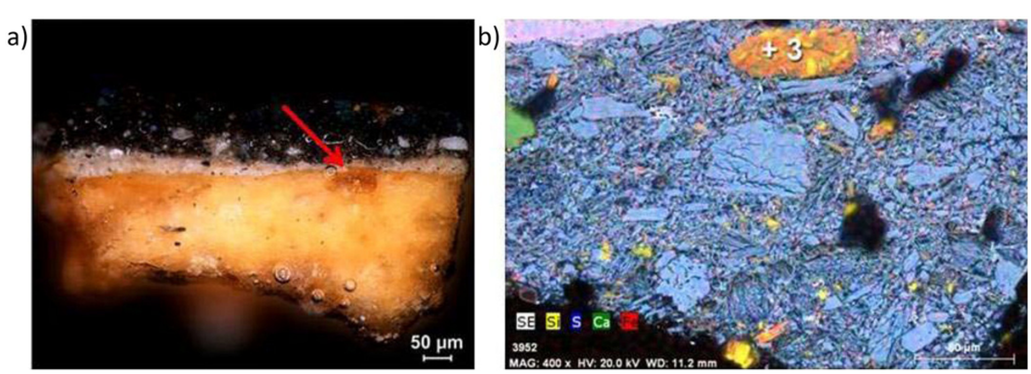

Fig. 4. a) OM image of sample 31-13-A2 of the painting Pentecost, assigned to Manuel Vicente, where the red arrow indicates the presence of an ocher grain in ground layer; b) SEM–EDS mapping of Si and Fe elemental distribution indicating with "+3" the same ocher grain in ground layer.

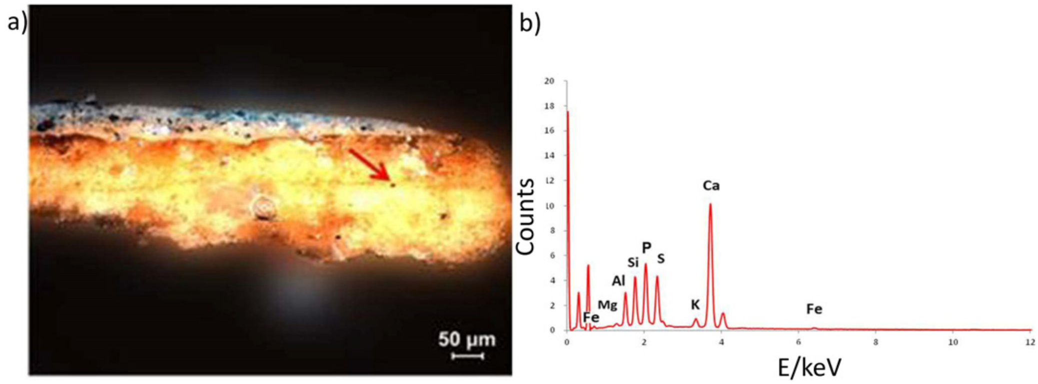

Fig. 5. a) OM image of sample 119-12A-4 of the painting Lamentation of Christ assigned to Bernardo Manuel, where the red arrow indicates the presence of a black grain in ground layer; b) EDS spectrum of the black grain, where the element P suggests the occurrence of bone black, Fe the presence of iron oxy-hydroxides and elements S and Ca propose the presence of calcium sulfate.

in ground and pictorial layer. In Fig. 7a we can observe the cross-section of the sample placed in vertical lecture, showing the pictorial layer on the left side (blue) and the ground layer on the right side (gray). In the lower region of the ground layer we can observe a bigger intensity of the oil band (red). This confirms the previous hypothesis that this accumulation can be due to the oil used in painting layers and to its penetration throughout the ground layer. In the painting layer (left side of the image) we can observe that the intensity of the oil is bigger (yellow) corresponding to higher absorption of this band. This discrepancy of intensity on the oil between ground and painting layer can also confirm the absorption of the oil by this calcium sulfate absorbent ground layer.

In Fig. 7b we can observe the spectra specifying the gray area containing the CH's band absorption region at 2926 cm^{-1}.

5. Conclusions

The microanalytical approach applied in this study allowed to improve the knowledge on the technical options of the artists face to the values of the time period under study. Critical analysis on the results obtained for inorganic materials and organic binders in ground layers brought novel conclusions relatively to the technology of execution and application regarding the paintings of Coimbra workshop, throughout three generations. Regarding the construction of altarpieces we can conclude that different ground layer materials may coexist in the same altarpiece, meaning that each altarpiece painting may have been executed by different hands or at different times, even with the visual homogeneity of the final work, easily identifiable with the same Coimbra workshop.

Using the same base materials, we can observe an evolution on the transformation technique of ground layers:

- Binders identified in the ground layer were oil and proteins, probably animal glue (Fig. 7a and b).
- In the end of the 15th century *gesso grosso* was mostly used (Fig. 6a).
- In the working period of Manuel Vicente we find the use of *gesso mate* probably with the addition of ocher pigments (Fig. 4a and b); this change was probably influenced by other painting workshops, such as Viseu Workshop [11].
- finally, by the end of the 16th century, Bernardo Manuel, the grandson, returns to the use of *gesso grosso* with pigments probably bone black and ocher already used by his father in *gesso mate* ground layers (Figs. 5a and b, 6b).

Heterogeneity may be found in a workshop throughout a century, from the end of the 15th century to the end of the 16th century. Although respecting the base materials chosen by their workshop, specifically addressing Coimbra workshop, the will of each author was mandatory in what concerns to the transformation of these materials. With this investigation it is possible to conclude that Bernardo Manuel followed the traditional *gesso grosso* technique used in the epoch of his grandfather, probably due to the greater stability of anhydrite compared to gypsum when it comes to thermo-hygrometric conditions.

This last painter gathered the know-how of both generations by using the same material that his grandfather but grinding this material thinly and adding colored pigments, as his father did, integrating both technologies learned in the transformation of *gesso grosso* and *gesso mate*.

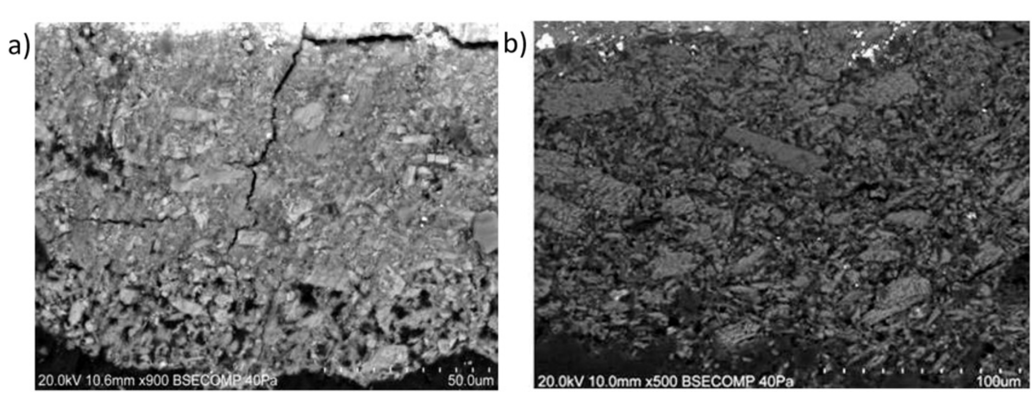

Fig. 6. a) SEM (BSE) image of sample 119-12B-3 of painting Christ Appearing to the Virgin, assigned to Bernardo Manuel, where is observed smaller dimensions of the grains; b) SEM (BSE) image of sample 20-08 A-6 of the painting Lamentation of *Santa Clara* altarpiece showing irregular grains of big dimensions in the ground layer.

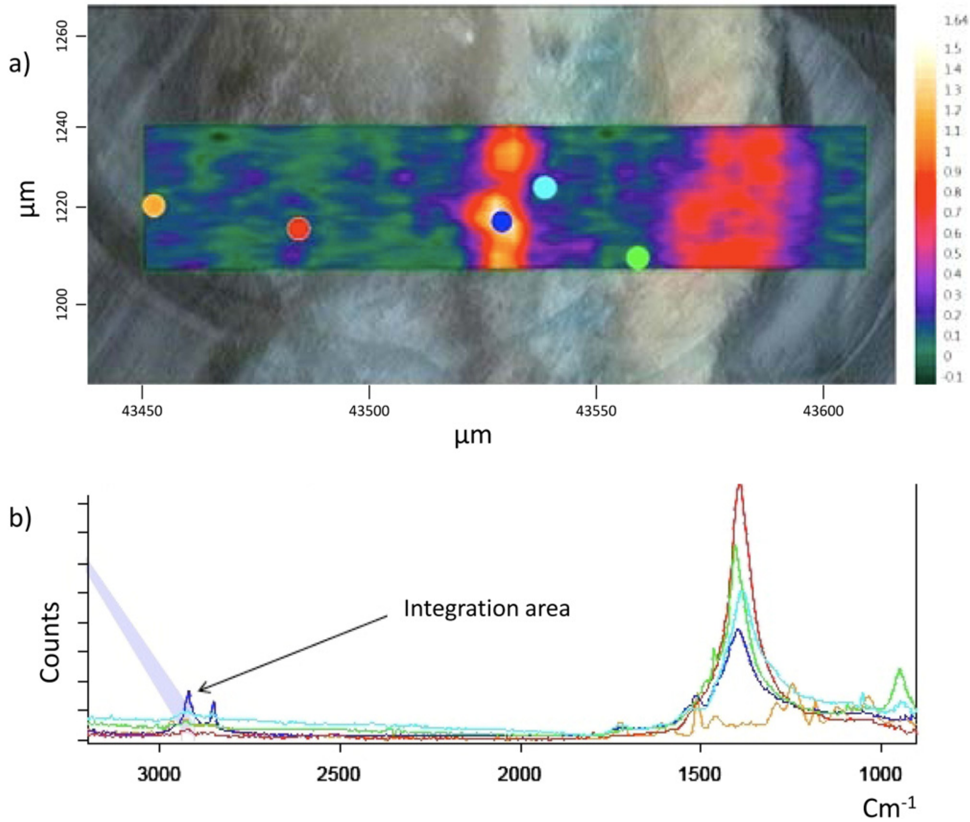

Fig. 7. a) μ-FTIR imaging mapping of sample 32-13-1 from the painting Assumption of the Virgin, assigned to Vicente Gil, showing a visible picture with false-color-plot of integration 2937–2902 cm^{-1} (gray area in spectra view) with a measurement of 5 × 1 ATR imaging map. The sample is placed in vertical lecture showing the pictorial layer on the left side (blue) and the ground layer on the right side (gray). The lower region of the ground layer shows bigger intensity of the oil band (red) while the painting layer (left side of the image) shows the biggest intensity of the oil (yellow), corresponding to higher absorption of this band. The right color scale is related to the microscope coordinates and not amplification. The amplification is reflected on the analyzed area 160 × 32 μm, resulting from the overlapping of 20,480 spectra; b) spectra from marked positions specifying the gray area (integration area) containing the CH's band absorption region at 2926 cm^{-1}.

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