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M. Guerra, M. L. Carvalho, A. Le Gac, M. Manso, C. Mortari, S. Longelin, and S. Pessanha



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New insights into the red and green pigments in the illuminated foral charter of Setubal (1515) by combined use of μ -Raman and X-ray fluorescence spectrometry

M. Guerra,^{1,2} M. L. Carvalho,^{1,2} A. Le Gac,^{1,3} M. Manso,^{1,4} C. Mortari,⁴ S. Longelin,¹ and S. Pessanha^{1,2,a)}

¹Laboratório de Instrumentação, Engenharia Biomédica e Física da Radiação, LIBPhys-UNL, 2829-516 Caparica, Portugal

²Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

³Departamento de Conservação e Restauro, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

⁴Faculdade de Belas-Artes da Universidade de Lisboa, Largo da Academia Nacional de Belas-Artes, 1249-058 Lisboa, Portugal

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The richly decorated *foral* charter attributed by D. Manuel I of Portugal, in 1515, to the village of Setubal, was studied using Energy Dispersive X-ray Fluorescence spectrometry and Raman micro-spectroscopy. An *in situ* characterization of the pigments used in the production of this masterpiece showed a very different pigment palette choice when compared to other similar Manueline charters. The red and green pigments are particularly puzzling, as the widely used mercury- and copper-based pigments, vermilion and malachite, respectively, were not found in the illuminated frontispiece. Instead, the cheaper lead-based pigment minium was used in the King's flag, while a mixture of copper sulfates was found for the green color, identified by means of micro-Raman spectroscopy. This result led to a new look at the conception that only one Royal workshop existed for the elaboration of Manueline *foral* charters. © 2016 AIP Publishing LLC.

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INTRODUCTION

In this study, a thorough spectroscopic evaluation was performed on the materials used in the manufacture of one of the most beautiful and richly illuminated charters of Portuguese cultural heritage, the *foral* charter of Setubal. The used pigments were evaluated by means of portable Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometry and Raman micro-spectroscopy (μ -Raman). Due to the inestimable value of the charter, every measurement had to be performed *in situ*, in the Portuguese National Archive (ANTT), except for the very few micro samples that were collected in a previous study and could be analyzed in the laboratory.

It was at the beginning of the 16th century that King D. Manuel I set forth the extensive restructuring of the *foral* charters that had been produced within the Portuguese kingdom since the 12th century. This was an ambitious project that aimed at renewing the *foral* charters and adapts them to a new language and the new aesthetic prevalent at the time. They were transcribed into renewed codices and adjusted to the present community rules, the *Leitura Nova* (new writing). The charters were written on parchment using gothic style characters and illuminated with various decorative elements, highlighting the heraldic motif. Examples of this are the coat of arms and the armillary sphere, used to express the King's

authority. In March 1249, Setubal received a charter granted by the Order of Santiago. Being Setubal land of this order, its charter consigned the rights and taxes due to the King and to the Order. Due to the progress and population growth, Manuel I granted a new charter to Setubal village on January 1515. This new charter stipulated clearly all rights and taxes charged in Setubal. The reform introduced, among others, changes on the system of fishing practices, registration, control, and receipt of salt rights. The richness of the village is expressed in the wealth of the adornments of the charter, which bills itself as one of the most impressive examples of this type.

The Manueline *foral* charters represent the most important written heritage of the Portuguese Art during the Renaissance. These documents have been the subject of numerous studies, given not only their historical value but also their artistic and technological excellence. Their aim was to understand the way in which the Manueline charters were created. In these investigations, the authors used different analytical methods, such as X-ray elemental analysis or scanning electron microscope coupled with energy dispersive spectrometer (XRF or SEM-EDS) combined with micro-spectroscopy techniques (Raman, FTIR, and/or UV-Vis fluorescence emission) and microscopy techniques (stereo-microscopy and digital microscopy) in which the charters were examined under normal and UV light. Some of these charters have been studied by Le Gac,^{1,2} Manso,³ Pessanha,^{4,5} and Moura.⁶

In order to enrich the range of information about the Manueline *foral* charters, the present work targets the study

^{a)}Author to whom correspondence should be addressed. Electronic mail: sofia.pessanha@fct.unl.pt

of the *foral* charter of Setubal especially for green and red characterization.

The illumination decorating the frontispiece is luxuriously ornamented (Fig. 1).

In the effort to accomplish a thorough pictorial characterization of this Manueline *foral* charter, nondestructive analytical techniques were used as much as possible. EDXRF analyses were carried out *in situ* for atomic characterization of the pigments used, as well as the characterization of the elements present in the parchment which may provide hints to the type of manufacture used. Raman analysis was also performed on the micro-samples to complement the information of molecular structures within the used materials.

MATERIALS AND METHODS

Portable energy dispersive X-ray fluorescence analysis

The spectrometer used in this work consists of an Eclipse IV Amptek X-ray tube (45 kV; 50 μ A) with a Rh anode. The outgoing radiation is collimated by a tantalum collimator, resulting in a 5 mm beam diameter at the sample surface. The sample is placed at a distance of 55 mm from the X-ray tube and at 10 mm from the detector Beryllium window. The system is equipped with two laser pointers to identify the central point of the X-ray beam at a 90° angle from the detector axis. This geometry allows partially polarized radiation with a high background reduction on Compton scattering. Samples were analyzed directly on air at room temperature.



FIG. 1. Frontispiece of the foral charter of Setubal.

The detector is a silicon drift detector (SDD) Amptek XR-100SDD with a 25 mm² detection area collimated down to 17.12 mm² and 500 μ m thickness (fully depleted) and a 12.5 μ m Be window. The dead layer has a thickness of 150 nm. This detector features an energy resolution of 125–140 eV at 5.9 keV. The acquisition time for each spectrum was 300 s. Spectrum evaluation was performed using the PyMca software package.⁷

Confocal micro Raman analysis

Raman spectra of the coloring materials were measured on micro-samples using a Horiba-Jobin Yvon XploRA confocal spectrometer, equipped with 3 laser diodes sources operating at wavelength values of 532 nm, 638 nm, and 785 nm, with maximum incident power of 2 mW. In this study, we have used an entrance slit of 100 μ m, and the scattered light collected by the objective was dispersed onto the air cooled CCD array of an Andor iDus detector by a 1200 lines/mm grating. A 100 \times magnification objective with a pinhole of 300 μ m was used to optimize the spatial resolution. These parameters allow us to perform Raman microspectroscopy typically in the range of 130–1800 cm⁻¹. Pigment grains were selected with the help of a microscope. To reach an accurate identification of the studied pigments, a polynomial baseline correction was carried out on the measured Raman spectra to remove the fluorescence contribution. The identification of pigments was made with good accuracy by using literature^{8,9} and several spectral databases (Crystal Sleuth, Spectral ID) implemented with some of our own reference spectra (pigments provided by Kremer).

RESULTS AND DISCUSSION

Parchment

The parchment is the end result of the special process animal skin undergoes in order to gain improved durability. The most common method of accomplishing this task is the procedure in which the raw hides are submerged in a lime bath; this causes the material to start dehairing.¹⁰ Other compounds were typically added at that stage to the lime to aid in the drying conservation process, such as sodium or potassium chlorides, ammonium chloride, or sulfate. In the following phase, the skin was stretched on a wooden frame and shaved with a knife on both sides. This was done until the desired thickness was obtained. In-between the scraping, the skin was left to dry, wetted, and stretched until the fiber network had obtained an almost horizontal structure. The parchment was produced for writing purposes, so the next step was to treat it with chalk and have its surface rubbed with pulverized pumice stone.¹¹ In the *foral* charter under study, certain elements could be detected by EDXRF analysis, these were calcium and chlorine together with traces of silicon, sulfur, potassium, iron, and nickel (Fig. 2(a)). The presence of calcium was already expected given that the treatments employed lime (CaO, Ca(OH)₂) and chalk (CaCO₃). Its purpose was to attain a whiter surface and to greatly reduce the moisture content of the hide.

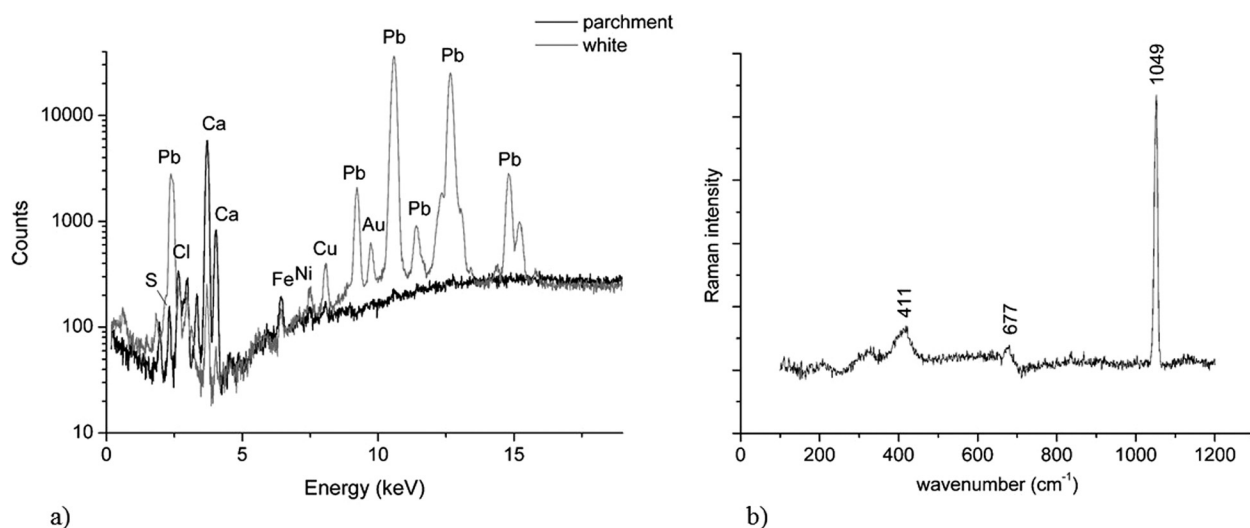


FIG. 2. (a) Comparison of the EDXRF spectra of parchment and white area. (b) Raman spectrum of the white sample ($150\text{--}1300\text{ cm}^{-1}$).

Pigments

White

The white color is prominent on the sides of the coat of arms, representing the regal flags. In almost all of the Portuguese *foral* charters, the King's flags were depicted in white and pink, white polished silver being used in the white section for greater visual impact. In this charter, however, the white part of the flag was found to be burnished white lead, due to the presence of the lead peaks in the EDXRF spectra (Fig. 2(a)). This polished white lead paint creates an extraordinary bright contrast with the leached parchment. White lead was the only white pigment available at the beginning of the 16th century and could be used in several different phases. Only the lead carbonate, hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) was identified by Raman spectroscopy (Fig. 2(b)).

Blue

In the blue areas, a copper-based pigment was found through EDXRF analysis (Fig. 3(a)). In addition to these

results, μ -Raman analysis was conducted, in which the azurite pigment ($2\text{CuCO}_3\text{Cu}(\text{OH})_2$) was identified (Fig. 3(b)). Azurite was commonly employed at the time, as shown in other studies about *foral* charters;^{1–3,6} however, it was rather a costly material in Portugal at that time and used with restraint. In this specific *foral* charter, the intense blue color has a significant implementation, which shows the exceptional richness of this masterpiece.

Yellow

The use of the yellow color is very limited in this charter. It can be seen in the landscape behind the coat of arms and the wings of the central angel. Through EDXRF analysis, the presence of lead (Pb) and tin (Sn) (Fig. 4) was detected, which might indicate the use of the pigment lead-tin yellow. In this case, type I lead-tin oxide (Pb_2SnO_4) is the most likely. Actually, two types of lead-tin yellow might be used, type I and type II containing silicon ($\text{Pb}(\text{Sn},\text{Si})\text{O}_3$). Type I found application in Europe from the 14th to the 18th century. The lead-tin yellow was manufactured by heating

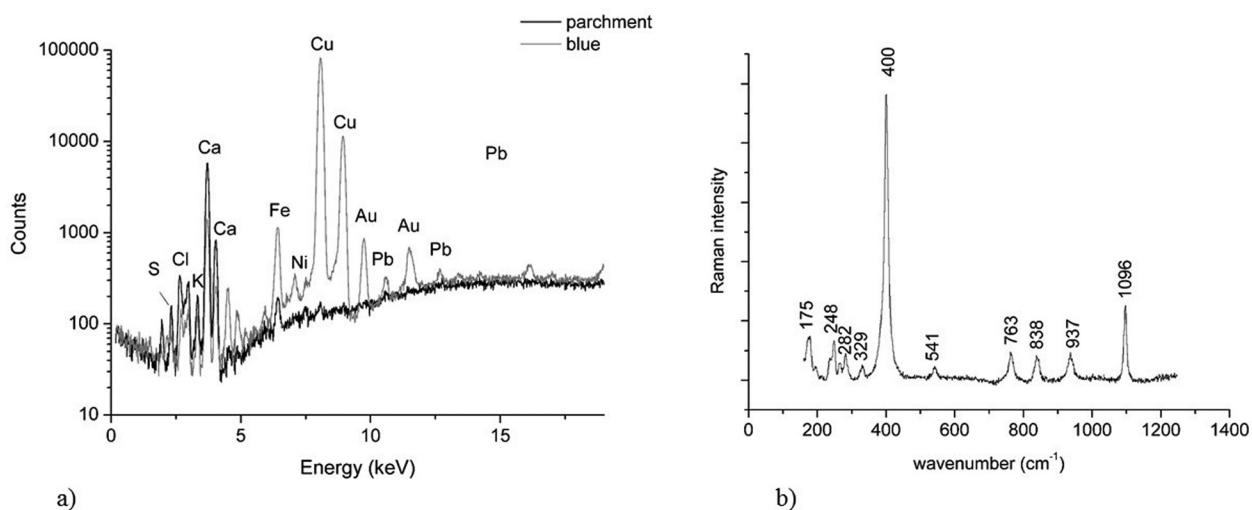


FIG. 3. (a) EDXRF spectrum of a blue area. (b) Raman spectrum of the blue sample ($150\text{--}1300\text{ cm}^{-1}$).

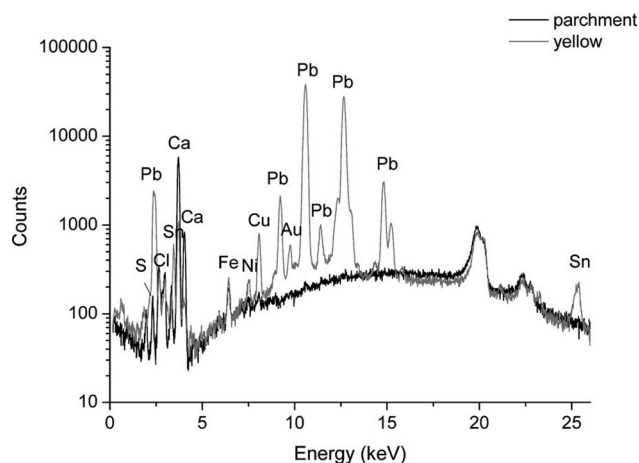


FIG. 4. EDXRF spectrum of a yellow area.

three parts of red lead oxide (Pb_3O_4) with one part of tin oxide (SnO_2) at a temperature between 650°C and 800°C . The synthesis of lead-tin yellow type II was a much more complicated process, and they were seldom found together. Furthermore, according to Martin and Duval¹² and Clark,¹³ lead-tin yellow type I was the most used from the second quarter of the 16th century onwards due to the easy manufacturing technique, and type II was no longer in usage in the 16th century.

Red

The very bright red present in this *foral* charter is of a much more orange shade than the red color applied in almost all of the other Portuguese *foral* charters, such as the charter of Sintra³ or the charter of Teixedo.¹ This led us to believe that the pigment employed in the illumination of the red parts of this charter was not the ubiquitous vermilion. The EDXRF spectra showed the presence of high amounts of Pb, and the absence of the characteristic Hg peaks confirmed that, in fact, the red pigment is minium (Pb_3O_4) instead of vermilion, Fig. 5(a). This choice is somewhat unexpected, as the richness of the illumination warranted the use of very high quality

materials, and vermilion was a much more expensive pigment at the time. The red paraphs and initials inside the written text, however, show the presence of cinnabar. It is well known that the illumination of the frontispieces was performed in different workshops than the writing of the juridical text, but it remains a puzzle why vermilion was not used here as well. We can only explain this considering that the painter did it on purpose. Essentially, minium gave special emphasis to the royal symbols and highlighted the winged angels. The presence of hydrocerussite [$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$] with the peak at 1049 cm^{-1} in the Raman spectrum can report to the origin of minium. The white pigment at 300°C combines with oxygen and gives a red pigment. It is the lead tetra oxide, Pb_3O_4 , identified by Raman spectroscopy in Fig. 5(b). However, this reaction usually results in a complete conversion of the hydrocerussite into minium, so the presence of the lead carbonate might be attributed to its use as an extender.

Green

The green color has a prominent role in the illumination, as it surrounds the name of the king in the central banderole. X-ray fluorescence spectra show that we are in the presence of a copper-based pigment, and from this information, it would be easy to conclude that malachite ($\text{CuCO}_3 \times \text{Cu}(\text{OH})_2$) was used Fig. 6(a). Actually, in the majority of the literature describing green colored materials used on ancient paintings, two copper greens are mainly cited: malachite and verdigris [$\text{Cu}(\text{CH}_3\text{COO})_2 \times [\text{Cu}(\text{OH})_2]_3 \times 2\text{H}_2\text{O}$]. The detection of blue grains of azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$) in the green paint could let us believe that the green was malachite, considering that these two minerals are often found associated in natural environment. But here, surprisingly, it is not the case at all. Actually, azurite seems to have been meaningfully used with another green pigment. The Raman analysis of a micro sample revealed that the expected copper carbonate, malachite, was not present in the green area, and that a copper sulfate could be found instead (Fig. 6(b)). Generally speaking, it is almost impossible to distinguish Antlerite [$\text{Cu}_3(\text{SO}_4)(\text{OH})_4$] and Brochantite [$\text{Cu}_4(\text{SO}_4)(\text{OH})_6$] from Langite [$\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot 2(\text{H}_2\text{O})$] or

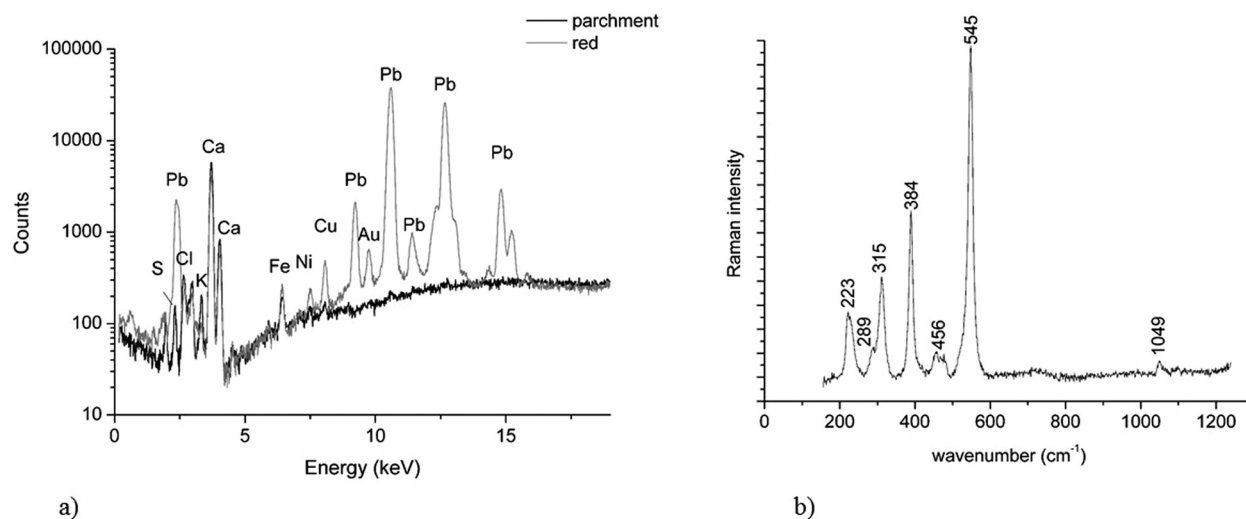


FIG. 5. (a) EDXRF spectrum of a red area. (b) Raman spectrum of the red sample.

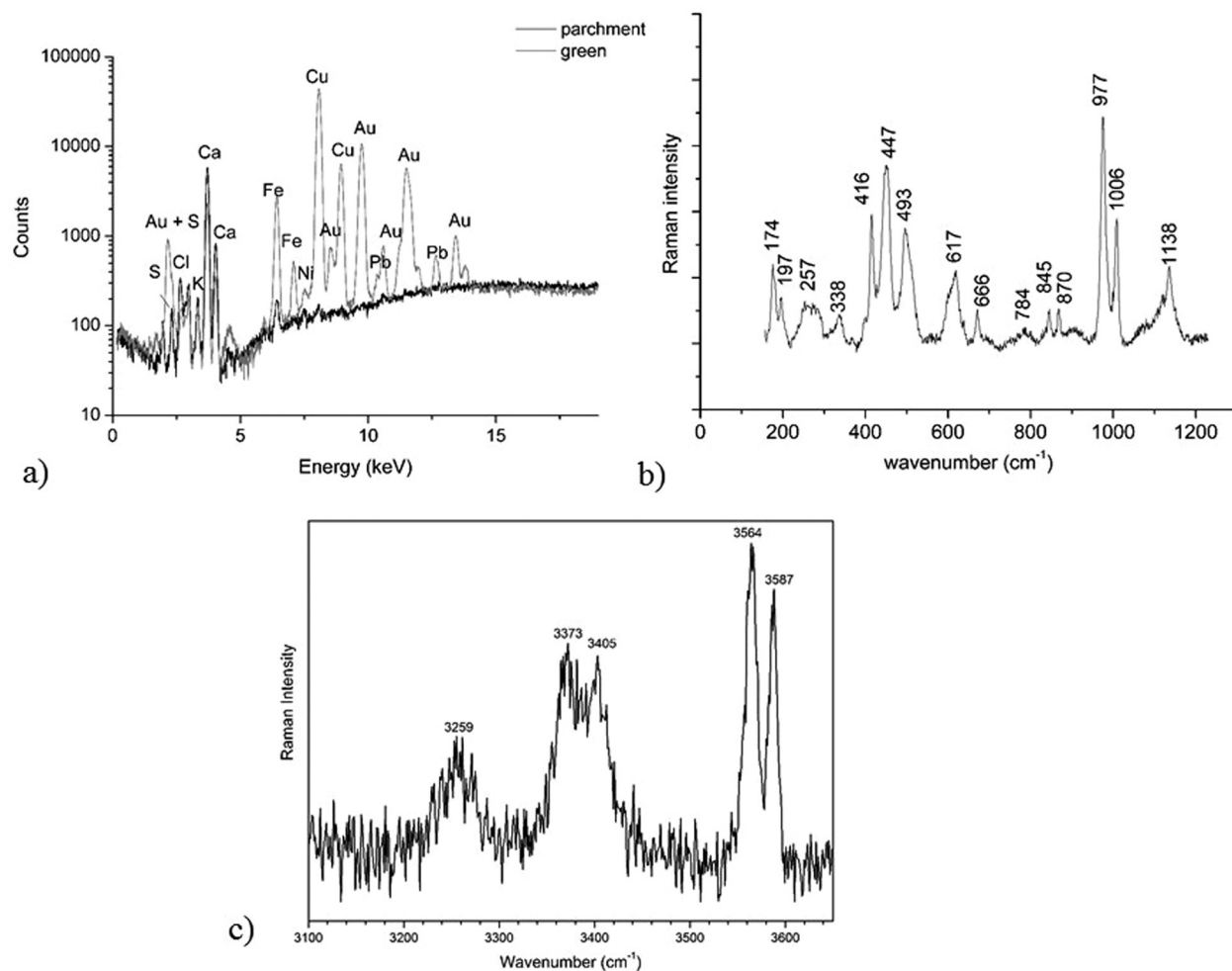


FIG. 6. (a) XRF of a green area. (b) Raman spectrum of the green sample ($150\text{--}1300\text{ cm}^{-1}$). (c) Raman spectrum of the green sample ($3100\text{--}3700\text{ cm}^{-1}$).

Posnjakite $[\text{Cu}_4(\text{SO}_4)(\text{OH})_6\cdot\text{H}_2\text{O}]$ by X-ray fluorescence, since their spectra are very similar. They all are copper sulfates, with different hydration degrees, and cannot be distinguished by XRF technique, based exclusively on elemental identification. The ratio Cu/S could be one possibility, since the amount of Cu is different in each one. Unfortunately, the presence of Au from the DOM MANVEL letters, or Pb is a constant and is overlapped with S lines, making the amount of sulfur impossible to be accurately defined. Distinguishing the several copper sulfates with Raman spectroscopy is also not straightforward as Martens *et al.*¹⁴ demonstrated, but considering the spectrum in the $3000\text{--}3700\text{ cm}^{-1}$ range (Fig. 6(c)), the presence of langite or posnjakite has to be taken into account. However, the peak at 257 cm^{-1} in Fig. 6(b) is consistent with langite. On the other hand, the peaks at 338 and 416 cm^{-1} indicate the presence of brochantite or antlerite but the shoulder at 517 cm^{-1} suggests the presence of brochantite.¹⁴ Gypsum was identified by the Raman band at 1006 cm^{-1} .

Langite and brochantite, in artworks, are usually associated with malachite, either as an impurity¹⁵ or a degradation product.^{16–18} However, no evidence of malachite was found in the spectra of green samples from these paintings where the copper sulfates were identified, supporting the idea they were used deliberately as pigments. The use of langite and brochantite as pigments is uncommon but not unreported in

easel paintings, frescoes, or illuminations from the fourteenth to sixteenth centuries.^{19–22}

Pink

The pink color has been used to decorate the robe of the angelic figure, the carnations, and some of the ornaments over the rectangular motif in gold. The EDXRF spectra of pink areas (Fig. 7) presented Ca and Pb, suggesting several

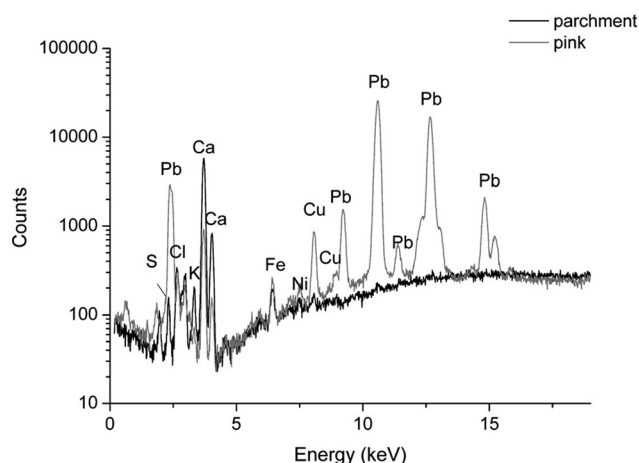


FIG. 7. Comparison of the EDXRF spectra of parchment and pink area.

possibilities for the employed colorants: we could be in the presence of hydrocerussite and/or minium explaining the presence of Pb and considering the choice for red and white pigments. Furthermore, the presence of high amounts of Ca could be due to the use of calcite as a mineral substrate in the creation of the red colorant. There are several references to different purple or red dyes in medieval texts that could have been added to white lead or red lead in order to produce a pink color, Brazilwood being one of them. Aluminum is often a component of the precipitant for red dyes; however, the capabilities of portable XRF setup are limited when concerning such low Z elements in low concentrations. Considering the colorants found in other foral charters, the combination of red dye and lead white seems the most probable.^{1,3}

Brown

The chestnut color can only be found around the illumination in a small casing that serves as a frame for the picture. Through EDXRF analysis, a small peak corresponding to aluminum was detected as well as manganese and iron (Fig. 8). The presence of this elements is indicative of umber pigment ($\text{Fe}_2\text{O}_3 \cdot (\text{H}_2\text{O}) + \text{MnO}_2 \cdot (n \text{H}_2\text{O}) + \text{Al}_2\text{O}_3$). This pigment was very commonly used, and its practice goes back to Prehistory.²³ It can be used as raw earth umber (Raw Sienna earth), in which case the earth was just mined and ground, or as burnt umber (Burnt Sienna earth), when the raw earth umber pigment was calcinated in order to get darker shades.

Inks

Iron gall

EDXRF spectrum analysis indicates the employment of iron-based ink, most likely iron gall ink (Fig. 9). Historically, this type of ink was the most typically used in European manuscripts. It was made from galls, vitriol (FeSO_4), gum arabic as a binder, and an aqueous vehicle such as wine, beer, or vinegar. Vitriol, being the main source of iron in these kinds of inks, could be obtained through mining, and therefore, it could also contain other metals such as copper, aluminum, zinc, or manganese, in addition to the iron sulfate. This

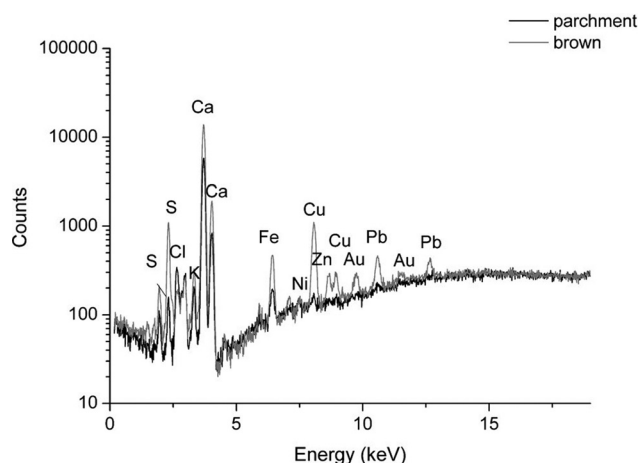


FIG. 8. Comparison of the EDXRF spectra of parchment and brown area.

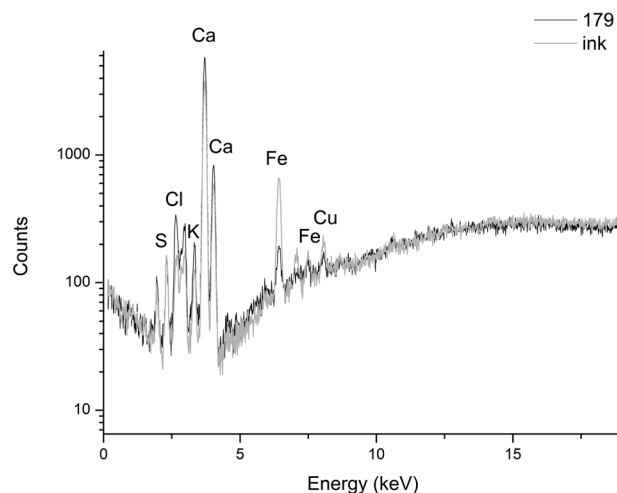


FIG. 9. Comparison of the EDXRF spectra of parchment and ink.

contamination depended on the mine, the galls were collected from Refs. 24–26.

CONCLUSIONS

The study of the *foral* charter of Setubal, performed both *in situ* and in the laboratory, allowed us to conclude that this is an exceptional artwork from many points of view. Although restricted to a dozen, the pictorial materials were subtly combined for the rich decoration of the charter, today in a remarkable state of preservation. The frontispiece defies to the common model by its chromatic expression and the profusion of Renaissance ornaments. Raman spectroscopy enabled the identification of copper sulfate minerals for the green color, instead of the malachite used in all of the studied charters.^{1,3,6} Another remarkable finding was the use of a very uncommon red pigment in Portuguese charters, minium, a very cheap red pigment, instead of cinnabar, the normally used red pigment. Cinnabar has not been identified on the border of the coat of arms, as this is recurrent in other charters.^{1,3,6} The use of red lead or minium on the flags is also unexpected but it better reflected the King's choice for his personal banner of white and red colors, while most of the foral charters exhibit a combination of silver and pink. Essentially, minium gave special emphasis to the royal emblems and highlighted the winged angels.

That contrasts also with the otherwise very rich pigments and metal coatings used profusely in the whole illumination. The palette of colors under consideration put in evidence the fact that pigments not only serve the King's assertiveness policy by their cost but also an important artistic purpose by their specific hue, while applied in documents that should convey the latest aesthetic trend.

This result led to a new look at the statement that a single Royal workshop existed for the elaboration of Manueline foral charters.^{27,28} If this was the case, the pigments used in the charter of Setubal should be the same as the ones employed in the charter of Teixedo,¹ Sintra,³ and Vila Flor.⁶ The pigments which were used in this work brought new horizons on this issue, suggesting that the idea of a unique workshop is incorrect.

ACKNOWLEDGMENTS

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