El Greco (1540-1614) was a famous Renaissance artist originally from Crete whose personalized and original artistic expression gained him fame all over Europe, especially in Spain. He had many followers and his works were copied extensively. The Fine Arts Museum of Seville keeps two interesting canvases in its collection. The first one is the original El Greco work *The portrait of his son Jorge Manuel* (towards 1600), while the second one, *The portrait of Fray Hortensio Félix de Paravicino*, was painted by an anonymous follower (2/2 16th century). The comparison of both portraits was of interest, especially with regards to the applied pigments, with the aim of finding possible similarities and differences. The elemental analysis was performed using non-destructive XRF, which permitted to examine the artworks *in situ*. The results of both paintings showed the use of lead white, yellow ochre, umbra, a copper-based green pigment and probably an organic red and black. But they also revealed important differences in the selection of red and blue pigments, which clearly distinguishes the original work from the anonymous one.

1 Introduction

Doménikos Theotokópoulos (1541-1614), known as El Greco, is considered to be one of the principal artists of the Renaissance. He was a painter, sculptor and architect, who made considerable changes in the artistic expression of the time. He was born in Crete, a Greek island, which at the time belonged to the Venetian Republic. Stylistically, it was a centre of Post-Byzantine Art in which El Greco was trained. Towards 1567 he travelled to Venice and Rome. During his stay in Italy, he changed his style according to the elements of Mannerism and Venetian Renaissance with painters such as Titian, Tintoretto and Veronese as well as Michelangelo. In 1577 he moved to Toledo in Spain where he worked until his death. In this last period of life he produced his best works, today spread among various museums and collections. His style is characterized by the contemporary Spanish mysticism, expressed by long figures and contrasts of light and shades, where colour plays a very important role. Although he was not accepted by the general artistic taste in his time, he gained his
reputation through the following centuries when numerous followers appeared and his works were copied extensively.

The Fine Arts Museum of Seville, the second most important gallery in Spain, has in its collection two interesting canvases. The first one, The portrait of his son Jorge Manuel (Figure 1), is original work painted by El Greco towards 1600. The second one is The portrait of Fray Hortensio Félix de Paravicino (Figure 2) and was painted in the second half of the 16th century by an anonymous follower of this famous Greek painter. Stylistically, both portraits are presented in a similar way, using dark tones for the background and the vestments, while the face and white gorget make strong highlights.1-6

The comparison of both portraits was of interest, especially regarding the pigments applied. Our work focused on finding possible differences that would permit to distinguish both artists on the basis of their use of pigments and painting techniques.

None of the examined canvases were under conservation-restoration, which is why the non-destructive X-Ray Fluorescence (XRF) technique was chosen for analysis.7-11 It permitted both selected paintings to be examined in situ, in the gallery space. The technique is very useful for non-destructive studies of art materials and objects. The XRF analysis provides data on elemental composition, revealing the chemical elements presented in the irradiated point. On the basis of the elemental composition it is possible to identify the majority of inorganic pigments; however the presence of organic pigments can not be confirmed, because usual XRF systems do not detect elements with a Z lower than 13 or 14.

2 Materials and Methods

The equipment used for the present work is a portable device, with an X-ray generator RX38 from EIS.S.L. with a W anode, while the detector is a silicon-drift one (SDD) with energy resolution of 140 keV. An Al-filter of 1 mm was coupled to the tube to suppress the characteristic W peaks from the anode in spectra obtained during the radiation. The analyses were carried out during the days when the museum is closed to the public (Figure 3). In the original work 63 points were analysed, while in the anonymous one 23 points were selected. All the measurements were done under the same fixed conditions: 80 µA of cathode current, 29.5 keV of applied high voltage and 300 s of preset live time. This permitted a comparison of the spectra to be made. Semi-quantitative analysis was done by using the areas of XRF peaks obtained in the multi-channel analyser. These areas can provide elemental concentrations, because they are proportional to the weight concentrations and their square root can serve as a measure of experimental error. Therefore, comparisons between the content of one particular element in different samples of similar composition can be made directly through the respective peaks of that element.

Pigments were identified according to the characteristic energy (keV) of the X-ray peaks in each obtained spectrum, which corresponds to specific chemical elements. The spectra were also compared with a
pigment database that was elaborated at CNA, analysing commercial pure pigments from old traditional recipes. Also, bibliography on pigments was consulted, in order to make attributions of the different pigments.12-22

3 Results and Discussion

3.1 El Greco: The portrait of his son Jorge Manuel

The most important chemical elements evident in the spectra obtained from this painting are Pb, Cu and Fe, which are present in all analysed points. In many of them also Ca, Mn and Hg can be detected. Calcium probably belongs to gypsum, used in the preparation layer.23

Lead peaks are the highest in all spectra and show the important role of a certain Pb compound (lead white, massicot, litarge or minium), not possible to identify with the XRF technique used. It must have been applied in the imprimation and not only as a colour. It is known that El Greco used lead white in his early painting imprimations, while in his later ones he used to apply minium.23 This must be also the case of Jorge Manuel’s portrait, since in some areas an orange-reddish under-layer can be observed. Lead counts vary depending on the area of the painting, being higher in the lighter areas (around 630 counts per second or cps) and lower in the darker ones (around 150 cps). However, it is surprising that these counts are lower in the spectra taken from the protagonist’s face carnation (around 260 cps) than in those from the dark background (around 460 cps). To find a logical explanation for this, additional complementary studies should be carried out.

The painting was executed using a mixture of different inorganic and organic pigments. For white colour, lead white was applied, found in the white gorget and cuffs, as well in all the highlights (high Pb peaks). It was also the basic pigment for carnations, made as a mixture with a small amount of vermilion (low Hg peaks) and probably some organic carmine (Fig. 4). Dark shadows were made with a diluted mixture of ochre (Fe) and some Cu-based pigment, probably azurite, characterized by higher Cu peaks in these areas.

A copper-based pigment, mixed with toasted ochre or umbra was used also for hair, beard, eyes and eyebrows of the protagonist. Carmine, a red organic pigment, is characteristic for El Greco’s palette,23 but it can not be detected by XRF. However, it must have been used also for the red lips, red corners of the eyes and in some parts of the left ear. In the spectra taken from these areas (Fig. 4a) no characteristic chemical elements for any inorganic red pigments are seen, although the red colour appears to be quite intense. This fact indicates the use of some organic red pigment, in this case probably carmine.

Figure 3: XRF measurements taking place in situ at the Fine Arts Museum, Seville, Spain.

Figure 4: XRF spectrum of Jorge Manuel’s carnation; the point under his left eye. The carnation is made of Pb white and small amount of vermilion (Hg), the shadows with a mixture of ochre (Fe) and Cu based green or azurite.

Figure 5: Comparison of two XRF spectra taken from the lips of both male figures: (a) Juan Manuel’s lips are made of red ochre (Fe) and probably carmine (no XRF information provided); (b) Paraviccino’s lips are painted with red ochre (more prominent Fe peaks) and vermilion (Hg).
Results of the dark greenish background show intense peaks of Mn, Fe and Cu (Fig. 6a). Mn and Fe peaks change simultaneously, demonstrating that they belong to the same pigment: umbra. The dark background colour is a mixture of natural or toasted umbra and some copper green pigment, which can not be identified more precisely. It was probably extended all over the painting surface. The author's signature on the background was written with an organic black pigment, not detectable by XRF.

The spectra of the dark colour of the black vestment (Fig. 7) show peaks of Fe, Cu and Pb, of which the counts are lower than those of the background. The principal pigment must be an organic black, mixed with some other pigments (ochres, azurite, and lead white) to obtain the desired tonality.

The palette and brushes in Jorge Manuel’s hands were painted with yellow ochre, shadows were modelled with a dark Cu-based green pigment, while the highlights were modelled with lead white. For the colours on the palette the painter used lead white (Pb), yellow ochre (Fe), red earth for light red (Ca, Fe) and a mixture of red earth and carmine (higher Ca peaks and lower Fe peaks) for the dark read colour. The dark, almost black colour is a mixture of umbra and a Cu-based pigment (Mn, Fe, Cu).

In some areas a low presence of Ba and Zn can be detected, indicating some later interventions with modern pigments (Zn white). In red areas signs of Cd were observed, demonstrating some cadmium red retouches.

3.2 Anonymous: The portrait of Fray Hortensio Félix de Paravicino

The spectra of the second painting, made by an anonymous author, gave quite similar results, however some important differences were found. As in the original El Greco’s canvas, high Pb peaks were detected in all the spectra also in the anonymous one. They indicate the existence of a lead compound, applied in the imprimation layer. With XRF it’s not possible to distinguish, if lead white or minium were used. Low Ca peaks must belong to a gypsum preparation layer.

The white pigment used for the white hood and for the carnation is lead white. The colour of carnation was obtained by adding a small presence of vermilion (Hg) and probably also some yellow ochre (Ca, Fe) to lead white. On the other hand, low peaks of Co and Ni (Fig. 8) revealed the use of blue smalt to obtain the cold face colour. In many cases the Kα Co peaks are overlapped by the Kβ Fe peaks and therefore are difficult to be identified, however in some cases are quite clearly seen. Neither yellow ochre nor smalt was found in the original El Greco painting, although the last one does belong to his palette, according to Garrido.23

Smalt was used by the anonymous author also for the dark areas of the hair, beard, and eyes, while the basic brown pigment for these areas is natural or toasted umbra (Mn, Fe). The pupil must have been painted with some organic black pigment. The lips of Fray Hortensio were made with a mixture of red ochre and vermilion, clearly seen by Fe and Hg peaks (Fig. 5b). So, apparently, there is no use of carmine (as it was the case in the original painting), which is another obvious difference between both portraits.

Figure 6: Comparison of two XRF spectra taken from the background of both paintings: (a) El Greco’s background (straight line) contents more Cu based green pigment, while (b) in the anonymous one (dot line) there is a very low content of it and Ca peaks are higher.

Figure 7: XRF spectrum of the black Jorge Manuel’s dress. A black organic pigment, mixed with some ochre (Fe) and azurite (Cu) was used.

Figure 8: XRF spectrum of the Paravicino’s carnation. A small presence of smalt (Co, Ni) can be observed, added to the Pb white, ochre (Fe) and vermilion (Hg) mixture.
The dark background was painted with a mixture of umbra (Mn, Fe) and some copper based green pigment; Cu is presented by much lower counts (0.5 cps) than in the original painting (12.4 cps, Fig. 6b). The dark vestment of the monk was made with natural or toasted umbra, as shown by Mn and Fe peaks whose counts are similar to those from the background spectra. However, higher Ca peaks can be observed in the vestment, identifying a possible use of some organic black pigment (bone or ivory black) mixed with the original brown colour. In some areas low peaks of Ti, Zn and Ba can be observed, revealing later interventions with modern pigments Ti and Zn white.

4 Conclusions

Two paintings from the collection of The Museum of Fine Arts in Seville were analysed by the non-destructive XRF technique. The first one is the original El Greco work The portrait of his son Jorge Manuel (towards 1600), while the second one, The portrait of Fray Hortensio Félix de Paravicino, was painted by an anonymous follower (2/2 16.century). The comparison of pigments in both canvases was of interest, allowing us to find similarities or differences. The XRF data for both paintings showed the use of lead white, yellow ochre, umbra, some copper-based green pigment and probably an organic black. But they also revealed an important difference in the presence/ absence of pigments between both paintings: the anonymous follower applied yellow ochre and smalt in carnation, hair and beard, which were not found in El Greco’s painting. The red pigment applied by El Greco was mostly organic carmine, while the anonymous author used red ochre and vermilion.

The original painting is characterized by intensive Pb peaks in all spectra, showing an important role of some lead compound used in the imprimation layer, probably minium. Lead white was applied in white gorget and cuffs, as well as the basic carnation pigment. In this case, some vermilion and probably some carmine, red organic pigment, were added. Carmine was used also for Jorge Manuel’s lips. The dark greenish background was made with umbra and some copper based green pigment, as shown by Mn, Fe and Cu peaks. The dark colour of the vestment was painted with some organic black pigment, mixed with ochre (Ca, Fe), azurite (Cu) and lead white (Pb). The painter applied the organic black pigment also for his signature on the right side of the painting. The palette and the brushes in protagonist’s hands were carried out with yellow ochre, while the colours are lead white, yellow ochre, umbra, red earth and carmine.

Also the second painting must have a lead compound imprimation, but on the basis of XRF spectra it is not possible to identify weather it is lead white or minium. The dark greenish background is carried out with a mixture of umbra (Mn, Fe) and some Cu based green pigment, the quantity of which is much higher in the original canvas. The carnation was made with lead white and some vermilion as in the Jorge Manuel’s portrait, but the analysis showed also some smalt and yellow ochre. Small was detected as well in the Fray Hortensio’s hair and beard. His lips were modelled with red ochre and vermilion and not with carmine as el Greco used to do. Umbra was applied for hair and the dark dress, maybe also some organic black was added to obtain a darker colour. In some areas posterior interventions with modern pigments Ti and Zn white were detected.

5 Acknowledgements

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6 References

11. S. Palazzi, Analisi chimica per l’arte e il restauro. Principi, tecniche, applicazioni, Nardini editore, Fiesole, Italy, 1997

