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Josefa d' Óbidos workshop from panel to canvas. Multianalytical approach to materials and technical evolution of the most significant Portuguese painting workshop of the 17th century

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ABSTRACT

In this work we address the study of three groups painted by Josefa d' Óbidos (1630–1684) and by her father Baltazar Gomes Figueira (1604–1674). These painters were the most important pair working in the 17th century in Portugal with a Proto-Baroque style and the materials and techniques used by their workshop are almost unknown.

Analytical procedures employed to characterize the materials and painting techniques involve molecular spectroscopy with μ-Confocal Raman (μ-Raman) and Fourier Transform Infrared Spectroscopy (μ-FTIR) in combination with other complementary methods such as X-ray Fluorescence Spectroscopy (XRF), μ-X-ray diffraction (μ-XRD) and Scanning Electron Microscopy with Energy Dispersive spectroscopy (SEM-EDS).

Results

are compared with the instructions of the most significant coeval Iberian painting treatises, with influence on Óbidos workshop.

Conclusions of this study bring the first insight on the materials used, technical procedures and evolution from panel to canvas of Óbidos painting workshop, particularly highlighting the work of Josefa d' Óbidos, the greatest female Portuguese painter of all times.

1. Introduction

Josefa d'Ayala e Cabrera, so-called Josefa d'Óbidos (Sevi1la, Spain 1630-Óbidos, Portugal, 1684), and her father Baltazar Gomes Figueira (Óbidos, Portugal, 1604–1674) were the most important group of painters of the 17th century in Portugal. Working under a Proto-Baroque style, both painters reflect the Iberian cultural diversity. During the Iberian union, direct influences from the most important painters working in Seville. such as Francisco de Herrera *el Viejo*, Juan del Castillo, Zurbarán, Murillo, or the treatisist Francisco Pacheco [1,2] are found. From the 17th century forward, the use of Iberian artistic materials increases in Portugal. Pigments are brought from Castile, specifically through its most important commercial and artistic trade market, Seville [3].

The materiality and painting techniques used in Óbidos workshop is practically unknown. This work studies a group of paintings assigned to both painters to define the materials used and the particular techniques employed, from ground to priming and painting layers.The earliest works, made in panel support (P1 and P2), and a painting in canvas support (P3), under the theme of the Holy family, dated and signed by Josefa d' Óbidos: "Josepha em Óbidos, 1674", from the last decade of the painter's life, nowadays in Évora Museum, Portugal, (Fig. 1) are studied.

The altarpiece of São Brás chapel (Bombarral, Portugal) (P1), has 8 panel paintings dedicated to this saint martyrdom, painted c. 1635–1640 by Baltazar Gomes Figueira. The altarpiece is directly influenced by t Zurbarán Spanish style in the dark backgrounds, and by the altarpiece of the "Martírios de São Brás", commissioned around 1580–90 to the counter-reformist painter Diogo de Teixeira for the Church of Santa Maria de Óbidos (Portugal), where Baltazar was buried. The painting included in this study, "The Rest on the Flight to Egypt" is the most significant and detailed of the 8 paintings, since it covers all the chromatic palette used by the artist in the altarpiece and is placed in a highlighted space over the altarpiece niche [4] (Fig. 2).

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Fig. 1. a) Panel altarpiece of São Brás chapel (Bombarral, Portugal) (P1), painted c. 1635–1640 by Baltazar Gomes Figueira; b) Panel painting of Santa Justa and Santa Rufina (P2), painted by Josefa d' Óbidos c. 1660, Chapel of Senhor Jesus da Boa Hora, in the village of Columbeira(Bombarral, Portugal); c) Canvas painting,the Holy family, dated and signed by Josefa d' Óbidos: "Josepha em Óbidos, 1674", nowadays in Évora Museum, Portugal.

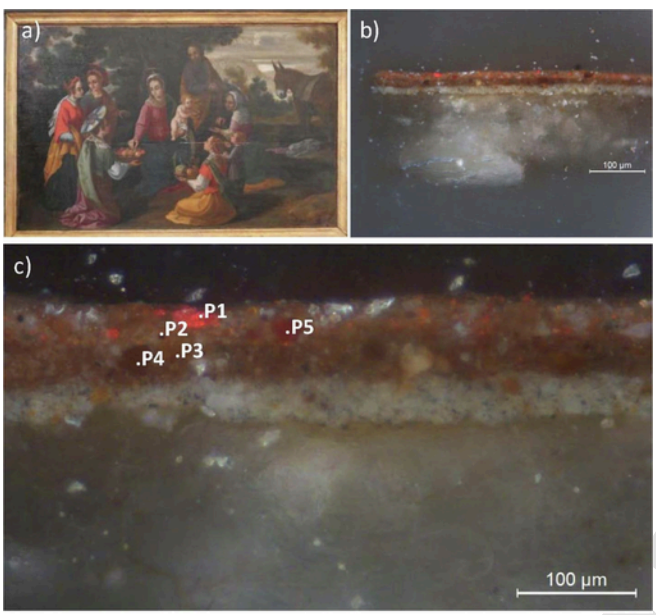

Fig. 2. ta) "The Rest on the Flight to Egypt" from altarpiece of São Brás chapel (Bombarral, Portugal) (P1), painted c. 1635–1640 by Baltazar Gomes Figueira and .P15 from carnation of the first figure at right; b) OM image of sample .P15 , with three painting layers and a thick ground layer; c) OM image of the same sample indicating the points analyzed by SEM-EDS technique.

The painting of Saint Justa and Saint Rufina (P2), patron saints of Seville, place of birth of Josefa d' Óbidos , was painted by this artist, c. 1660, to the Chapel of Senhor Jesus da Boa Hora (former Chapel of Saint Justa and Saint Rufina), in the village of Columbeira, Bombarral, Portugal.This painting style follows the Sevillian canons , with great influence of the work of Zurbarán and Murillo [5–9].

Analytical procedures employed to characterize the materials and painting techniques involve molecular spectroscopy with µ-Confocal Raman (µ-Raman) and Fourier Transform Infrared Spectroscopy (µ-FTIR) and µ-X-ray diffraction (µ-XRD) in combination with other complementary elementary composition methods such as X-ray Fluorescence Spectrometry (XRF) and Scanning Electron Microscopy with Energy Dispersive spectroscopy (SEM-EDS).

Results are compared with the instructions brought by coeval painting treatises: the 1615 "Arte da Pintura", written by the Portuguese Filipe Nunes [10], and the namesake treatise "Arte de la pintura", finished in 1641, by the Spanish painter Francisco Pacheco that influenced directly Óbidos workshop [2].

2. Materials and methods

2.1. Sample collection and preparation

Collection of samples was carried out after the exhaustive visual observation of the material conservationof the paintings, helped by microphotography, and after preliminary elementary identification carried out *in-situ* by portable Energy Dispersive X-ray Fluorescence Spectroscopy (EDXRF). Areas of bigger degradation (lacunae) were chosen to collect samples. For each painting (P1, P2 and P3) samples were taken, prepared and analyzed in a comparable group of colours, light and dark tones, to evaluate materials and techniques. Samples from the background, carnation and hair, palm leaves, perizonium and mantles were taken in order to cover the artists palette. Analyses were carried out on the samples using Micro-Fourier Transform Infrared spectroscopy. Afterwards, part of the samples were assembled on epoxy resin supports (Epofix©) and polished with micromesh of silicon carbide in order to perform analysis using Optical microscopy (OM), Confocal Micro-Raman spectroscopy (µ-Raman) and Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS).

2.2. Confocal Micro-Raman spectroscopy (µ-Raman)

The XploRA confocal Raman spectrometer from Horiba-Jobin Yvon equipped with an air-cooled CCD array of an AndoriDus detector was used. Spectra were acquired using a 785 nm Laser diode, a pinhole of 300 µm, an entrance slit of 100 µm, and a 1200 lines/mm grating. The 100 × objective was used in combination with a 1% filter rendering an incident power on sample of 0.20 ± 0.02 mW (lasercheck®, Edmund optics). Spectra deconvolution was performed using LabSpec (V5.78). Literature and Raman databases (Spectral ID™ from Horiba, Crystal Sleuth and RRUFF [11]) were used in order to identify the compounds of P1 and P2.

2.3. 5-Portable energy dispersive X-ray fluorescence spectroscopy (EDXRF)

Determination of elementary composition for each color was achieved with an XRF portable setup consisting of an Amptek Mini-X Rh X-ray generator (50 kV, 200 µA max.) and an Amptek XR-100CR silicon PIN detector with a 7 mm^2 detection area and 300 µm thickness, and a 25 µm Be window. The angle between the incident and the emitted beam is 90°. This geometry allows for a reduction of the background due to Compton scattering [12]. X-ray generator was operated at 30 kV and 15 µA during 120 s. Energy resolution was 140 eV at 5.9 keV. Spectra were acquired using DppPMCA software.

2.4. Optical microscopy (OM)

A Leitz Wetzlar dark and light field microscope for assessment to cross-sections was used. The microscope is coupled to a Leica DC500 digital camera for image acquisition, equipped with visible light.

2.5. Scanning Electron Microscopy with energy dispersive X-ray spectroscopy (SEM-EDS)

A Hitachi S—3700 N scanning electron microscope coupled to a Bruker XFlash 5010 SDD energy dispersive detector was used to carry out SEM imaging (Back Scattering Electron mode). SEM-EDS analysis was used to identify elementary composition in cross-sections of the paintings. Accelerating voltage used was 20 kV. Cross-sections were analyzed in variable pressure to preserve samples for subsequent analytical methods.

2.6. Micro-Fourier Transform Infrared spectroscopy

Fourier Transform Infrared spectroscopy (μ-FTIR) analysis was performed to confirm binders and pigments in ground and paint layers. A microscope Hyperion 3000 controlled by software OPUS 7.2 from Bruker and a Mercury Cadmium Telluride detector are coupled to a Bruker spectrometer Tensor 27 model at medium infrared region (MIR), in transmission mode, with a 15× objective and a diamond compression microcell EX'Press 1.6 mm, STJ-0169 was used. A working range of 4000–600 cm^{-1} and 64 scans were recorded. For each spectrum, a spectral resolution of 4 cm^{-1} was performed.

3. Results and discussion

3.1. Pigments in the altarpiece of São Brás (P1), c. 1635–1640, Baltazar Gomes Figueira

3.1.1. White

White light tone in the sleeve of the 1st figure in the right side shows by XRF technique the following elements: Pb and Fe. In sample BOM2-1 cerussite (1055 cm^{-1}) was identified by μ-Raman technique (Table 1).

3.1.2. Yellow

Yellow light tone in the robe of the 2nd left figure shows by XRF technique the elements Pb, Fe, Ca and Hg. In sample BOM2-29 were identified by μ-Raman technique the compounds hematite (295 and 419 cm^{-1}), cinnabar (250 and 343 cm^{-1}) and cerussite (1053 cm^{-1}) (Table 1).

Yellow light tone from the dress of the 1st right figure shows by XRF technique the following elements: Pb, Hg and Fe. In sample BOM2-3 were found the compounds cerussite (1055 cm^{-1}), cinnabar (254, 285 and 342 cm^{-1}) by μ-Raman technique (Table 1).

3.1.3. Carnation

SEM-EDS performed in sample BOM2-15, carnation of the 1st right figure identified the presence of Pb, ocurring in lead white, together with Hg and S,present in vermilion (Fig. 2c, P1), and a red lacquer with Al (alum) (Fig. 2c, P5), Ca existing in particles of calcite (Fig. 2c, P4), Mn and Fe-rich particles (Fig. 2c, P2 and P3), probably of yellow and red ochre, and umber . Several points were analyzed, and lead-tin yellow pigment was not detected. Cerussite, hydrocerussite, gypsum, calcite, kaolinite, oil and lead carboxylates compounds were identified by μ-FTIR. The use of white, vermilion and red lacquer are advised by the Portuguese treatisist Filipe Nunes for the making of the carnations [10].

3.1.4. Rose

Rose color from the Virgin's tunic displays by XRF technique the presence of the elements Pb and Hg. Micro-Raman technique identified in sample BOM2-24 the use of cinnabar (252 and 343 cm^{-1}).

3.1.5. Red

Red light tone from the tunic of the 1st right figure when analized by XRF technique exhibits the elements Hg, Fe, Ca, Cu and Pb. Micro-Raman technique identified in sample BOM2-9 the use of cinnabar (250, 281 and 341 cm^{-1}). It is also possible to observe the

Table 1
Comparison between pigments found by color in P1, P2 and P3.

Color	P1	P2	P3
White	cerussite, carbon black	cerussite, cinnabar, carbon black, oil, lead carboxylates	cerusite, metal carboxylates, oil
Yellow	cerussite, cinnabar, hematite	cerussite, cinnabar, goethite, yellow ochre carbon black	calcite, gypsum, oil, yellow ochre, proteins
Carnation	cerussite, hidrocerusite, vermilion, red lacquer, calcite, yellow ochre, red ochre, umber, gypsum, kaolinite, lead carboxylates	yellow ochre, cerusite, hydrocerusite, carbon black, cinnabar, gypsum,calcite, oil, lead carboxylates	lead white, oil, proteins
Rose	lead white, cinnabar	-	oil, proteins, lead white, metal carboxylates
Orange	-	-	calcite, silicates, oil
Red	cinnabar, red lacquer, azurite, cerusite, hidrocerusite, calcite, kaolinite, gypsum, oil, protein	cinnabar, red lacquer, kaolinite, hydrocerusite, calcite, oil, lead carboxylates	red lacquer, lead white,chalk, yellow ochre, oil
Blue	azurite, cobalt blue, cerussite, hidrocerusite, calcite, kaolinite, oil, protein, lead carboxylates	azurite, cobalt	silicates, linseed oil, proteins, lead white, metal carboxylates, silicates (kaolinite?)
Green	gypsum, goethite, hematite, azurite,calcite, lead-tin yellow type I,cerussite, caulinite, oil, protein	verdigris, carbon black, yellow ochre, azurite, hematite, lead-tin yellow type I cerusite, hydrocerusite, oil, copper carboxylates, lead carboxylates, calcium oxalates	calcite, yellow ochre, oil, calcite, kaolinite, carboxylates, oil, azurite
Purple	cinnabar, cerussite, hematite, minium, azurite, hydrocerussite, calcite, kaolinite, oil, lead carboxylates	cerusite, purple dye, hydrocerusite, bone black, quartz, oil, protein, lead carboxylates	-
Brown	cinnabar, goethite, hematite, cerussite, anhydrite, lead-tin yellow type I, calcite, litharge, massicot, dolomite	cinnabar, yellow ochre, cerusite, carbon black, azurite, massicot, lead -tin yellow type I	calcite, gypsum, yellow ochre and oil, kaolinite, proteins
Gray	-	-	lead white, oil, metal carboxylates, yellow ochre, kaolinite
Black	-	cinnabar, bone black, red ochre, yellow ochre, kaolinite, hydrocerusite, calcite oil, protein, lead carboxylates	lead white, oil, proteins

presence of bigger particles of red lacquer in darker tone mixed with cinnabar by OM UV (Fig. 3).

Red light tone from the tunic of the 2nd figure to the left displays by XRF technique the presence of the element Hg. Micro-Raman technique in sample BOM2-31 dispalyed the use of cinnabar (252 and 340 cm^{-1}). In the same sample azurite, kaolinite, cerussite, hydrocerussite, calcite, gypsum (traces), oil and protein compounds were identified by μ-FTIR.

3.1.6. Blue

XRF technique shows for the blue color used in the sky the elements Cu and Co. Sample BOM2-21 allowed to identify azurite (310, 400, 760, 844, 1089 and 1426 cm^{-1}) by μ-Raman technique. The Co identified by OM and XRF technique is probably due to smalt, used as a drying material for the oil painting, but also used in mural painting [10].

Sample BOM2 – 23, the Virgin's mantle, shows a red surface layer with azurite, cerussite, hydrocerussite, calcite, kaolinite, oil, protein and lead carboxylates compounds identified by μ-FTIR. In a 1st blue layer , the same technique allowed to find azurite, hydrocerussite (traces), kaolinite and protein.

3.1.7. Green

Green color dress of the 3rd right figure , when analyzed by XRF technique, displays the elements Fe, Cu, Pb and Ca are highlighted. Micro-Raman technique identified in sample BOM2-16 the use of gypsum (502 and 1010 cm^{-1}), goethite (316 and 388 cm^{-1}), hematite (218, 301, 398, 497 cm^{-1}), azurite (246, 394, 845 and 1056 cm^{-1}) and calcite (277, 712 and 1087 cm^{-1}).

Green light tone of the tunic of the 1st figure from left displays by XRF technique the elements Pb, Fe, Cu and Sn. Micro-Raman technique identified in sample BOM2-25 the use of azurite (248, 400, 853 and 1052 cm^{-1}), lead-tin yellow type I (197, 286, 456 and 487 cm^{-1}) and cerussite (1052 cm^{-1}).

Green “changeant” tone of the tunic of the 3rd figure to the left shows by XRF technique the elements Cu and Fe. Micro-Raman technique identified in sample BOM2-33 the use of goethite (296 and 408 cm^{-1}), azurite (249, 401, 521, 675, 767 and 869 cm^{-1}) and hematite (223, 294, 408 and 600 cm^{-1}).

In green light tone of the mantle of the 1st figure to the right , was identified by XRF technique the elements Ca, Fe, Cu and Pb. Micro-Raman techniquedisplays in sample BOM2-7 the use of hematite (219, 295, 404 and 606 cm^{-1}) and azurite (232, 398, 835 and 1098 cm^{-1}). In the shadow tone of this color (sample Bom2-8) a green layer having azurite, kaolinite, calcite, gypsum, oil, and protein compounds,identified by μ-FTIR technique.

3.1.8. Purple

In Purple shadow color of the skirt of the 1st figure to the left , XRF technique has shown the elements Pb, Fe and Ca. Micro-Raman technique identified in sample BOM2-28 the use of cinnabar (249 and 345 cm^{-1}), cerussite (1050 cm^{-1}), hematite (224, 293 and 407 cm^{-1}) and minium (223, 312, 385 and 545 cm^{-1}).

In sample BOM2 - 22, St. Joseph purple tunicwere identified azurite, hydrocerussite, calcite, kaolinite, oil and lead carboxylates, revealed by μ-FTIR.

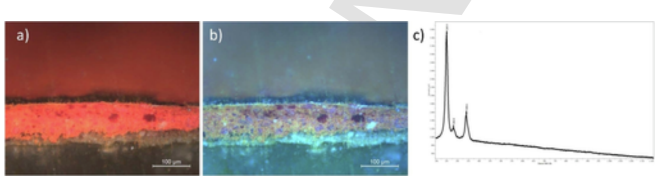

Fig. 3. a) OM image of sample from the tunic of the 1st figure on the right (P1); b) OM image of sample under UV light showing the presence of bigger particles of red lacquer in darker tone; c) Raman spectrum of sample BOM2-9 shows the use of cinnabar (250, 281 and 341 cm^{-1}).

3.1.9. Brown

Light brown tone in the robe of 3rd figure to the left shows the following elements: Hg, Pb, Ca, Fe and Cu, identified by XRF technique. Sample BOM2-34 allowed to identify cinnabar (252 and 344 cm^{-1}), goethite (297 and 398 cm^{-1}), cerussite (1049 cm^{-1}) and anhydrite (415, 618, 871, 1010 and 1134 cm^{-1}) by μ-Raman technique.

Light brown tone in the ground displays by XRF technique the following elements: Sn, Pb and Fe. Sample BOM2-5 allowed to identify hematite (220, 298 and 405 cm^{-1}), lead tin yellow type I (194, 272 and 456 cm^{-1}) and goethite (301, 405 and 610 cm^{-1}) by μ-Raman technique.

Brown color in the hair of the 3rd figure to the left displays the elements Hg, Pb, Fe and Sn when analysed by XRF technique. Micro-Raman technique performed in sample BOM2-11 allowed to identify cinnabar (253, 284, 343 cm^{-1}), hematite (293, 405, 597 cm^{-1}), goethite (214, 402, 567 cm^{-1}) and calcite (1087 cm^{-1}).

When analysed by XRF technique, the shadow brown color of the donkey shows the elements: Fe, Sn and Pb. Sample BOM2-19 allowed to identify hematite (222, 406 and 606 cm^{-1}), litharge (160, 382 and 396 cm^{-1}), massicot (157, 300 and 399 cm^{-1}) and dolomite (282 and 1084 cm^{-1}) by μ-Raman technique.

3.2. -pigments in panel painting (P2), c. 1660, Josefa d'Óbidos

3.2.1. White

White light tone in the book of Saint Rufina shows by XRF technique the element Pb. Sample COL-13 allowed to identify cinnabar (241 and 340 cm^{-1}), cerussite (1056 cm^{-1}) and carbon black (1295 and 1563 cm^{-1}) by μ-Raman technique.

XRF technique displayed in white shadow tone of Saint Justa book the elements Pb and Fe. Sample COL-2 allowed to identify cerussite (1050 cm^{-1}), carbon black (1388 and 1578 cm^{-1}) and cinnabar (249 and 338 cm^{-1}) by μ-Raman technique (Table 1). In the white and varnish superficial layers hydrocerussite, oil and lead carboxylates compounds were identified by μ-FTIR.

3.2.2. Yellow

Yellow color of of Saint Rufina veil, when analized by XRF technique, displayed the elements Pb, Sn, Fe and Hg. In sample COL-23 were identified cerussite (1051 cm^{-1}), cinnabar (252 and 343 cm^{-1}), goethite (251, 29, 395, 482 and 559 cm^{-1}) and carbon black (1323 and 1576 cm^{-1}) by μ-Raman technique.

Yellow light tone in Saint Justa mantle shows by XRF technique the elements Pb,Sn and Fe. Micro-Raman technique performed in sample COL-4 allowed to identify carbon black (1345 and 1591 cm^{-1}), yellow ochre (319, 400 and 529 cm^{-1}) (Table 1).

3.2.3. Carnation

Carnation light tone in the right hand of Saint Rufina shows by XRF technique the elements Fe, Pb and Hg.In sample COL-21 were recognized yellow ochre (302 and 410 cm^{-1}) and cerussite (1050 cm^{-1}) by μ-Raman technique. Carnation shadow tone shows by XRF technique the same elements: Fe, Pb, Cu and Hg.In sample COL-22 carbon black (1321 and 1602 cm^{-1}), cinnabar (251 and 341 cm^{-1}), yellow ochre (302, 391 and 583 cm^{-1}) and cerussite (1052 cm^{-1}) were detected by μ-Raman technique. In the white layer of this sample kaolinite, hydrocerussite, calcite (traces), oil and lead carboxylates compounds were identified by μ-FTIR.

Carnation light tone in the right hand of Saint Justa when analyzed by XRF technique displays theelements Hg, Fe and Pb. In sample COL-8 were identified yellow ochre (301, 400 and 552 cm^{-1}), gypsum (435, 1002 and 1158 cm^{-1}) and rutile (226, 441, 605 cm^{-1}) by μ-Raman technique (Table 1).

3.2.4. Red

Red color from the ribbon in the hair of Saint Justa displays by XRF technique the presence of the elements Hg, Fe, Cu and Pb. Micro-Raman technique identified in sample COL-10 the use of cinnabar (252 and 344 cm^{-1}).

Red color from Saint Rufina belt strap distinguishes by XRF technique the presence of the elements Hg and Pb. Micro-Raman technique found in sample COL-18 the use of cinnabar (250 and 340 cm^{-1}) (Table 1).In the same sample a 2nd red and varnish layer having kaolinite and hydrocerussite, compounds were identified by μ-FTIR. In the same layer the presence of calcite (traces), oil and lead carboxylates compounds were confirmed by μ-FTIR. In the 1st gray layer kaolinite, hydrocerussite, calcite (traces), oil and lead carboxylates compounds were also identified by the same technique.

3.2.5. Blue

Blue color in Saint Justa head tie ,when analyzed by XRF technique shows the elements Cu, Co and Fe. In sample COL-11 were recognized yellow ochre (296, 407, 674 cm^{-1}), azurite (201, 400, 537, 645, 849 cm^{-1}), ochre red (227, 294, 487 cm^{-1}) by μ-Raman technique.

Shadow blue color in the sky shows by XRF technique the following elements: Pb, Fe, Cu and Co. Sample COL-26 allowed to identify cerusite (1048 cm^{-1}) using μ-Raman technique. Light brown tone composing the floor, when analized by XRF technique reveals the elements Pb, Fe, and Cu. Sample COL-27 allowed to identify goethite (297, 337, 398 and 548 cm^{-1})and carbon black (1315. 1650 cm^{-1}) by μ-Raman technique (Table 1).

3.2.6. Green

Light green tone from the trees displays by XRF technique theelements Pb, Fe, and Cu. Micro-Raman technique identified in sample COL-29 the use of azurite (267, 400, 752, 831 and 1081 cm^{-1}).

Green shadow tone from the trees, when analized by XRF technique,reveals the elements Cu and Fe. Micro-Raman technique determined in sample COL-30 the use of carbon black (1306 and 1604 cm^{-1}), yellow ochre (301, 401, 464 cm^{-1}), azurite (247, 327, 402, 715, 834 and 1099 cm^{-1}), hematite (221, 292, 405 and 603 cm^{-1}) and cerussite (1049 cm^{-1}).

Light green tone from the palm leaf of Saint Justa displays by XRF technique the elements Pb, Fe, Ca, Sn and Cu. Micro-Raman technique identified in sample COL-31 the use of hematite (223, 293 and 404 cm^{-1}) and lead-tin yellow type I (127, 195, 267 and 453 cm^{-1}). Green shadow displays by XRF technique the presence of the elements Pb, Fe, Ca ,Sn and Cu. Micro-Raman technique revealed in sample COL-32 the use of verdigris (360, 601 and 973 cm^{-1}) [13].

In the green color of Saint Justa palm leaf , the analysis of sample COL-32, performed by SEM-EDS(Fig. 4a,b and c), has identified in the green upper layer Cu (Fig. 4a, P4, P6), probably azurite, particles presenting Sn and Pb, presumably lead-tin yellow (Fig. 4a,P3), Hg and S (Fig. 4a,P1), most likely vermilion. Particles of Iron were also identified (Fig. 4a, P5), possibly yellow ochre. In the varnish layer, μ-FTIR technique allowed to identify calcite, oil, copper carboxylates and calcium oxalates compounds. In a 2nd green layer, calcite, gypsum, oil and copper carboxylates and calcium oxalate compounds were also identified by this technique, such as in the 1st light brown layer of kaolinite, hydrocerussite, calcite (traces), oil and lead carboxylates. The composition of this color is in accordance to the writings of Filipe Nunes to make a green color mixing “cinzas” (azurite) and massicot (lead-tin yellow) [10,14]. The 2nd yellow layer of this sample would bring light to the upper green layer- as revealed by the treatisist Pacheco, citing Lomazzo, a color cannot be seen without light and the painter should be an expert in the light effects [2]. Pb, most probably lead white (Fig. 4a,P7) was also found, Al in a red matrix (Fig. 4a,P6), possibly red lacquer, and an organic non-identified yellow compound, possibly saffron, as advised by Nunes for the making of the green “Verdete” [10] (Table 1).

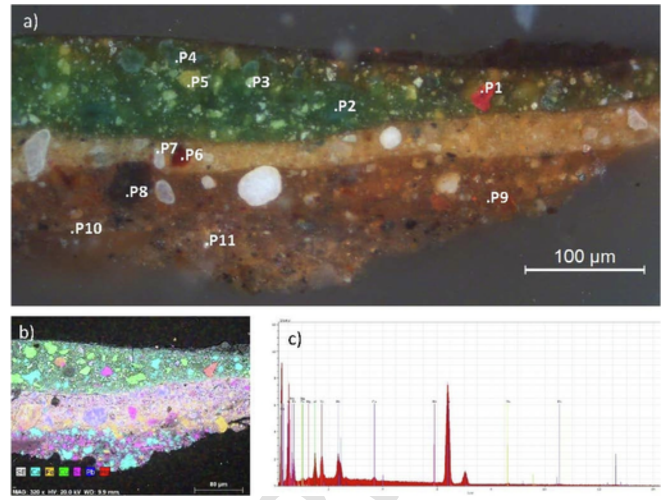

Fig. 4. a) OM image of the green color of Santa Justa Palm tree, sample COL-32, indicating the points analyzed by SEM-EDS technique (P1-P11); b) SEM-EDS mapping of Ca, Fe, Cu, Si, Pb and Hg elementary distribution in cross-section from the same sample and .P9 pointing EDS analysis; c) EDS spectrum having the elements Fe, Al and Si, probably yellow ochre (.P9).

3.2.7. Purple

Purple light tone from Saint Rufina tunic exhibits by XRF technique the presence of the element Pb. Micro-Raman technique identified in sample COL-19 the use of cerussite (1048 cm^{-1}). Purple shadow tone from the same tunic displays by XRF technique theelements Pb and Co. Micro-Raman technique identified in sample COL-20 the use of carbon black (1343 and 1600 cm^{-1}) and quartz (223, 294, 413, 464, 638 cm^{-1}). In sample COL-6, purple light tone of the Virgin's tunic, the pink and varnish superficial layer displays hydrocerussite, lead carboxylates and oil compounds were identified by μ-FTIR. This technique also allowed to find in the 2nd pink and brownish varnish layer, hydrocerussite, calcium phosphate, oil, protein and lead carboxylates; In the 1st white layer, hydrocerussite, oil and lead carboxylates were also identified by the same technique.

Purple shadow tone from Saint Rufina cloak displays, by XRF technique, the elements Fe, Pb and Co. Micro-Raman technique identified in sample COL-17 the use of carbon black (1323 and 1556 cm^{-1}). Purple light tone from Saint Justa tunic ehxibits by XRF technique the elements Pb and Fe. Micro-Raman technique performed in sample COL-6 revealed the use of carbon black (1314 and 1593 cm^{-1}) .XRF technique identified in purple shadow from Saint Justa tunic the elements Pb, Fe and Co (Table 1).

3.2.8. Brown

Brown color of Saint Justa's hair, when analyzed by XRF technique, reveals the elements Fe and Co.In sample COL-12 was identified cinnabar (252 and 340 cm^{-1}) by µ-Raman technique.

XRF technique displays the following elements in brown color of Saint Rufina's hair: Pb, Fe, Cu and Hg. Sample COL-24 allowed to identify cinnabar (253 and 340 cm^{-1}), yellow ochre (302, 403, 477 and 568 cm^{-1}), cerussite (1054 cm^{-1}) and carbon black (1324 and 1587 cm^{-1}) by µ-Raman technique.

Brown shadow tone in the ground , when analyzed by XRF technique , displayed the following elements: Pb, Fe and Cu. In sample COL-28 were found azurite (248, 399, 764, 859 and 1096 cm^{-1}), cerussite (1054 cm^{-1}), massicot (276 cm^{-1}) and lead-tin yellow type I (129, 196, 291 and 454 cm^{-1}) by µ-Raman technique (Table 1).

3.2.9. Black

Black color of the book of Saint Rufina shows, by XRF technique, the presence of the elements Fe and Pb. Micro-Raman technique performed in sample COL-15 revealed the use of carbon black (1327 and 1593 cm^{-1}). In the surface varnish layer, kaolinite, bone black, hydrocerussite, calcite (traces), oil, and protein compounds were identified by µ-FTIR. (Table 1).SEM-EDS technique has proved that in the black color of Saint Rufina book (sample COL-15) P was absent in the black particles, being probably a black with vegetable origin.This material is advised by the treatisist Pacheco who states that carbon black should be used since is softer in contrast to make the shadows and the black colors [2]. In this layer, Fe-rich particles were also found, being probably red and yellow ochre and other particles with Pb, most probably lead white, and Ca, as calcite particles (Table 1).

XRF technique performed in Saint Justa's book the elements Cu, Hg and Fe. Results ofµ-Raman technique performed in sample COL-3 revealed the use of cinnabar (249 and 341 cm^{-1}) and carbon black (1310 and 1578 cm^{-1}) (Table 1). Micro-FTIR technique identified in the surface and varnish layer of the same sample, kaolinite and hydrocerussite, bone black, wax, oil, protein and lead carboxylate compounds .

3.3. Pigments in canvas painting (P3), Josefa d'Óbidos, 1674

3.3.1. White

White sample from the towel (E6) displays three layers. A 3^{rd} organic layer, a 2^{nd} white layer with white, black and red particles and a 1^{st} priming layer having white, black, yellow and brown particles, visible by OM. XRF technique, in the area of sample E6, identified the elements Pb, Fe, S, Hg, Ca, Si, Cu, Mn and K. Micro-FTIR analysis has shown the following materials present in sample E6 (layer 2, varnish): lead white (3536, 1707, 1521, 1509, 1406, 1099, 1045, 839, 771, 720, 682 cm^{-1}), oil (linseed) (2921, 2851, 1707, 1521, 1509, 1099, 1045 and 682 cm^{-1}) and metal carboxylates (1521, 1541 v (COO-), 1406, cm^{-1}), a metal soap, product of lead white pigment degradation in mature linseed oil [15–19].

It was also detected in the varnish layer, the presence of a previous restoration with Rembrandt Picture Varnish Glossy (oil colors) (2925, 2854, 1706, 1455, 1448, 1347, 1256, 1120, 1042, 958 cm^{-1}) (Table 1).

3.3.2. Yellow

Micro-FTIR analysis performed to the yellow halo of Jesus, has shown the following materials in sample E1 (layer 1): calcite (1797, 1436, 876 and 669 cm^{-1}), gypsum (3414, 1710, 1693, 1188, 713 and 669 cm^{-1}) and oil (linseed).

Sample E10, the ochre of St. Joseph's mantle, displays by OM a 3^{rd} layer, organic, a 2^{nd} yellow layer with white, black and red particles and a 1^{st} priming layer with white, yellow and brown particles, as shown by OM. XRF technique, for the same area , identified the elements Pb, Fe, Ca, Hg, S, K, Cu, Mn and Si. Micro-FTIR analysis has shown the following materials present in the same sample : (layer 2, layer 3)calcite, yellow ochre (3555, 3550, 1705, 1050, 1034, 914, 875, 794 cm^{-1}), oil (linseed) and proteins (1635 amide I and 1521 d (CNH) cm^{-1}) (Table 1).

3.3.3. Carnation

In sample E2, the carnation of the neck of Jesus, is visible a 3^{rd} layer, in an organic matrix, a 2^{nd} white layer with white, transparent and black particles, and a 1^{st} priming layer with white, black, yellow, and brown particles, identified by OM,. Micro-FTIR analysis has shown the following materials in sample E2 (layer 2, varnish): lead white, oil (linseed) and proteins (3292, 2922, 2852, 1648, 1458, 1411, 1322, 1115, 1039, 782 and 670 cm^{-1}) (Table 1).

3.3.4. Rose

Sample E3, rose of Jesus tunic, right shoulder area, displays a 2^{nd} organic matrix (red glaze) and a 1^{st} red layer with white red and black particles by OM. Micro-FTIR analysis has shown the following materials present in sampleE3 (varnish), the presence of a previous restoration Rembrandt Picture Varnish Mat (3383, 2921, 2851, 1710, 1521, 1447, 1406, 1318, 1274, 1254, 1233, 1209, 1189, 1117, 1097, 1067 and 1044 cm^{-1}). In layers 2 and 1 was identified by this technique, besides the presence of a previous restoration Rembrandt Picture Varnish Mat, the oil (linseed), proteins, lead white and metal carboxylates (Table 1).

3.3.5. Orange

In sample E8, the orange color of the carrots, is observable by OM a 4^{th} layer with Varnish, a 3^{rd} red layer with white, red and black particles, a 2^{nd} white layer with white and black particles and a 1^{st} priming layer with white, black, yellow and brown particles. XRF technique, in the area of sample E8, identified the elements Pb, Hg, Fe, Ca, S, K, Cu, Mn, Si,and Ti, being this last the result of a restoration intervention. Micro-FTIR analysis has shown the following materials present in sample E8 (layer 3, varnish): calcite, silicates and oil (linseed) (Table 1).

3.3.6. Red

In the red color of the Virgin's tunic (sample E18), is visible by OM a 3^{rd} layer with an organic matrix (dye?), a red glaze, a 2^{nd} red layer with red and white particles and a 1^{st} yellow layer with yellow particles. XRF technique, in the area of sample E18, identified the elements Fe, Pb, Hg, Ca, Cu, K, S, Mn and Si. Micro-FTIR analysis has shown for sample E18 (varnish), the presence of a previous restoration Rembrandt Picture Varnish Glossy (oil colors) as a superficial intervention layer. In layer 2, the presence of lead white, oil (linseed) and metal carboxylates (1522 cm^{-1}), and in the 1^{st} layer chalk, yellow ochre and oil (linseed) (Table 1).

3.3.7. Blue

Sample E5, the light blue tone from the mantle of Jesus, displays by OM a 4^{th} light blue layer, where blue and white particles are visible; a 3^{rd} gray layer with white, black, yellow and red particles; a 2^{nd} organic layer and a 1^{st} priming layer with white, black, yellow and brown particles. XRF technique, in the area of sample E5, identified the elements Fe, Pb, Ca, S, Mn, K, Cu, Si, Ti, Zn and Cr, being these last the result of a restoration intervention. Micro-FTIR analysis has shown the following materials: lead white, metal carboxylates, silicates (kaolinite?) and oil (linseed) (layer 4, layer 3) (Table 1).

The dark blue of Jesus mantle's fold (sample E4), displays by OM a 4th blue layer having white and blue particles, being also visible a 3rd white layer with white, red and black particles in an organic matrix, a 2nd black layer with black particles and a 1st priming layer having white, black, yellow and brown particles. XRF technique, in sample E4, identified the elements Fe, Pb, Ca, S, K, Mn, Cr, Hg, Cu, Si, Zn and Cr, being these last the result of a restoration intervention. Micro-FTIR results have shown the same restoration Rembrandt Picture Varnish Glossy and other materials as silicates, linseed oil, proteins and lead white (Table 1).

3.3.8. Green

In sample E12, the dark green shade effect of the Virgin's veil, is visible by OM a 3rd yellow layer with yellow, white and brown particles, a 2nd dark yellow layer with yellow, white, black, red (pigment and dye) and brown, and a 1st blue layer with blue, white and black particles. XRF technique, in the area of sample E12, identified the elements Pb, Fe, S, Ca, K, Cu, Mn, Si, Zn and Ti, being these last the result of a restoration intervention. Micro-FTIR analysis has shown the following materials present in sample E12 (global): calcite, yellow ochre and oil (linseed) (Table 1).

The light green tone of the same area (sample E13), shows by OM a 2nd gray layer having white black, yellow and red particles and a 1st priming layer with white, black, yellow and brown particles. Micro-FTIR analysis has identified calcite, kaolinite, carboxylates (malachite?) and oil (linseed) as main materials(Table 1).

Green-brownish color of the carrots leaves (sample E17) displays by OM a dark brown/bluish layer containing white, yellow, red (pigment and dye), black, green and blue particles. XRF technique, in the area of sample E17, identified the elements Cu, Pb, Ca, Fe, S, Hg, K and Si. Micro-FTIR analysis has found oil (linseed), calcite and azurite (3429, 2921, 2851, 2511, 1417, 1047, 952, 876, 836 and 713 cm^{-1}) (Table 1).

3.3.9. Brown

The bread's brown color , sample E11, displays by OM a 5th organic layer, a 4rth white layer having white, red and yellow particles, a 3rd red layer (red dye) is visible, a 2nd layer with black and white particles and a 1st layer in Red (red dye and red pigment) having white, red and black particles. XRF technique, in the area of sample E11, identified the elements Pb, S, Fe, Cu, Ca, K, Si and Mn. Micro-FTIR analysis has confirmed the occurrence of a previous restoration,Rembrandt Picture Varnish Glossy (oil colors), in the superficial layer; in layer 3, the presence of lead white, yellow ochre and Oil (linseed); in layer 2 and layer 1, the use of calcite, yellow ochre, oil (linseed) and gypsum (3405, 1601, 1051, 712, 670 cm^{-1}) (Table 1).

In sample E14, the background (dark brown), is possible to identify by OM a 2nd layer of organic matrix and a 1st dark brown layer with brown, black and white particles. Micro-FTIR analysis has shown for sample E14 (global)the presence of kaolinite, oil (linseed) and proteins (Table 1).

Brown color of the table, sample E15, ehxibits by OM a 4th dark red layer with red (pigments and dye), black and white particles, a 3rd layer having brown, black, red, orange and white particles, a 2nd organic layer (sizing) and a 1st priming layer with white, black, yellow and brown particles. Micro-FTIR analysis performed in sample E15 (results for layers 3 and 4 were similar to layers 1 and 2): oil (linseed), proteins and kaolinite (3700, 1034, 1009, 914, 795 and 699 cm^{-1}). In layer 1 was identified by μ-FTIR the presence of yellow ochre, oil (linseed) and vestiges of proteins (Table 1).

3.3.10. Gray

In sample E7, the gray of the dish, is visible by OM a 2nd white layer having white and black particles and a 1st priming layer with white, black, yellow and brown particles. Micro-FTIR identified in E7 (layer 2), the presence of lead white, oil (linseed) and metal carboxylates; in layer 1 yellow ochre, lead white and oil (linseed) were identified by the same technique (Table 1).

In sample E9, the gray towel, is observable by OM a 4th layer of organic matrix, a 3rd gray layer having white, black and red particles, a 2nd organic layer and a 1st layer with white, black, yellow and brown particles. For the area of sample E9, XRF technique identified the elements Pb, Fe, S, Hg, Ca, Cu, Mn, K and Si. Micro-FTIR analysis for sample E9 (varnish), confirmed the existence of restoration Rembrandt Picture Varnish Glossy together with kaolinite (Ochre), lead white, metal carboxylates, oil (linseed) and yellow ochre; and in layer 1, the presence of yellow ochre and oil (linseed) (Table 1).

3.3.11. Black

The black color of the salt container, sample E16, displays by OM a single black layer having black, white red and brown pigments. XRF technique forsample E16, identified the elements Pb, Fe, S, Hg, Ca, Cu, K, Mn, Si, Zn and Ti, being these last the result of a restoration intervention. The materials identified by μ-FTIR in the same sample were lead white, oil (linseed) and proteins (Table 1).

3.4. Pigments discussion

The three paintings show a similar technique of mixed binding media, using linseed oil and protein. The number of layers diverges from one to three for each color . The palette of Óbidos workshop comprises eleven different colors for the three paintings. To achieve these colors, a mixture of 2 (in white) to 12 different pigments (in carnation) by color iscombined. Light tones are obtained by adding lead white, and dark tones of the same color are accomplished by adding umber and carbon black, as stated by Pacheco [2], being these the most repeated pigments by color, in order to carry out the volume of the figures and the perfect merge between colours [2]. The density for each color is achieved by adding calcite, and/or gypsum as fillers.These materials are also used to increas of transparency, such as in the case of the carnations. By adding these lower refractive index fillers to other pigments a bigger transparency and realistic technical accomplishment of the flesh color is accomplished, letting know the intelligence of the artist, as stated by Pacheco, citing Vasari [2]. The mixture of pigments for the making of each color is also similar in the three paintings: for the white color cerussite, cinnabar and carbon black; for the yellow color cerussite, cinnabar, hematite, goethite, yellow ochre, carbon black, calcite and gypsum. These pigments are advised by Pacheco for the yellow color [2]; the carnation is achieved by mixing lead white, vermilion, red lacquer, calcite, yellow ochre, red ochre, umber, cerussite, carbon black, cinnabar and gypsum, a stated by Nunes [10]; for the orange color calcite and silicates (ochres) were used,; in the rose color lead white and cinnabar were found. Pacheco advises to the perfect m ix of this color, white and carmine should belayed over a first layer of vermilion in order to perpetuate the color [2]; for the red color, cinnabar, red lacquer (probably carmine, as stated by Pacheco [2]), lead white, chalk and yellow ochre; for the blue color azurite, smalt, lead white, and silicates (kaolinite?); The use of smalt mixed with azurite for the sky (P1 and P2) is a technique also stated by Portuguese and Spanish treatisists, as siccative, with a bluish transparency effect [2,10].Pacheco states that smalt thinly grind and mixed with blue (azurite) are the key to conserve the blue color unchangeable, since this color has the tendency to turn darker through time [2];for the green color, azurite and lead-tin yellow type I, as advised by Nunes [10], having also gypsum, goethite, hematite, calcite, cerussite, verdigris, carbon black, yellow ochre and kaolinite; for the purple color smalt (P2), purple dye, azurite, cinnabar, cerussite, hematite, minium, hydrocerussite, calcite, kaolinite and carbon black; for the brown color, cinnabar, goethite, hematite, cerussite, anhydrite, lead-tin yellow type I, calcite, litharge, massicot, dolomite, yellow ochre, carbon black, azurite, gypsum and kaolinite; for the gray color, lead white, yellow ochre and kaolinite; for the black color, cinnabar, carbon black, red ochre, yellow ochre and lead white.

The presence of oxalates and metal carboxylates in the painting layers point out to, a chemical degradation in need to be stabilized.

3.5. Sizing, ground and priming layers and underdrawing results and discussion

3.5.1. Altarpiece of São Brás (P1), c. 1635–1640, Baltazar Gomes Figueira

In P1 a thick (c. 180 µm) (Fig. 2b) white calcium sulfate ground layer is observed by OM and confirmed by µ-FTIR, in the samples analysed for the color layers, as being gypsum and anhydrite with protein binder, probably animal glue. Over this layer a 2nd thinner (c. 5–10 µm) yellow layer and a 3rd whitish-yellow layer (c. 10–15 µm), both corresponding to priming layers. This preparation of panel paintingsis reported by the treatisist Filipe Nunes.After a first sizing layer with animal glue, two gypsum and glue ground layers were laid out, scraped and smoothed, after drying. Over the ground layer were spread one or two layers of priming, also smoothed when dryied [10].After these procedures the panel was prepared to be drawn. Uncessefull attempts of infrared photography and reflectography area exams were made. Most probably a non-carbonaceous-based ink was used, since previous studies indicate this ink as almost imperceptible [20–25]. An iron-gall ink could have been used, since it can be found in some Portuguese-Flemish paintings from the beginning of the 16th century [20]. The second priming layer was made in a lighter whitish tone and thicker than the first priming yellowish-brown layer in order to receive the drawing and painting layers (Fig. 2).

3.5.2. Panel painting (P2), c. 1660, Josefa d'Óbidos

SEM-EDS has shown that in P2 brownish priming layer has Fe—Mg-rich particles, probably aluminosilicates (Fig. 4a, P10) and calcium particles (Fig. 4a, P11) (sample COL-32).

Micro-Raman technique performed in sample COL-30 highlighted the use of a gypsum ground layer (434, 625 and 1004 cm^{-1}).In the 2nd reddish priming layer, SEM-EDS technique provided the elementary analysis of particles having Fe and Fe—Mg (Fig. 4a, b and c, P9), probably yellow ochre, umber (Fig. 4a, P8) and kaolinite. Micro-FTIR confirmed the presence of kaolinite, calcite, gypsum, hydrocerussite, oil, quartz and lead carboxylates compounds in the ground layer, being this last a product of degradation. Underdrawing was not visible by infrared photography technique probably due to the brown color of priming, ground layers and drawing ink. Ground layer is thinner (63–68,9 µm) than in P1. This aspect leads to a very thin ground layer under an also thin priming of 32–36 µm, totalizing both layers 76–97 µm (sample COL-21, Fig. 5).

3.5.3. Canvas painting (P3), Josefa d'Óbidos, 1674

The canvas painting (P3), is composed by a first sizing layer (usually animal glue), visible by OM, explained by Nunes as the first

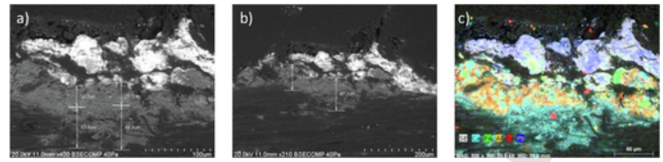

Fig. 5. a) SEM image (BSE) of sample COL-21showing priming layer thickness of 32–36 µm and ground layer thickness of 63–68,9 µm to the wooden support of Saint's carnation; b) SEM image (BSE) of the same sample showing the total thickness of priming and ground layer from 77 to 97 µm over the wood; c) SEM/EDS mapping of Ca, Fe, Al, Si and Pb elementary distribution of cross-section from the same sample , differing from the ground (mostly Ca) and priming layer (mostly Al and Si).

layer to spread over the canvas [10]. The brown color priming includes white, black, yellow and brown particles; µ-FTIR technique has found the pigments lead white, chalk, yellow ochre, gypsum and the binders oil (linseed) and proteins (Fig. 6c). SEM-EDS has confirmed through samples taken from the orange color of the carrots (E8) and Saint Joseph's yellow mantle the presence of a priming layer containing Fe-rich particles, probably aluminosilicates (highly Ti enriched and no Mn detected) (Fig. 6a, P1, 2 and 3), particles with similar proportion of Ca—Mg, probably dolomite (Fig. 6a, P4) and Ca as calcite particles (Fig. 6a, P 5).This layer is thinner (with maximum thickness of 225 µm) than the ground layer used in panel painting P1.Nunes reveals that canvas priming should be spread thinly to avoid its flaking, "contrary to certain Roman painters that use a soft thick priming layer , flaking at minimum mistreatment" [10].

4. Conclusions

Pigmentsby color and the use of and mixed media technique (linseed oil and protein)are similar for the three paintings.Overlapping 1 to 3 layers for each color is also a common technique in these paintings.

Thus, the colouring technique and ideology show an evolution from Baltazar to Josefa: the father paints the S.Brás altarpiece from light to shadow and prepares his work according to the Portuguese counter-reformist tradition, with single white calcium sulfate ground layer and proteins (animal glue) and lighter primings. Twenty years later, his daughter, Josefa d'Óbidos, paints from the shadow to the light, seeking not only the ideology but also technical innovation and material influence of Seville, her land of birth: an intermediate phase with P2, using brownish ground and priming layers.A ground layer in a gypsum matrix, material used by her father, having in adittion other raw materials such as ochre, calcite, quartz and kaolinite; a dark priming layer having these raw materials and hydrocerussite; a 2nd phase with a different technique is identified in Josefa d' Óbidos tec-

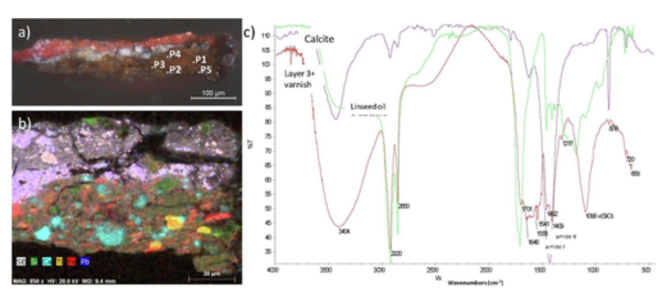

Fig. 6. a) OM image of the orange carrots (E8) indicating the points analyzed by SEM-EDS technique; b) SEM/EDS mapping of Si, Ca, Ti, Fe, and Pb elementary distribution of cross-section from the same sample; c) Micro- F TIR spectrum showing calcite, varnish and linseed oil bands.

nique - sizing and dark priming having ochres, calcite and dolomite over canvas support (P3)), lacking a calcium sulfate ground layer. .

Technical evolution from panel to canvas is also visible by layer thickness measurement. Ground layers decrease from panel painting P1 to P2, disappearing in canvas painting (P3). Priming layers increase its thickness in panels P1 to P2, evolving into a different technique with a unique and thicker priming layer in canvas painting, the latest support used by Josefa d'Óbidos.

One of the earlier works assigned to Josefa d'Óbidos and the unique wooden panel in the painter's career (P2), concerns a middle evolutionary process, from panel to canvas, of Óbidos workshop technique, in a proto-baroque style.

Conclusions on this study bring the first insight on the materials used, technical procedures and evolution from panel to canvas of Óbidos painting workshop, highlighting in particular the influences and technical advance of Josefa d' Óbidos, the greatest female Portuguese painter of all times.

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