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MATERIAL CHARACTERISATION OF A FLORENTINE PAINTER IN PORTUGAL IN THE LATE 19TH CENTURY: PAINTINGS BY GIORGIO MARINI

Rui BORDALO[1,2*], Carlo BOTTAINI[1,3], Claudia MORICCA[1], António CANDEIAS[1,2]

[1] HERCULES Laboratory, University of Évora, Largo Marquês de Marialva, 8, 7000-809 Évora, Portugal
[2] Laboratório José de Figueiredo, Direção Geral do Património Cultural, Rua das Janelas Verdes, 37, 1300-001 Lisbon, Portugal
[3] CIDEHUS, University of Évora, Largo Marquês de Marialva, 8, 7000-809 Évora, Portugal

Abstract

This paper presents the analytical characterisation of a series of paintings authored by Giorgio Marini (1836-1905) from the Museum of Évora. Marini was an Italian painter who lived in Portugal in the 19th century. He was a very prolific painter and his works, most of them portraits commissioned by urban and rural bourgeois and noble elites, are dispersed all over the country. The general good conservation state of most paintings prevented the collection of micro-samples for detailed study. Hence, material identification of the painting materials was performed primarily by XRF, given its non-destructive and non-invasive nature, and it was complemented when possible by auxiliary techniques optical microscopy, Raman spectroscopy, and SEM-EDX. Pigments and fillers such as yellow and red ochre, lead white, zinc white, barium white, chrome yellow and green chrome are among the identified pigments. This is the first time the palette used by Giorgio Marini was identified, helping to characterised the pigments used by foreign painters during the 19th century in Portugal.

Keywords: Portable XRF; Raman spectroscopy; SEM-EDX; Pigment analysis

Introduction

The study of the painting materials used by foreign painters working in Portugal in the second half of the 19th century is of especial interest to study the use of new pigments at the time. Giorgio Marini (1836-1905) was a Florentine painter who worked in Portugal from the 1860s until his death. His paintings have never been studied. Not much is known about his life. He worked in Ponta Delgada (Azores), where he made some orders for the main church and several portraits [1]. He later moved to continental Portugal in 1870 and it is known that he lived in Évora for many years after which he moved again in 1902 to Castelo Branco. He worked primarily portraying the urban and rural bourgeois and noble elites. His technique was quite excellent although his quality varied substantially with each order. His paintings are dispersed all over the country, in both public and private collections, probably being one of the most prolific painters in Portugal never studied. His portraits are generally simple and with sober colours, face being the most detailed area, sacrificing the background and clothes to a simpler treatment. From a commercial point of view, this may have been needed since the face was the focus and the prices would have to be competitive. He also painted landscapes and religious and historic themes.

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* Corresponding author: rmbordalo@gmail.com

This paper showcases the use and methodology followed of a portable non-invasive atomic spectrometry technique such as XRF for the identification of painting materials with the aims of characterising the materials used by Giorgio Marini. The use of Raman spectroscopy as a secondary technique further allowed the molecular characterisation of same materials invisible to XRF. Also, the use of SEM-EDX further allowed the atomic characterisation of some pigment particles, mainly for the detection of low-Z elements which were beyond the capabilities of XRF.

Paintings

The Museum of Évora has a small collection of paintings by Giorgio Marini, which was used in this study to characterise his palette. The paintings were examined in situ at the Conservation Laboratory of the Museum of Évora. A total of 13 oil paintings, from which 12 are dated and signed, were analysed. The paintings are dated from 1887 to 1897. The paintings are summarised in Table 1.

Table 1. Summary of the paintings by Marini from the Museum of Évora included in the study.

Code	Title	Authorship	Date	Dimensions (h x w, cm)	Technique and support
ME 783	Beggar	Attributed	-	40x32	Oil on canvas
ME 957	Landscape with Swimmers		1887	35.5x25.5	
ME 958	Landscape/Study of an Old Man		1887	35x25	Oil on tin-plated iron sheets
ME 959	Corn Harvest/Study of an Old Man		1887	35x23.5	
ME 1281	Portrait of Frei Manuel do Cenáculo		1887	73x58	
ME 1276	Portrait of a Gentleman	Signed	1891	70.5x59	
ME 1139	Portrait of Augusto Filipe Simões		1893	76x64	
ME 1399	Portrait of a Gentleman		1896	73x60	Oil on canvas
ME 1440	Portrait of José Vicente da Rocha		1897	72x59	
ME 964	Portrait of a Lady		1897	73x59	
ME 977	Portrait of a Lady		1897	75x60	

One of the earliest paintings (1887) is a copy of an 18th century portrait of Frei Manuel do Cenáculo (1724-1814) (Fig. 1), archbishop of Évora and whose art collection, displayed at the Public Library of Évora during the 19th century, was the base for the creation of the Museum in 1915.

Fig. 1. Examples of three paintings of the collection before conservation (from left to right): Study of a Beggar (ME783, undated), portrait of Frei Manuel do Cenáculo (ME1281, 1881), and portrait of José Vicente da Rocha (ME1440, 1897).

The rest of the collection, dated from 1891 to 1897, is composed of portraits of several people, known and unknown. Unlike all the other paintings, one of them - a study of a beggar -, is not signed nor dated. It was decided to include this painting in the study given its attribution to Marini in the Museum inventory.

The paintings' preferred support is canvas, although there are three paintings on metal support (dated 1887) approximately of the same size, two of them painted in both sides of a tin-plated iron support with a study of an old man on one side and an idyllic landscape on the other (Fig. 2). These metal sheets were often sold by itinerant peddlers and Marini could have been perhaps influenced to experiment with this support from the large ex-voto collections, largely painted on metal supports, which exist in religious centres near Évora.

During the research, it came to our attention that Marini had preferred colours to sign. On the paintings with a light background colour, he used to sign using a dark brown to black colour (paintings ME964, ME977, ME1139, and ME1440) while on dark background colours he preferred using yellow (ME1399, ME1281, ME1276, and both ME958 and ME959 portraits) and orange (landscapes of ME958 and ME959).

Fig. 2. Two double paintings executed in tin-plated iron support before conservation: landscape and portrait study (ME958, 1887) (left), and Corn Harvest and portrait study (ME959, 1887) (right).

Experimental part

In order to characterise painting materials, a set of several analytical techniques are usually used for which micro-sampling is required. Nevertheless, the paintings were generally in good condition and only some of them had lacunae from which borders the micro-samples could be taken off ethically without damaging the paintings. In case of the paintings on metal support, despite having several lacunae, sampling was not possible due to the paint layers' poor structural strength. Thus, it was only possible to sample the paintings ME783, ME964, and ME1281. Unfortunately, they were not enough to obtain a sample from all the colours used. Thus, portable non-invasive XRF was used to determine the elemental composition of the pigments present and optical microscopy (OM), Raman spectroscopy and Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy (SEM-EDX) were used to characterise the materials contained in the micro-samples.

XRF spectra were recorded with a Brüker TRACER III-SD handheld portable spectrometer equipped with a rhodium tube and silicon drift detector. The equipment is equipped with an X-ray tube Rh target; it has a 10mm^2 XFlash SDD, Peltier cooled, and a typical resolution of 145eV at 100000 counts per second (cps). The analysis was performed with an Al/Ti filter (304.8μm aluminium/25.4μm titanium). The operating conditions were 40kV, 12.5μA current and 30 seconds acquisition time. The incident beam on the sample is an elliptic spot size of 3x4mm. To perform the analysis, the instrument was positioned in a stable tripod in front of an easel with the paintings, bench top configuration for the analysis procedure.

The equipment was placed in direct contact with the painting surface, minimising thus atmospheric interference. The spectra were acquired using Brüker's S1PXRF v.3.8.30 and ARTAX v.5.3.0.0 software.

After the XRF analysis, micro-samples were taken with a scalpel from selected areas in paintings ME783, ME964, and ME1281, and prepared by embedding them in EpoFix resin.

Optical microscopy was carried out on the micro-samples with a Leica DM2500M coupled with a Leica MC170 HD digital camera and equipped with a UV ebq 100-04 light source. This allowed the preliminary investigation, identification of the painting stratigraphy and colour layers as well as to locate areas of special interest for further analysis.

μ-Confocal Raman analysis was performed using a Horiba-Jobin Yvon XploRA confocal μRaman spectrometer coupled to an Olympus X41 microscope equipped with a digital camera. The instrument is equipped with two laser sources (= 638 and 785nm), whose laser beams were focused through two objectives of 50X and 100X. Exposure time of 15 seconds and 15 accumulations were used with a grating of 600g/mm. A pure silicon standard was used to calibrate the wavelength scale prior to any analysis. Raman spectra were acquired using LabSpec software. No baseline correction was performed.

Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy (SEM-EDX) analysis was performed with a Variable Pressure SEM-EDX Hitachi S-3700N coupled to an X-ray Spectrometer Brüker Xflash 5010 SDD detector. Given the variable pressure capability, it was not necessary to coat the micro-samples with a conductive layer, allowing later study using other techniques. The samples were analysed using an acceleration voltage of 20kV to detect heavier elements such as Pb, and a pressure of 30Pa. The data acquisition was performed using the Brüker Esprit v.1.9 software. EDX was used to determine and map the elemental composition present in the cross-sections. Element detection from the equipment was screened by analysing a blank, made of transparent plastic.

Results and discussion

In the analysis of oil paintings, Raman spectroscopy is more suitable for the identification of inorganic samples since the presence of the medium, typically drying oils, induces a fluorescence phenomenon that interferes with the assignment of Raman bands. Nevertheless, Raman analyses to the cross-sections revealed a constant peak in some samples at $1868cm^{-1}$ which may be attributed to cyclopropenoid fatty acids [2, 3] which are well known components of seed oils [4], confirming thus the use of a seed-based oil medium. Indeed, cyclopropane has a characteristic absorption at around $1870cm^{-1}$ is due to the C=C stretching vibration of the cyclopropene ring in the fatty acid chain [2, 3].

A total of 126 spot analyses were performed by XRF on the 13 paintings. Table 2 summarises the results of the main elements and their corresponding counts per second (cps) of the tin-plated paintings and table 3 summarises the same data from paintings ME783, ME1139, ME1276 and ME1281, shown as example. XRF detailed results from all the paintings can be found as supplementary material to this article.

White

XRF results show that all the paintings are characterised by the presence of elemental lead in every area analysed (Table 2). The presence of lead in paintings is commonly associated with white lead (basic lead carbonate, $2PbCO_3 \cdot Pb(OH)_2$) which was historically the most important and widely used white pigment until mid-19th century when zinc white became a substitute, thus overcoming lead's toxicity problem. The widespread presence of lead white in all the paintings regardless of the colour suggest that this pigment was used in the ground layer but also in colour layers. The use of lead white in the paintings can be differentiated according to the painting support. While the five tin-plated paintings (ME957, ME958 and ME959)

contain approximately an average of between 6000 and 8000cps (Table 2), the canvas paintings have an average of approximately 13000cps (Table 3). This difference is justified by the thinner layers and absence of a thick ground layer as used in the canvas paintings. Lead white was used in colour layers by itself, such as in the white beard of the portrait of ME958, or mixed with other white pigments, such as identified in the landscape of ME958.

Table 2. XRF results from the tin-plated paintings by Marini, expressed as counts per second (cps) and rounded to the nearest unit, after normalisation (based on Rhodium values). More results are provided as supplemental data.

Code	Painting	Ba	Ca	Co	Cr	Cu	Fe	Hg	Ni	Pb	Sn	Zn
Emission line		L	K	K	K	K	K	L	K	L	K	K
ME957	12.Lacunae	9	54	50	2	7	1312	74	2	2487	1064	1
	5.Yellow	9	3	0	5	9	12	60	1	13166	539	2
	4.Orange	10	3	18	10	7	207	521	1	7095	1056	2
	9.Red	13	16	31	7	8	483	171	0	8947	871	2
	10.Carnation	14	15	27	32	7	912	66	0	4394	956	1
	6.Green	9	6	26	4	8	203	106	1	6799	1066	0
	1.Blue	10	5	59	1	7	282	47	8	7061	889	2
	3.Brown	8	8	48	3	8	390	225	5	6328	1061	1
	11.Grey	9	12	14	6	9	307	355	2	8081	1047	2
ME958 Landscape	8.White	15	2	8	1	7	163	22	0	10015	752	10
	11.Yellow	11	11	26	5	6	591	100	1	6635	1053	6
	2.Pink	13	5	11	1	5	123	231	1	10726	651	90
	5.Red	15	12	19	4	8	754	213	1	5650	1045	49
	7.Green	13	7	26	22	8	447	37	2	7648	864	8
	6.Blue	12	13	41	4	6	499	37	4	6119	1091	109
	4.Brown	12	33	37	4	6	1768	17	0	2656	1074	20
ME958 Portrait	5.White	13	9	4	0	9	82	27	0	12666	398	1
	1.Yellow	10	32	30	1	6	1090	5	0	2324	1116	1
	4.Brown	17	25	24	0	7	1107	8	0	4195	929	0
ME959 Landscape	7.Yellow	18	17	28	41	8	830	173	1	6154	809	1
	10.Red	22	51	43	5	8	1892	13	0	1908	1002	1
	1.Green	18	5	90	1	7	397	48	7	6947	872	1
	9.Green	19	12	27	59	8	641	23	1	7388	824	1
	11.Blue	20	5	26	2	7	293	18	2	8318	833	2
ME959 Portrait	1.Red	22	15	38	2	7	674	336	2	4849	911	0
	2.Yellow	21	8	26	1	9	551	15	0	6558	896	3
	3.Brown	19	14	82	0	7	1022	59	8	4917	1012	2
	4.Yellow	18	13	15	57	8	435	254	0	6862	879	2
	6.White	21	10	11	0	12	215	54	1	10947	616	2

The presence of lead white was also confirmed by Raman spectroscopy in several analyses. The strongest carbonate stretching vibrations of hydrocerussite occurs at 1049-1053cm^{-1} while for cerussite (anhydrous lead carbonate, $PbCO_3$) it is present at 1052cm^{-1} [5-8]. A weak but consistent peak at 1053cm^{-1} appeared in all the Raman spectra that were performed to the micro-samples (Figure 3a) indicating the presence of a lead carbonate in both the ground and colour layers although the identification of which carbonate present cannot be made based on this band alone. Thus, it is likely that the lead white is composed of a mixture of both.

XRF also confirms the presence of calcium, barium and zinc, all elements associated with white pigments. Calcium is associated with calcite (calcium carbonate, $CaCO_3$) and gypsum (calcium sulphate, $CaSO_4$), also widely used in ground layers. The contribution of sulphur could not be determined by XRF since its energy overlaps that of lead, which is much stronger. Also, Raman analysis to the ground layers was not effective due to the fluorescence effect and only some weak, albeit clear bands, were detected. A sample from ME964 identified a weak band at 1088cm^{-1}, which is associated with aragonite ($CaCO_3$), while ME1281 revealed a similar peak at 1080cm^{-1}. No peaks associated with calcium sulphate were detected. The use of calcite is dependent from the colour where it is applied. For example, in three paintings

(ME964, ME997 and ME1139), the lighter areas (white/yellow) have lower cps (<10cps) than darker areas (grey/black).

Table 3. XRF results from paintings by Marini, expressed as counts per second (cps) and rounded to the nearest unit, after normalisation (based on Rhodium values). More results are provided as supplemental data.

Code	Painting	Ba	Ca	Co	Cr	Cu	Fe	Hg	Ni	Pb	Sn	Zn
Emission line		L	K	K	K	K	K	L	K	L	K	K
ME783	2.Pink	17	7	2	0	6	89	46	0	13075	35	148
	1.Red	20	6	2	2	9	105	43	2	13896	32	138
	4.Blue	7	18	252	1	4	177	44	37	11987	26	396
	3.Brown	23	14	30	1	7	597	46	2	11181	21	921
	5.Background	11	33	17	2	6	697	118	1	10443	17	1024
ME1139	5.White	6	5	0	1	9	14	28	2	13771	29	49
	1.Red	6	20	56	1	7	307	190	6	12953	25	62
	2.Carnation	7	6	3	0	7	48	43	1	13061	24	63
	3.Brown	7	53	10	1	7	310	34	2	12257	21	448
	4.Grey	5	33	0	1	4	89	17	1	11284	19	3761
ME1276	7.White	15	5	0	1	10	40	38	1	14118	26	11
	1.Yellow	6	22	3	12	10	210	45	1	13359	26	7
	5.Pink	16	8	2	1	11	41	62	1	13256	25	8
	6.Red	15	14	2	4	8	394	273	1	13443	29	12
	4.Brown	21	27	0	7	9	613	106	0	14137	32	14
	2.Grey	15	21	2	0	8	185	43	0	13050	26	10
	8.Background	20	50	3	1	10	450	49	1	13360	28	17
ME1281	11.White	6	28	12	32	6	603	24	0	12790	28	5
	10.Yellow	5	26	7	44	6	655	30	0	13654	34	3
	4.Red	8	22	94	2	5	416	238	8	13351	28	5
	3.Carnation	4	14	19	3	7	166	58	4	14084	32	3
	12.Green	5	44	26	60	7	581	25	2	13056	35	6
	9.Brown	5	15	23	34	7	1201	26	0	13474	30	5
	8.Grey	5	20	12	5	8	81	30	0	13738	32	6
	13.Black	5	63	0	6	7	651	21	0	13123	29	8

Concerning the structure of the ground layers, ME964 may be taken as example. SEM-EDX analysis revealed two ground layers, which is typical, one lower largely composed of large amounts of calcium and some lead, corresponding to calcite and lead white as confirmed by Raman spectroscopy, and an upper one of mostly lead white and some calcite. Often it was not possible to distinguish from calcium carbonate from calcium sulphate since the S K-line (2.31keV) is almost coincidental with Pb M-line (2.35keV) and the EDX system resolution did not allowed their separation.

Barium was also detected by XRF and it is an indication for the presence of barium white (Barium sulphate, $BaSO_4$), which was used primarily as extender for lead white after 1820s. The use of barium across the paintings is more or less constant, even in the paintings with tin-plated support, except for ME1139, ME1281, and ME1399 where their counts is approximately below 8 cps. One of the areas with a higher count is a white area (53cps) of ME1140 which is double than in the background (26cps). One of the most common peaks detected in most Raman analyses to both ground and colour layers is a peak located at 998cm^{-1} (Figure 3b). This peak may be associated with an intense symmetric stretching mode ($_1$) of the S-O bond, common to several sulphates such as celestite (1003cm^{-1}, $SrSO_4$), barite (989cm^{-1}, $BaSO_4$) or anglesite (978cm^{-1}, $PbSO_4$) [7-9].

Zinc was also detected by XRF in many paintings although its use was not constant (Table 2). For example, in ME957 and both paintings from ME959 only some trace were found (<2cps). In ME958, it can be seen that the use of zinc white was intentional since in the portrait there are only trace amount (<1cps) while in the landscape zinc value go up to 50 to 1109cps in some areas while others are under 20cps. As these are all tin-plated supports, this may be due to the thin layers or lack of a ground layer. Nevertheless, the canvas paintings also have generally

low zinc cps, such as ME1281 with <8cps. Exceptions are three areas (grey, brown and blue) with high zinc counts, up to 6357cps. One of the main differences between the undated and unsigned painting (ME783) and the others by Marini is in the use of zinc, since the unsigned painting has constantly higher zinc cps than the other paintings. This could be due to the fact that this painting could belong to a painter or period other than Marini. Zinc is mainly linked to the presence of zinc white (zinc oxide, ZnO), a synthetic pigment after mid-19th century. The main Raman feature of zinc white is a distinctive peak at 438cm^{-1} which was not found in any spectra. However, a consistent peak located at 430cm^{-1} does appear in several spectra from ME964 and ME1281. This peak is typical for wurtzite [7-9] which is a zinc iron sulphide mineral ((Zn, Fe)S), despite its brown colour. Wurtzite is often found in association with barite [10]. Its presence would require further confirmation but it could perhaps be present as an impurity from zinc sulphide. Zinc could also have been used as zinc sulphide mixed with barium sulphate (BaSO$_4$+ZnS), assuming the commercial name of litophone. This mixture presents weak signals at 222cm^{-1} and 349cm^{-1} from zinc sulphide [11] and 988cm^{-1} from barium white. The use of lithopone is not clear since Raman spectra do not show the peak at 453cm^{-1}.
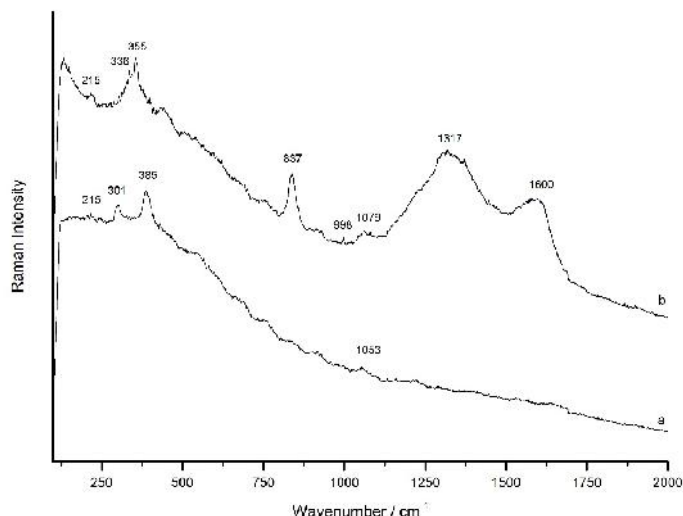

Fig. 3. Raman spectra of two particles from ME1281: a) red particle from the ground layer shows peaks associated with iron oxides (385, 301, and 215cm^{-1}) and lead white (cerussite, 1053cm^{-1}); b) a particle from the top green layer shows characteristic peaks of chrome yellow (355 and 837cm^{-1}) and bone black (broad bands at 1317 and 1600cm^{-1}).

An elemental analysis by EDX performed to the white ground layer from ME783 determined that it is composed of lead white, calcium sulphate (Ca+S), barium sulphate (Ba+S), and zinc. Lead, barium and calcium were also found together mixed in colour layers, such as in a red layer of ME783, as identified by SEM-EDX.

Furthermore, EDX detected some particles with a high content of aluminum and silicon, although further confirmation of white alumino-silicates could not be determined. This could be due to the fact that the materials are poor Raman scatterers or that their characteristic peaks are below the equipment cut-off such as those, for example, from kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$).

Yellow

After lead, iron is the most common element in the yellow areas, such as the carnations, as identified by XRF (Table 2). Yellow iron oxides are very common and are among the oldest pigments known. The use of yellow iron oxides is confirmed by the high counts of iron in paintings such as ME1281. However, a note should be made for the high iron counts of the tin-

plated metal supports which are undoubtedly due to their core iron content. This is supported by the iron comparison of the XRF analysis of ME957. The highest content of iron was measured in a lacuna with no paint traces (1312cps) which contrasts with a yellow area with just 12 cps. This is related to the fact that this last area has also the highest cps of lead which may have acted as a buffer for the iron from the core of the support.

An XRF analysis of the bright sunset yellow sky of ME957 (Figure 2) detected lead followed by tin and chromium, all commonly associated with yellow pigments. However, it should be taken in consideration that the support is tin-plated and that the cps value of tin is the lowest among all the analyses to this painting by which a tin-based yellow pigment would not be a viable option. In the 19th century there were available several lead-based yellow pigments although since no antimony or arsenic were detected and lead-tin pigments were not used between 1750 and their rediscovery in 1940 [12], we are inclined to the presence of either yellow lead (lead(II) oxide, PbO) or, given the presence of chromium, chrome yellow (lead(II) chromate, $PbCrO_4$). In the same painting, the three highest cps of chromium are located in one orange area (cloud) and two yellow areas (carnation and sunset), by which the use of chrome yellow is very likely. Still in ME957, when analysing the elemental composition of two yellow areas, the sunset sky and a carnation, it can be seen that the chromium content is similar (5 and 7cps, respectively) while the iron content is diverse, being quite low (12cps) in the sky and high in the carnation (912cps) which indicates that a yellow iron oxide was mixed, most likely yellow ochre. Raman or SEM-EDX analyses on these areas were not possible due to the lack of samples. In all the other paintings, it can be observed that chromium always has higher cps in yellow and green colours.

Chrome yellow was also used mixed with green in the background of ME1281 as identified by its characteristic Raman bands at 355(s)cm^{-1} and 837(vs)cm^{-1}, the later corresponding to the Cr-O stretching vibration (Fig. 3b).

Although both portraits of ME958 and ME959 are almost entirely made in yellow and earth tones, XRF analysis of the paintings identified that chromium is only present in the signature of both portraits, with 35 and 57cps, respectively, confirming thus the presence of chrome yellow. The use of chrome yellow may have been due to the fact that Marini needed a tonality that would stand up from the other warmer yellows. No chromium was identified in the other three signatures of the two paintings, except iron. A high content of iron, associated with yellow and brown iron oxides, was also observed although this may be due to the underlying background layer. Concerning the potential use of yellow lead (PbO), it can be observed in Table 2, for instance, the distribution of elemental lead in the portrait of ME958, where all non-white areas present a similar cps (between around 2300 to 5700cps against 12666cps in the white area), and that in all the paintings cps values of elemental lead do not present a significant difference between yellow and other areas. Thus, the use of yellow lead in the areas of that colour is unlikely.

Red

The main red pigment used through the paintings is vermilion (mercury sulphide, HgS), as identified by XRF by the presence of Hg (Table 2). Iron is also always present in all the red areas, such as the lips, showing the presence of a red iron oxide. Mercury is found in both red and yellow areas, such as carnations, showing that Marini used vermilion mixed with both red and yellow ochre (for instance in ME958, ME959, ME964, ME977, and ME1139).

EDX analysis of the red particles of ME783 indicates the presence of both iron and silicon. Iron oxides may have diverse compositions such as 20%-50% iron oxide with high concentrations of silicon which may be from clays or quartz (SiO_2) [13-17]. In a sample from the red signature of ME964, it was observed by EDX that the top red particles contain a high amount of iron, followed by silicon and magnesium, and that no mercury was present. The use of red ochre by the artist was later confirmed through the analysis by the Raman analysis of a

sample from ME1281, where some few isolated particles were found within the top green colour layer, identified by their characteristic bands at 290 and 405cm^{-1}.

Also, lead is always present, which could indicate the presence of lead-base red pigments such as minium (Pb_3O_4), although this is constant throughout all the XRF analysis and is most likely due to lead white presence in all the layers and may be the sole origin of lead in XRF.

A micro-sample of the red lip from Study of a Beggar (ME783) was further analysed by SEM-EDX and Raman. The top red layer presents a very large variety of different particles of red, purple, ochre and white colours (containing lead, barium and calcium). Both ochre and purple particles have similar composition of iron, silicon, magnesium and aluminium, suggesting the presence of different types of ochres. The red colour is given from small dispersed particles of vermillion and large particles of either bright red iron and silicon-based particles, suggesting the presence of several red iron oxides.

An EDX analysis of the red particles of the signature of ME964 identified the presence of Fe, followed by Si, Mg and K, indicating the presence of potassium, ferro-magnesian aluminosilicate mineral. However, Raman spectroscopy did not provide with a positive identification of this mineral.

In ME 1281, a sample was taken from the side of the canvas and further analysis confirmed the presence of a brown coloured layer, composed of diverse particles, underneath the white layer. One of these, of red colour, was analysed by Raman and despite its high fluorescence; it identified the peaks at 385(m), 301(w), and 215(vw)cm^{-1} (Figure 3a) which are very similar to another sample at 389(m), 302(w) and 215(vw)cm^{-1}. These peaks correspond to the most relevant peaks of goethite (hydrous ferric oxide, a-FeOOH), namely 387 and 300cm^{-1} [18] or 386, 298 and 215cm^{-1} [19]. Another important peak at around 552cm^{-1} is hardly visible due to the fluorescence. The peak at 385 cm^{-1} is assigned to iron oxide in hydrated form. However, the particles are red and not yellow, although they could not be from haematite (anhydrous ferric oxide, a-Fe_2O_3), whose peaks are located at 291, 299, and 411cm^{-1} [20]. Thus, the peaks are closer to yellow ochre than red ochre, despite the particle colour. An explanation of this could be related to the presence in low percentage of pure iron trioxide (Fe_2O_3), which adds a reddish hue [18], or to a partial calcination of yellow ochre. In another red particle from the same painting, most peaks correspond to red ochre (302, 410, 503, 614cm^{-1}) [20].

Green

XRF analysis of the green pigments identified a consistent presence of both iron and chromium as shown, for example, in the landscape of ME958 where there are only trace values of chromium (<4 cps), except for a green area with 22 cps. However, the presence of chromium may be related to the use of chromium yellow and not of a chromium-based green as it was observed by Raman spectroscopy in a sample from ME1281, identifying characteristic bands of chrome yellow at 356 and 838cm^{-1}. The yellow particles mixed within the green layer can be observed by optical microscopy (Figure 4). However, the presence of a green pigment could not be identified by Raman spectroscopy since no characteristic peaks, such as 487cm^{-1} from Viridian green, could be detected [21-24].

Green earth is a pigment with diverse minerals although it is most commonly constituted by clayed micas celadonite and glauconite. According to Ospitali *et al.* [25] it is possible to differentiate among the several mineral by their composition ratio. EDX analysis of the green background colour of ME1281 (Figure 4) resulted in the identification of Si > Mg > Al (relative atomic % Si = 1.58; Mg = 0.32; Al = 0.05; Fe = 4.39) which is consistent with the trend verified by authors for celadonite [25]. Its chemical composition is, approximately, $K[(Al,Fe^{3+}),(Fe^{2+},Mg)](AlSi_3,Si_4)O10(OH)_2$ with low Al content.

In ME958, two areas of the green vegetation with different tonalities were analysed by XRF (Table 2) and while they both show a high and constant iron content, only one shows an

increase in the chromium cps (from a trace value of 3cps to 22cps), which may be from the use of both green and brown earths and chrome yellow or green. The landscape of ME959 presents a similar tendency. In this painting, the corn leaves are both green and yellow but they are so small that it was not possible to perform differentiated elemental analysis to that area. The XRF analysis detected lead, iron and chromium, most likely from both green earth and yellow ochre. The green background of the portrait (ME959), however, contains no chromium, just iron, confirming thus an iron-based green.
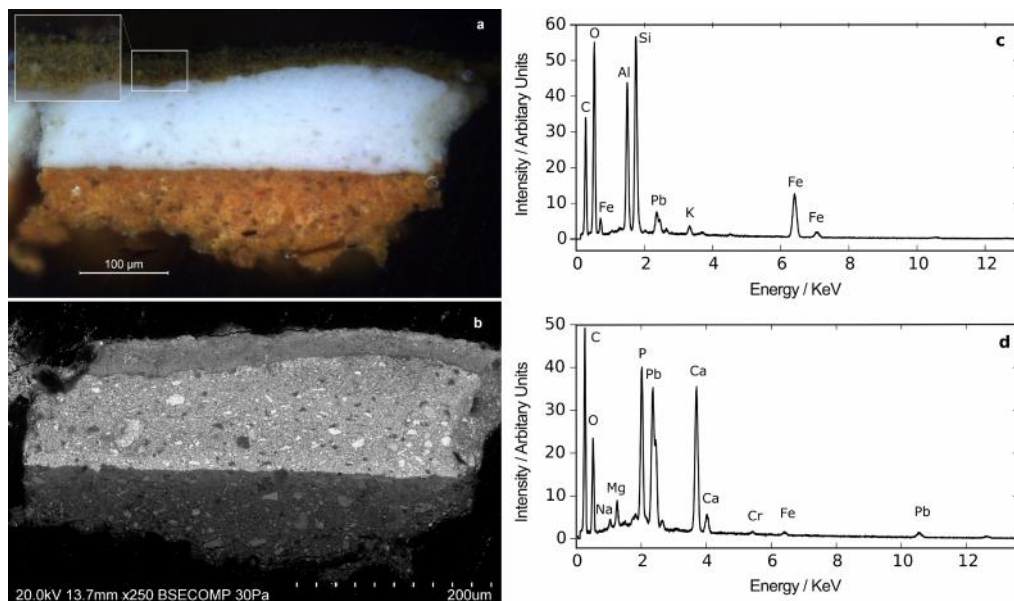
Fig. 4. Cross section from the green background of *Portrait of Frei Manuel do Cenáculo* (ME1281): a) light microscopy with a detail of the chrome yellow particles in the top green layer; b) microphotography of the same area where the distribution of particles can be observed in a four-layer structure; c) EDX area analysis of the brown ground layer, showing high contributions of an alumino-silicate (Si+Al) followed by iron oxides (Fe); d) EDX spot analysis of a particle from the green layer showing the presence of lead white (Pb), bone black (Ca+P) and low contributions of iron and chromium-based pigments.

Blue

Blue was scarcely used and, even then, just in small areas or heavily mixed with other colours. Four different blue areas (sky, water, and a shirt) were analysed by XRF in the landscape of ME958 and in ME997. After lead, the most common denominator is the presence of iron and a varying presence of zinc, from zinc white, which was used to whiten the several tonalities. The presence of iron in blue areas suggests the presence of Prussian Blue, an iron (III) hexacyanoferrate(II) of general formula $[Fe(II)(CN)_6]^{4-}$. The presence of iron has been observed in all blue areas of the several paintings. A similar iron-rich composition was found in a blue handkerchief from a figure in ME959. However, it should be kept in mind that XRF would not detect any of the elements that compose ultramarine blue (sodium alumino-silicate, $Na_8[Al_6Si_6O_{24}]S_n$), by which this possibility cannot be set aside.

Cobalt was also detected in several paintings, which is usually associated with blue pigments such as smalt (cobalt(II) silicate, $CoO \cdot nSiO_2$), Thénard's blue ($CoAl_2O_4$), and cerulean blue ($CoSnO_3$), but also in other red, violet and green pigments. ME783 shows a high content of cobalt (252cps) in a blue area (shoulder), although it could be a posterior intervention since it does not seem to belong, colour and style-wise, to the painting. This same area also revealed the presence of nickel, which is a common impurity of cobalt ore [26], suggesting a correlation that

is illustrated in Figure 5 that plots the cps for nickel (K cps) versus cobalt (K cps), with a correlation of R = 0.80. High cobalt cps have also been detected in some areas of ME1281 (Table 3), namely in the red lips and brown eyes (86 and 94cps, and 107cps, respectively), while in other areas the values are almost negligible. An example of this is that in another two brown areas, the cps values drop from 107 to 16, while in other four areas there are only traces (<3cps). In other paintings, such as ME964, cobalt is virtually non-existent in any of the areas analysed which confirms that its presence is related to the use of a pigment. Unfortunately, neither Raman spectroscopy nor SEM-EDX were detected any cobalt-based pigment.
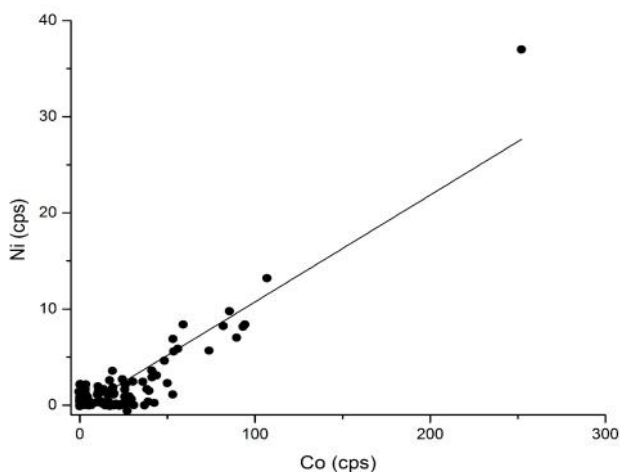

Fig. 5. Plot of K Ni cps versus K Co cps measured on the paintings (linear fit: R=0.80).

Browns

Ii can be observed in Table 2 that in each painting, the brown areas are the ones with the highest iron cps, suggesting that the brown is from an iron-rich pigment. For example, brown areas such as brown clouds of ME957 and ME958 (in ME958, the iron cps is four times higher than the other areas), a brown eyebrow of ME959, and brown hair of ME1139, also present a similar composition of mainly iron, indicating the use of a brown iron-oxide. EDX analysis of a sample from the background of ME964 detected several particles with composition of Si, Al, Mg and K. Unfortunately, none of the acquired Raman spectra of the brown areas reported any contribution from brown ochres.

Black

One of the most common black pigments, and also one of the most ancient, is bone black, which is made of charred bones. This makes it the usual suspect to look for when analysing black paintings. The markers of bone black are phosphorus and calcium given the presence of calcium phosphate ($Ca_3(PO_4)_2$) from hydroxyapatite, the main inorganic component of bone (up to 84%) [27]. The presence of phosphorus was not identified by XRF since phosphorus' atomic weigh (Z = 15) is below the equipment operating conditions limit. The absence of phosphorus in two otherwise identical XRF spectra from a black and a white area may also be a potential indication of the presence of this pigment, as it happened in the analysis of ME1276. However, the presence of bone black was confirmed in the unsigned painting (ME783), and signed paintings ME964 and ME1281, both by Raman spectroscopy and EDX.

The Raman spectrum of bone black has two characteristic broad bands at approximately 1360 and 1590cm^{-1}, both of which were present in several spectra. In a micro-sample from ME783, some few bone black particles were also observed by chance dispersed in the white

ground layer. This identification was also confirmed by EDX which detected both phosphorus and calcium. Two micro-samples of ME964 detected particles of bone black, identified by a high amount of phosphorous and calcium, followed by Fe, Mg and Si, which are likely from nearby particles. In ME1281, an XRF comparison between the grey cassock's collar and the black cassock indicates a higher cps of both iron and calcium in the black area and of lead in the grey area. This indicates that the collar was painted with an excess of lead white and calcium, since the variation cannot correspond to its content in the ground layer, it surely corresponds to calcium phosphate from bone black, which was also confirmed by Raman analysis.

Marini's Palette

Marini was a painter that worked mostly producing portraits by commission. He often used a simple formula, of the portrayed in the centre over a background of solid colour. Assessing by the pose, it is likely that they were made based on a photographic print and not with live models. In most of his paintings, the portrayed has a dark suit or dress which clashes with colourful but very simple and small decorations, such as tie pins. Table 4 summarises the pigments identified in the 13 paintings by Giorgio Marini analysed in this study. He recurrently used lead white, vermilion, cobalt blue and brown ochre as they were identified in all the paintings. Barium and zinc white were also detected in most but not all paintings. Calcite was detected in the ground layer of those paintings that were sampled and, as a typical material; it is very likely that it was used in all the paintings. Some pigments may not be present in a certain painting due to the limited colour variety of Marini's compositions although chrome yellow, yellow and red ochre, an iron-based blue and green earth were only found in few paintings. Bone black was only found in the three paintings that were sampled although, as one of the most typical blacks, it is likely that Marini used it in all his paintings.

Table 4. Distribution of the pigments found in the painting collection from Marini, ordered by year. Some pigments were only identified through sampling (indicated by an asterisk) by which a pigment which is not indicated in a given painting may have been used in that painting.

Pigments	ME783* undated	ME957 1887	ME958 1887 L	ME958 1887 P	ME959 1887 L	ME959 1887 P	ME1281* 1887	ME1276 1891	ME1139 1893	ME1399 1896	ME1440 1897	ME964* 1897	ME977 1897
Lead White	•	•	•	•	•	•	•	•	•	•	•	•	•
Barium White	•	•	•	•	•	•		•			•	•	•
Zinc White	•		•					•	•	•	•	•	•
Calcite							•					•	
Yellow ochre		•	•	•	•	•	•					•	
Chrome yellow	•			•		•	•					•	
Vermilion	•	•	•	•	•	•	•	•	•	•	•	•	•
Red ochre	•						•					•	
Green earth						•	•						
Iron-based Blue			•		•								•
Cobalt blue	•	•	•	•	•	•	•	•	•	•	•	•	•
Brown ochre	•	•	•	•	•	•	•	•	•	•	•	•	•
Bone black	•						•					•	

Note: L: Landscape; P: Portrait.

Conclusions

The present study aims to identify for the first time the painting materials from a collection of easel paintings by Giorgio Marini, an Italian painter settled in Portugal in the last quarter of the 19th century. Due to the impossibility to sample most paintings, the chosen methodology was to use a non-invasive portable XRF in combination for optical microscopy, Raman spectroscopy and SEM-EDX performed for the selected samples. A total of 126 XRF point analyses were performed to 13 paintings. Most evidence for pigment identification was

obtained by comparative analysis of the data collected by XRF and SEM-EDX, despite their limitation to elemental identification. Raman spectroscopy, despite its molecular analytical capabilities, did not resulted in clear identification of many of the pigments, either by the materials' low scattering or due to fluorescence. Nevertheless, the combination of these techniques allowed to overcome the limitation of the XRF elemental analysis and indicated the presence of lead white, barium white, calcite, zinc white, yellow and red ochre, vermilion, chrome yellow, two blue iron- and cobalt-based blues, green earth, brown ochre, and bone black. All the pigments found were commonly used in the nineteenth century. Marini's choice of pigments was very conservative given the variety of many other pigments that were available at the time. The present collection gathers works from 1887 to 1897, from when Marini was 51 to 61 years-old, which is likely the last representative period of his live.

Acknowledgments

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