Article / Artigo

Application of energy dispersive X-ray fluorescence spectrometry to polychrome terracotta sculptures from the Alcobaça Monastery, Portugal

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Abstract
Portable energy dispersive X-ray fluorescence spectrometry (EDXRF) was used in the Alcobaça Monastery, in order to study the chromatic coatings applied to terracotta statues that belong to two seventeenth-century monumental groupings. The main goal of this scientific approach consisted in determining the elemental composition of the constitutive layers and in trying to reconstitute the existing polychromy, taking into account the technical aspects observed at naked eye. The measurements carried out by EDXRF allowed a first material characterization of these artworks. By comparing the results obtained in each statue, it was possible to attest the application of a seventeenth-century coating to each one and at least a subsequent intervention in the form of a refurbishment or a new polychromy. According to the materials employed in their production, it appears that the refurbishment is likely dated from the 19th century while the new polychromy is still dated from the 18^{th} century.

Keywords
EDXRF
Sculpture
Polychromy
Pigments
Terracotta
Cultural Heritage

Aplicação da fluorescência de raios X dispersiva em energia a esculturas em terracota policromada do Mosteiro de Alcobaça, Portugal

Resumo
A técnica portátil e não invasiva de fluorescência de raios X dispersiva em energia (EDXRF) foi utilizada no Mosteiro de Alcobaça. Foi aplicada ao estudo científico dos revestimentos cromáticos de estátuas em terracota pertencentes a dois conjuntos escultóricos datados do século XVII. Tratou-se de determinar a composição elementar dos estratos constituintes e tentar reconstituir os tipos de policromia aplicados com base em exames prévios feitos à vista desarmada. As medições efectuadas por EDXRF permitiram contribuir para uma primeira caracterização material destas obras. Comparando entre si os resultados obtidos, comprovou-se a presença de policromias seis-centistas e de pelo menos uma intervenção posterior à manufactura das esculturas. Chegou-se à conclusão que a datação do estrato superficial que visava o conserto ou a repolicromia das peças poderia ser datado do século XVIII numa obra e do século XIX na outra, pelo tipo de materiais empregues nas suas realizações.

Palavras-chave
EDXRF
Escultura
Policromia
Pigmentos
Terracota
Património Cultural

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Introduction

As the parent complex of the Cistercian community in Portugal, the Royal Abbey of Saint Mary of Alcobaça (hereinafter referred as Alcobaça Monastery) goes on holding several sets of monumental polychrome terracotta statues mostly produced by the monks during the 17th century [1].

Two of these sets are especially relevant for the present study: *1)* the composition of thirteen sculptures depicting the *Delivery of the Keys* (also called the *Apostleship*, in which Christ is giving the key of the kingdom of heaven to St. Peter), intended for the former Chapel of Saint Peter and known as the early work of the 17th century; and *2)* the set of sixteen sculptures the Abbot Friar Sebastian de Sottomayor commissioned during one of his three-yearly mandate (1675-1678) for the reredos of the presbytery, completed by the statues of *St. Gabriel* and the *Virgin Mary* depicting *The Annunciation*, which overhanged the choir on either side of the main chapel.

Figure 1. Statue of the *Virgin Mary* which was part of the set of monumental terracotta statues commissioned by the Abbot Friar Sebastian de Sottomayor during his three-yearly mandate (1675-1678) for the choir of the Alcobaça Monastery.

These two groupings were dismantled in the 1930s. The former is actually housed in the storage space available at the abbey, where most of the constitutive sections (*tacelos*) of the disassembled statues were stored separately, and not piled up to avoid more extensive damage to the set. The latter is displayed in the chapter house along the four walls, each sculpture having been reassembled. In this new arrangement, *St. Gabriel* and the *Virgin Mary* are flanking the entry of the chapter house as they originally flanked the chancel of the church.

In the framework of the three-years national project *TACELO - Studies for the conservation of monumental terracotta sculptures from Alcobaça monastery* (PTDC/CTE-GIX/111825/2009), the current study focuses on the application of portable energy dispersive X-ray fluorescence (EDXRF) spectrometry to the polychromy of two terracotta statues belonging to the aforesaid ensembles.

Energy dispersive X-ray Fluorescence (EDXRF) spectrometry is a non-invasive technique that provides information on the elemental composition of the constituent materials of the objects under study.

The portable instrument was designed at the Atomic Physics Center of the University of Lisbon to provide on-site analysis in the better condition of measurement, taking into consideration the spatial geometry of each sculpture. The technique is totally non destructive since it does not require any sampling.

Methodology

The methodology adopted in this study took into consideration several aspects:

Apostles' polychromy

According to *1)* the manufacture of the *Apostles'* ceramic body, divided into sections to facilitate the drying of the clay, the firing procedure and the permanent reassembling of the figures in their resting place [2], and *2)* the final coating applied to give them a more realistic appearance matching the Baroque taste, the upper section consisting of the bust and head is the most representative of the palette used for each statue. This section comprises as much the polychromy applied to the garment as the one rendering the hair and flesh, and moreover, any layers that may have been added in subsequent intervention(s). It should be noted that the face was always the main focus and object of worship, and could be refurbished over time independently of the other parts of the image. Given this factual situation, the upper section (*tacelo*) corresponding to the bust of an *Apostle* (still not identified and designated as *Apostle 2*) was selected in order to assess the elemental composition of the distinct polychrome areas by in situ EDXRF analysis.

Virgin's polychromy

The sculptures of the choir were entirely painted white, probably in the late 18th century or the early 19th century to bring them into fashion according to the Neoclassic style then in force. Even though the set goes on exhibiting this monochrome overpaint, the *Virgin Mary*, from the pair of statues depicting *The Annunciation*, gave rise to the removal of this outer coating to reveal the polychromy underneath. This earlier polychromy applied to the entire figure (only partially preserved nowadays) is giving evidence of an abundant use of gilded surfaces and a larger palette of colors.

This polychromy presents similar features to the ones of the selected *Apostle* and the other statues of the same set, and is believed to be the original coating achieved in the last quarter of the 17th century. It was also studied by EDXRF and further compared to the *Apostle'* finishes.

Primary sources and other references

The polychrome coatings actually visible on the two statues under consideration are imitating golden brocade fabrics to achieve the surfaces of the clothing, by evidencing paint layers which were applied over gilding and stripped off according to specific patterns to expose the shiny gold beneath. These characteristics readily refer to the seventeenth-century treatises by Filipe Nunes [3] and Francisco Pacheco [4], and more specifically to the technique of *sgraffito* (*estofado* in Portuguese) well described by these authors. Therefore their works were considered of primary importance to further interpret the EDXRF spectra, besides other treatises deemed relevant in this research. Portuguese contracts of polychromy were also consulted as valuable art technological sources for the additional information they provide. Moreover, any study on Portuguese polychrome sculpture with similar features and recent findings on the materials used in sculpture and painting were also taken into account, to verify whether the elemental composition of the different matrices analyzed are pertinent to the material and technical particulars from the 17th century or expected in latter times.

Layers build-up

In research involving pictorial layers on three-dimensional artworks, special attention has to be paid to the fact that, from one area to another, the number of layers may vary considerably: either because certain final optical effects may require a more complex build-up than others [5], or because, as already mentioned, some areas would have been the subject of occasional interventions when others would have remained untouched. An inventory of areas of interest was made. Wherever possible, when some losses within the polychrome surface allowed the analysis of an underlaying ground, metal coating or paint, its measurement was performed individually to better understand its contribution within the spectra.

Figure 2. Detail of the statue of the *Virgin Mary*'s back showing the seventeenth-century original polychromy actually visible after subsequent interventions have been removed.

Experimental procedure / Analytical protocol

The EDXRF equipment used in this study for elemental analysis consists on the Amptek XR-100SDD, thermoelectrically cooled and the X-ray generator Amptek ECLIPSE IV with Rh anode. For collimating the beam an acrylic and brass support with a 2 mm pinhole in Ta was used. The components are assembled on an aluminum structure in a 45º geometry. A macroscopic screening of the statues was made, and 11 measurements were performed *in situ* for the upper section of the *Apostle*, and 15 for the statue of the *Virgin Mary*. All spectra were acquired during 150 s under working conditions of 40 kV and 40 μA.

Results and discussion

Tables 1 and 2 provide the potential interpretation of the overall data gathered in the areas analyzed by EDXRF technique on the *Virgin Mary* and the *Apostle 2*, respectively.

Virgin's polychromy

The statue of the *Virgin Mary* was studied first since the ground layer, the bole layer, gilding, the colored surfaces and other potential superficial finishes examined in several areas could be analyzed separately (Figures 1 and 2). The EDXRF measurements were carried out in this specific order to better assess the elemental composition of each layer.

Black substance

A black layer remained visible in the mortise made in the *Virgin*'s left wrist and on the surface of the sleeve as well, where this black substance seems to have run over.

The spectrum of this black layer (Figure 3) provides essentially the elemental composition of the ceramic body itself, since the main elements detected were Fe, Ca, K, Mn, Sr, Rb and Zr. The elements Mg, Al and Si, also specific to clay, have very low energy fluorescence lines and are strongly attenuated in the air path to the detector, so their detection was not expected by EDXRF. This composition is especially consistent with calcium-rich clay mineralogy as described by Coroado and co-workers in a research carried out on monumental terracotta sculptures from Alcobaça Monastery [6]. The study was done by X-ray diffraction and showed the presence of quartz, calcite, gehlenite and alumino-silicates as moscovite and feldspars phases. It should be noted that these phases, in particular the presence of calcite and gehlenite together, allowed to estimate the firing temperature round about 850 ºC [6].

Because of the specific location of the black substance in what was a tenon-and-mortise joint, this substance likely refers to the wax-based mixture used to fix the hand in place. Although basically composed of wax and natural resin(s), this kind of organic cement (called *betume* in Portuguese) could contain inorganic additives, such as a mineral powder [2, 7] and sometimes an earth pigment [8], to increase its viscosity, strength and chemical compatibility with the terracotta elements that were to be assembled [9-10]. In case a mineral was added to the cement, it is expected to be either powdered bricks or crushed recovered fired pottery, thus of the same nature as terracotta, or powdered marble or lime, thus calcium-rich materials. All of them are hardly distinguishable from the ceramic body itself. The same can be expected from earth pigments. This could explain why no other elements have been found. On the other hand, the search for a black pigment, able to justify the color observed, is not

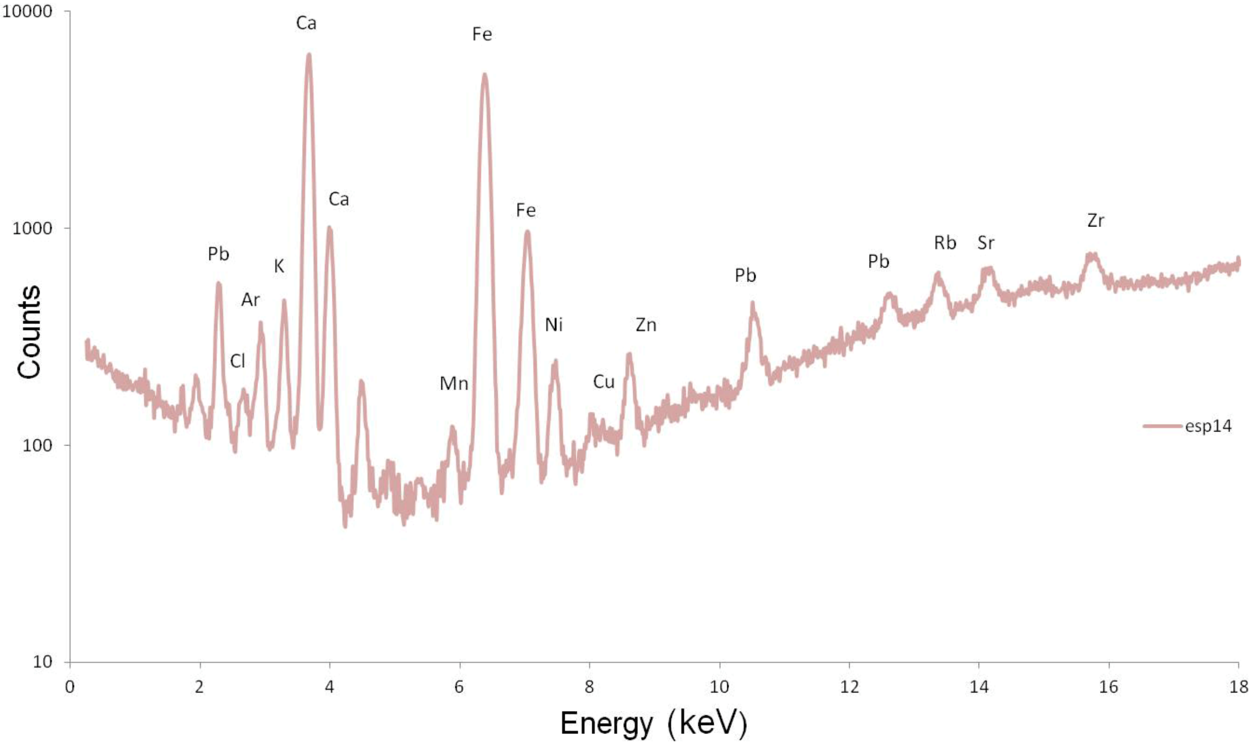

Figure 3. EDXRF spectrum of the black substance observed on the *Virgin*'s sleeve.

Table 1
Virgin Mary — Potential interpretation of the overall data obtained by EDXRF

EDXRF spectra	Detected elements	Interpretation
All spectra (Priming) 05 - Original ground layers 06 - Original ground layers (2) 11 - Overpaint ground layer	Ca / S (?)	Chalk / Calcite: $CaCO_3$ One or more phases of calcium sulfate: Anhydrite / *Gesso grosso*: $CaSO_4$ Dihydrate or synthetic gypsum / *Gesso mate*: $CaSO_4{\cdot}2H_2O$
09 - Pink layer 13 - Flesh tone (hand) 10 - White overpaint	Pb	One or more phases of white lead: Plumbonacrite: $Pb_5O(OH)_2(CO_3)_3$ Hydrocerussite: $2PbCO_3{\cdot}Pb(OH)_2$ Cerussite: $PbCO_3$
All spectra (with *estofo*) 04 - Bole	Fe	Bole / Kaolinite / Fine clays + iron oxide (II): $Al_2Si_2O_5(OH)_4$ + FeO
04 - Bole 13 - Flesh tone (hand) 15 - Red sleeve 03 - Black hair	Pb	Red lead: Pb_3O_4
04 - Bole 13 - Flesh tone (hand) 09 - Pink layer – *estofo* 15 - Red sleeve – *estofo* 03 - Black hair	Fe	Hematite: Fe_2O_3
15 - Red sleeve 13 - Flesh tone (hand)	Hg	Vermilion: HgS
All spectra (with *estofo*) 04 - Bole 03 - Black hair / gilding 14 - Black layer (wist)	Fe	Goethite / Ocher – Earth pigments containing Fe: FeO(OH)
04 - Black hair / gilding	Mn	Manganese dioxide (IV): MnO_2
03 - Black hair / gilding 14 - Black layer (wist)		Carbon black: C Bone black (containing hydroxiapatite): C + $Ca_5(OH)(PO_4)_3$
07 - Blue	Co / Ni / Fe / Ca / K	Smaltite: $(Co, Ni)As_{3-2}$ Cobaltite: (Co, Fe)AsS
07 - Blue 08 - Blue 2	Cu	Azurite: $Cu_3(CO_3)_2(OH)_2$
07 - Blue 08 - Blue 2	Ca	Indigo – blue organic dyestuff Precipitated over calcite?
15 - Red sleeve – *estofo* 09 - Pink layer – *estofo* 07 - Blue – *estofo* 12 - Bole – *estofo* 03 - Black hair / gilding	Au	Gold leaf – precious metal Gold alloy or pure gold? The composition should be analyzed by other methods

conclusive. A carbon black of an uncertain origin, called *pó de sapatos* (literally "black from shoes") remains obviously under the limit of detection; it was a synthetic pigment widely used in Portugal, obtained by combustion of vegetable matters by collecting the resulting soot [11]. The presence of phosphorus specific to an animal carbon black containing hydroxiapatite, with the formula $Ca_5(OH)(PO_4)_3$, is challenging, since the Kα peak of P at 1.94 keV overlaps with the existing Ca escape peak at 1.92 keV. Finally, a black earth, such as the one designated as *terra preta* in the account books of the Tibães Monastery [12], only confuses matters for it is expected to contain calcium carbonate, iron, manganese and silica [13].

Ground layer

Besides the elemental composition specific to the ceramic body, in which Ca, Fe and Sr were mostly identified, the EDXRF spectrum characterizing the white ground layer (Figure 4, red line) put in evidence three elements which may relate to the inert — or inerts — employed at the priming stage: Ca, eventually related with a calcium-based material; S, which may be associated to Ca in case calcium sulfate-based layers were applied; and Pb, referring to a white lead-based ground. In the 17th century, in Portugal, a whiting — thus made of chalk ($CaCO_3$) — is very unlikely because it was more specific to the northern region of Europe, while a ground made

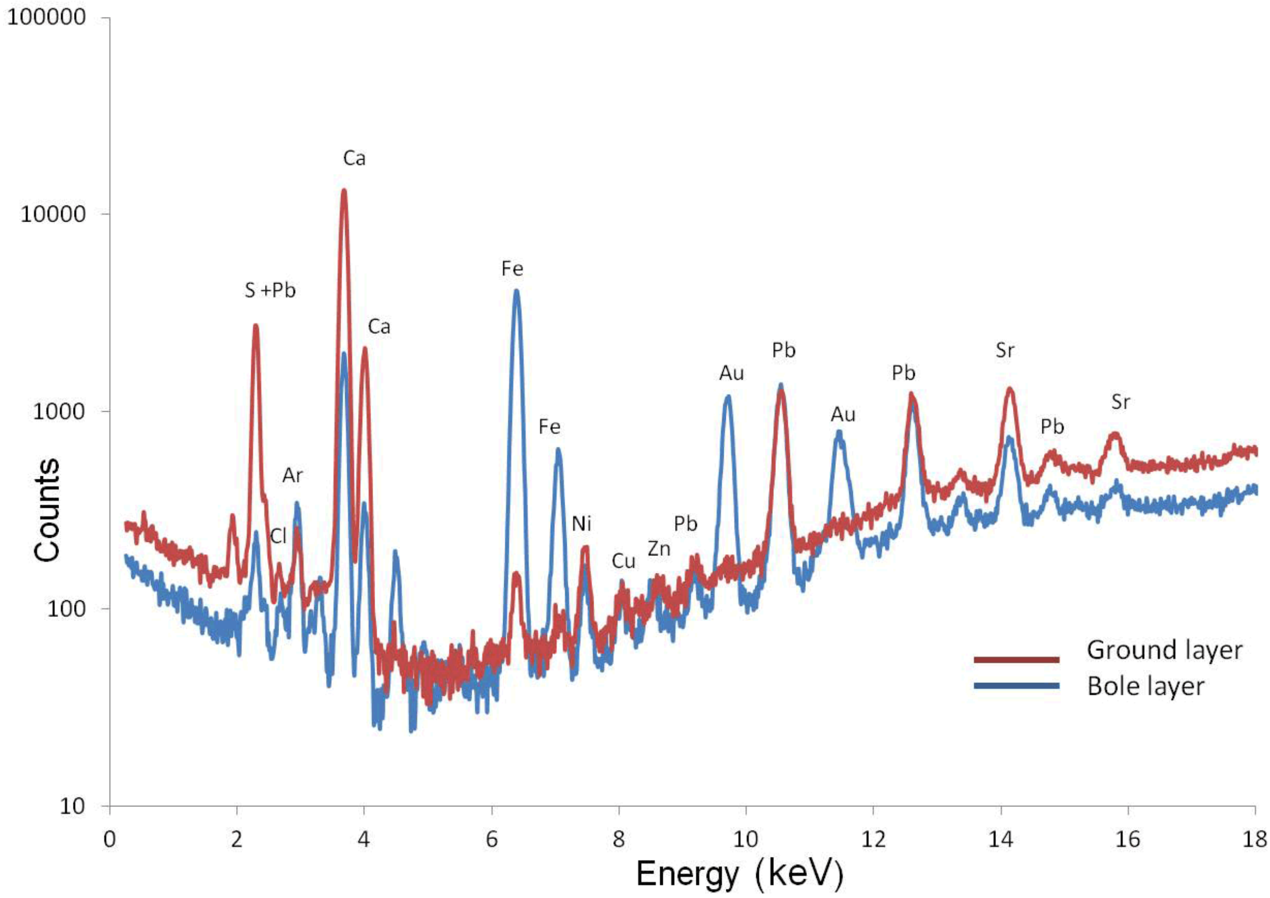

Figure 4. Comparison between the EDXRF spectra of the original ground layer and the bole layer observed on the statue of the *Virgin Mary*.

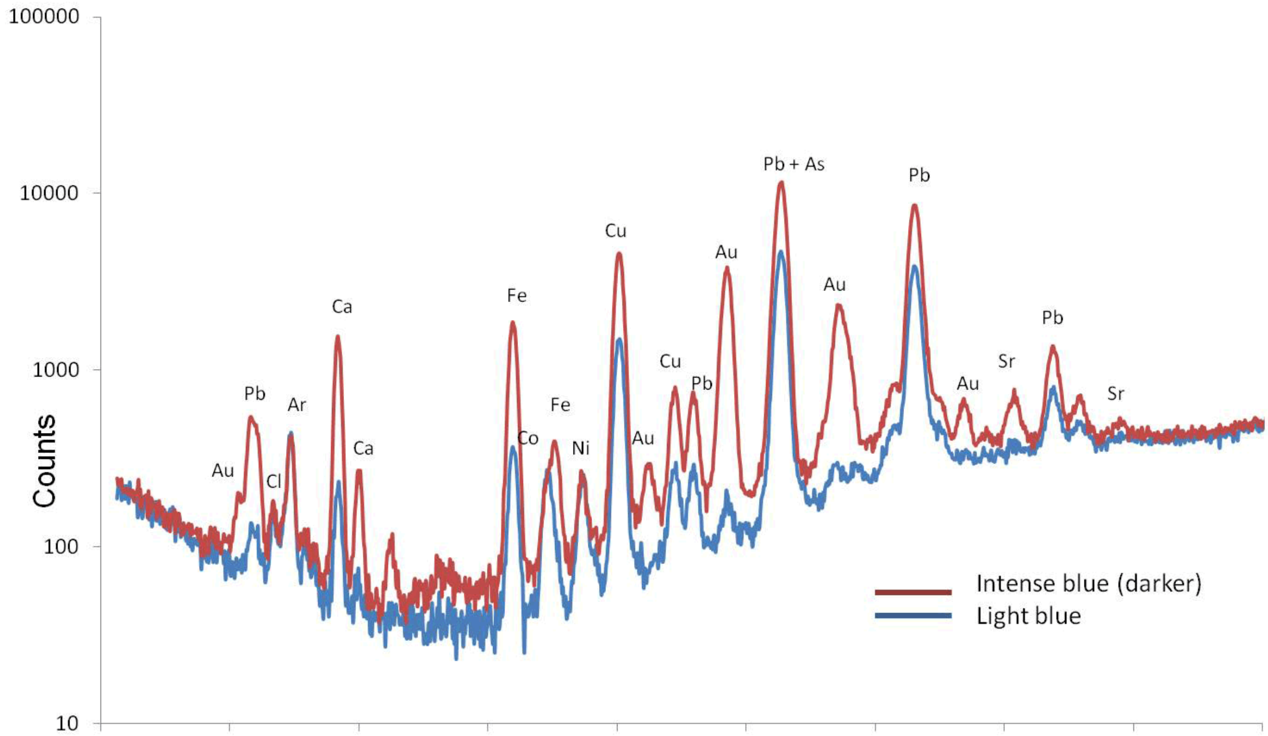

Figure 5. Comparison between the EDXRF spectra of the darker blue paint and the lighter blue paint observed on the *Virgin*'s cloak.

of gypsum ($CaSO_4·2H_2O$) perfectly fits the material most available in southern Europe and the practices then involved in sculpture. A double ground implying a base layer of *gesso grosso* consisting of synthetic anhydrite ($CaSO_4$) and a top layer of *gesso mate* consisting of synthetic dihydrate or gypsum ($CaSO_4·2H_2O$), as mentioned by Nunes [3] and Pacheco [4], was, in fact, the most in usage in water gilding and *sgraffito* technique performed on Baroque wooden images [9, 14-20] and terracotta statues as well [18, 21]. Its use is attested within the materials purchased by the Benedictine monks in 1682 for the terracotta monumental grouping displayed in the sacristy of the Tibães Monastery [12]. Even though a lead-based priming was far from being habitual, it is not excluded. This kind of ground layer was already identified in other Portuguese wooden or terracotta sculptures produced during the 17th century [18, 22]. It should be noted however that, in the statues from Alcobaça, the presence of Pb may be rather justified by the subsequent application of the white and monochrome overpaint branded with the Neoclassic style (discussed below). The recurrent detection of Pb in all spectra irrespective of the material to be analyzed, likely due to particles of white lead trapped within the damaged original polychrome coating, seems to validate this latter explanation.

Bole layer

A reddish bole was systematically observed in many losses of the gilded surfaces. The comparison between both spectra of the ground layer and this bole layer (Figure 4, blue line) stresses the fact that the main detection of Fe within the bole is directly related to the iron oxide typical of the earthy clay, precisely red, employed as the base for the gold leaf. Even though the bole was native from Armenia as Vasari referred to it [9, 23] — thus its name 'Armenian bole' already employed over time and in Portuguese contracts of polychromy [14-17] — nothing is less certain that, in Portugal, this material ever came from this region in the last quarter of the 17th century [9]. Further analysis, by means of X-ray diffraction for example, should be carried out to distinguish the true quality of this bole: whether it is the Portuguese fine ocher Cennino Cennini spoke highly of [24], the color of which has been reinforced by the addition of red iron oxide for example [9], or one of the famous boles then sourced in Spain [4], as the one called *bolo de Llanes* from Castilla [25-26].

Gilding

The detection of Au in the spectrum of the bole layer (Figure 4, blue line) aided the shiny yellow metal coating to be readily identified as the most precious metal, here laid on the statue in the form of hand-beaten gold leaf. Neither Ag nor Cu was detected. This suggests that the gold was not alloyed, or that Ag and/or Cu present in very low amount remained under the limit of detection, all the more because the metal leaf is extremely thin, expected to be less than 1 micron thick [27]. The deep hue of this gold and its bright appearance are in agreement with a high-grade gold, certainly pure, therefore non-corrosive, and in usage to transmit both the symbolisms of perfection and transcendence of the Virgin Mary. Gold leaves were place side by side (and slightly overlapped on the edges) until covering the whole surface of the garment prior to the application of specific colors to reinforce the iconography of the Virgin.

Blue cloak

While the color blue symbolizes virginity, two superposed shades of blue were observed on the *Virgin*'s cloak, in the depressions of the volumes where the color paints were better preserved over time.

Darker blue paint

The blue color paint in close contact with gilding, and supposedly applied over it immediately after the gold coating was burnished, to obtain the intricate design of a blue brocade fabric, is the more intense one. Marked in red color in Figure 5, the EDXRF spectrum of this darker blue paint shows a complex elemental composition resulting from the combination of the bole, gilding and blue constituents. Given that Pb present peaks of a more significant expression than in the aforesaid spectra, one wonders to which topographic level within the layered structure a lead-based pigment should correspond: whether *1)* to a high reflective underlayer of the blue color, made of white lead as Pacheco recommended it in his treatise "in order to lay the color in a more appropriate manner"? [4]; or *2)* to an admixture of white lead within the blue pigment to produce a lighter tone?; or *3)* to the eighteenth- or nineteenth-century monochrome overpaint already removed but remaining everywhere in the cracks of the original polychromy? Only a cross-section of the blue areas under consideration would shed further light on this question. Whatever the answer, the clear detection of Cu, not to be confused with the tiny Cu peak originating from the collimator (Figure 4), suggests the use of the blue basic copper carbonate mineral known as azurite or fine blue, with the formula $2CuCO_3·Cu(OH)_2$. In Baroque Portuguese sculpture, this pigment was considered as the most appropriate to depict the *Virgin Mary*'s blue garments and was quite indispensable to express her transcendental nature. The recurrent use of azurite in three-dimension artworks during the 17th and 18th century appears to have lasted longer than in painting [18, 28-29].

Lighter blue paint

Regarding the other blue color, of a paler shade, the EDXRF analysis (Figure 5, blue line) put in evidence the elements Co, Ni (accusing here a greater intensity) and As, besides Cu already found in the underlaying blue paint, and Pb as well. The presence of Co, Ni and As suggests the use of smaltite with the formula (Co, Ni)As_{3-2}, member of the cobalt iron nickel arsenide minerals sourced from Saxonia, or erytrite with the formula $(Co,Ni)_3(AsO_4)_2·8(H_2O)$. Both are consistent with the blue smalt pigment, a potassium glass colored with cobalt oxide. The simultaneous use of cobaltite, (Co, Fe)AsS, sourced from Sweden [30-31], is not excluded. Whether all these compounds were present in the pigment should be further studied in order to better define whether the marketed product was of one or more origins. Even though blue smalt was far from being the pigment reference in Portuguese polychrome sculpture during the 17th [9, 32] and 18th century [17], it was widely used in painting since the 16th century onwards [33-34] and also in wall painting, in the chapel over which altarpieces were set to make a handsome contribution to the whole decoration [15, 17]. In this case study, the use of smalt allows at least the identification of a new coating, different from a material viewpoint but respectful of the original color scheme from an iconographic perspective.

Black hair

The same cannot be said with regard to the *Virgin*'s hair. It is mostly black but with gold areas amid the dominant color. Even with a microscopic examination, it proved difficult to determine whether the hair was first entirely gilded, with oil gilding over mordant according to Nunes and Pacheco's treatises [3-4] and then painted black in a subsequent intervention corresponding to the smalt blue paint of the cloak; or originally painted black with glints of gold applied over the color, according to the technique of *peleado* Pacheco fully described [4].

The EDXRF spectrum of the black hair (Figure 6, blue line) put in evidence three elements: Pb, which may relate to the mordant (or *mordente* Nunes referred to [3]), an oily substance made dryer by adding lead-based metallic oxides in it and used to attach the gold leaf in the gilding process [3-4]; Au, which fits the gold coating (either totally or partially laid over the hair); and Cu. The presence of this latter element corresponds perhaps to a low-grade gold, in this case a binary alloy containing a certain amount of copper (Au+Cu); unless it results from the influence of a blue adjacent area of the cloak painted blue with azurite. The fact that the color black is characterized by no element in particular, not even by the presence of P typical of a black pigment of an animal origin (such as bone black), implies that the coloring agent was either pure carbon, of an organic source (like the aforesaid *pós de sapatos*), or a mineral matter (the already mentioned *terra preta* or black earth pigment [12]), the elements of which may be misleading with the underlaying ceramic body and ground layer.

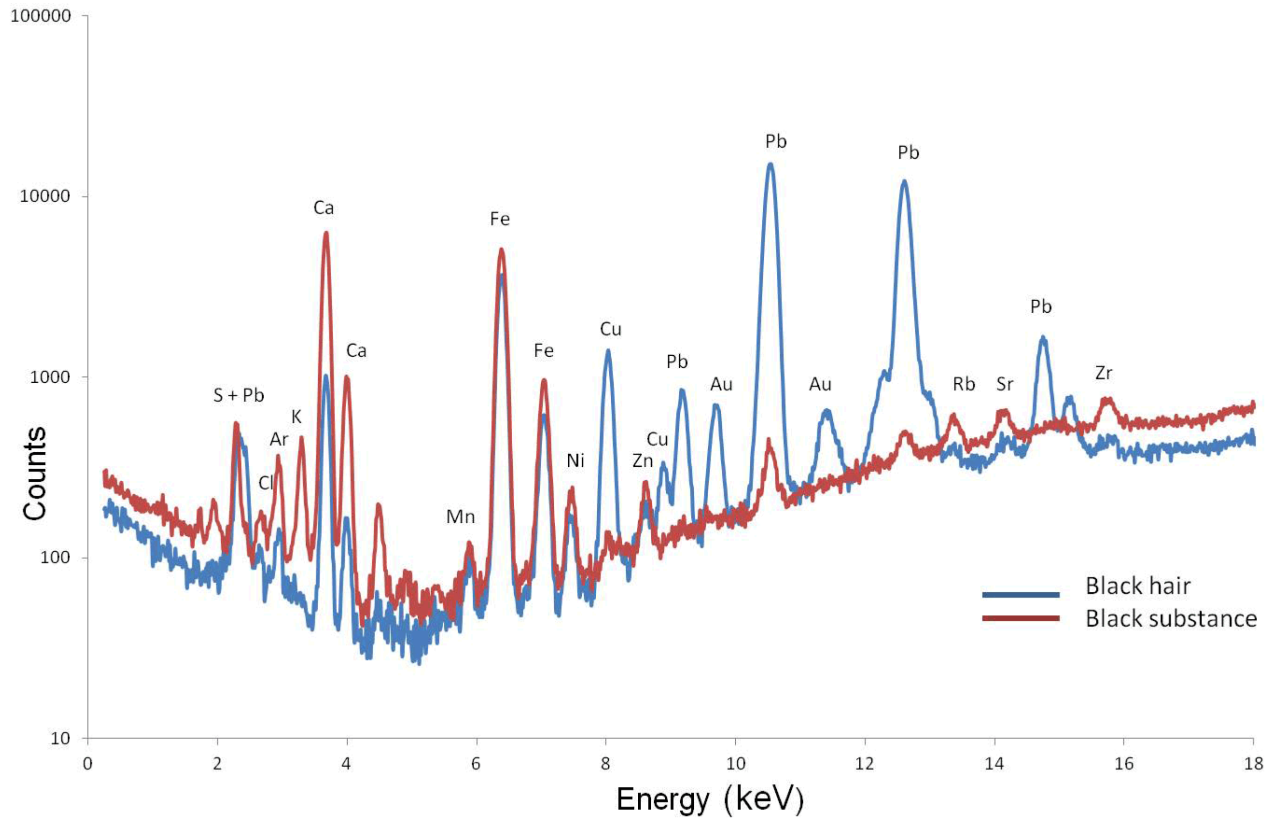

Figure 6. Comparison between the EDXRF spectra of the black paint of the *Virgin*'s hair and the black substance observed on her left sleeve.

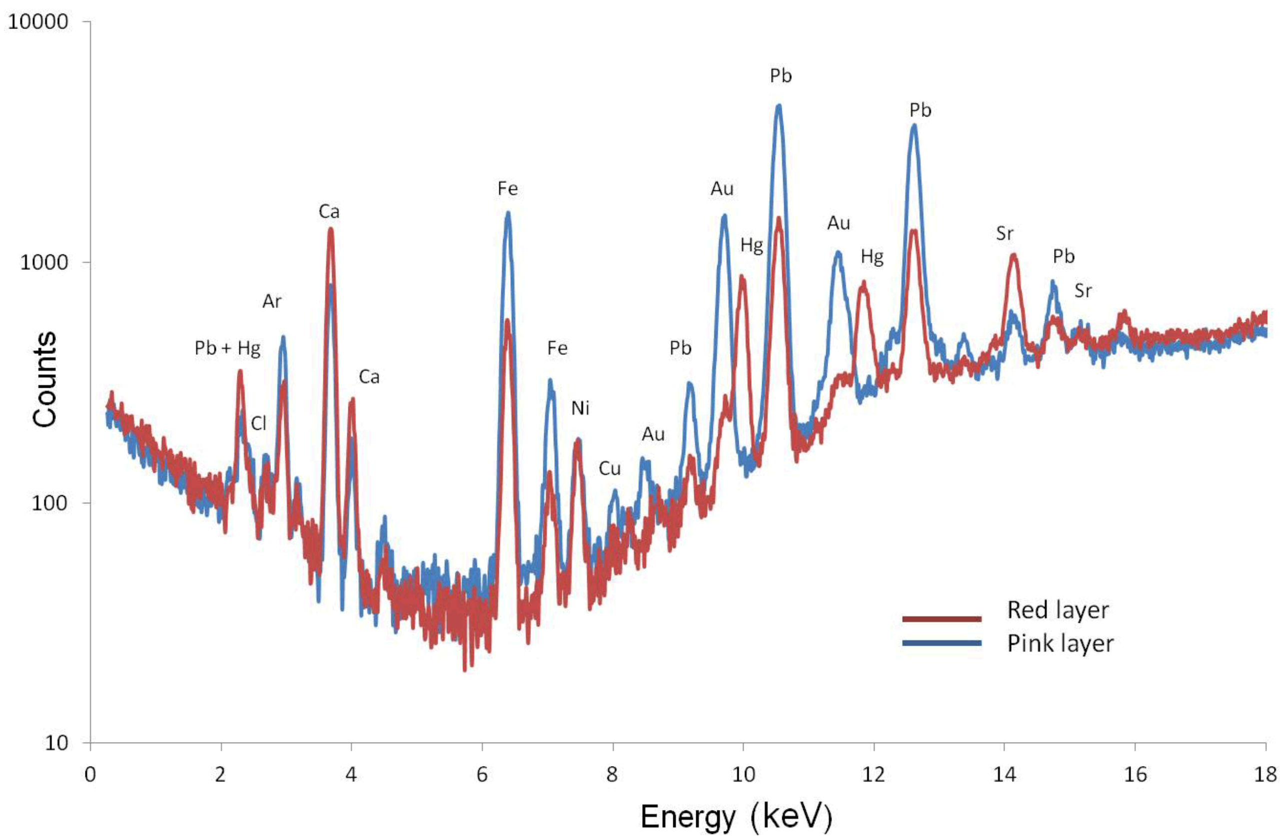

Figure 7. Comparison between the EDXRF spectra of the red paint and the pink paint observed on the *Virgin*'s dress.

Dress of a warm color — red and pink

Regarding the *Virgin*'s dress, it was painted twice over: first red, then pink. This scheme remained visible on her right sleeve.

Red layer

In the red layer applied over gilding, Hg, Au and Pb were detected besides other elements characteristic of the underlaying substrates (Figure 7, red line). The presence of Hg refers undoubtedly to vermilion or mercuric sulfide with the formula HgS, an opaque and costly pigment of a brilliant hue, very often labeled fine (*vermilhão fino*) in Portuguese lists of painting materials [12, 16]; and Au, to the gold coating applied beneath. Pb arose the same considerations as the ones already drawn regarding the blue paints, because it proved difficult to determine, only on the basis of the EDXRF measurement, the material and layer this element matches with.

Pink layer

By comparison of this spectrum with that of the pink color (Figure 7, blue line), the increase of Fe and Pb suggests a mixture containing red iron oxide (Fe_2O_3), also designated as hematite and called *almagre* in Portuguese, and white lead, the so-called *alvaiade* in Portuguese, without excluding red lead (Pb_3O_4), the so-called *zarcão* or *azarcão* [12, 16]. As for the blue paints, this second intervention on the dress conformed to the chromatic relation first established, in accordance with the iconography of the Virgin Mary in which the warm hue symbolizes the Passion of Christ. In this case, the pink color of the dress was probably in keeping with the blue cloak covered with smalt, thus betting on the harmony of two paler shades branded with the Rococo style, typical of the 18th century. In any case, the detection of Pb, as resulting from the Neoclassic white general overpaint, cannot be discarded either.

Flesh tone

The EDXRF analysis of the flesh tone preserved on the *Virgin*'s right hand (Figure 8) showed a specific relationship between the elements Ca, S, Fe, Pb and Hg. Taking into account the recipes by Nunes [3] and Pacheco [4] to render a flesh tone in the 17th century, Pb and Hg make sense. These elements reinforce the idea that white lead was mixed with vermilion to obtain a bright pink color. The two pigments were the most employed for depicting a splendorous completion, especially well adapted to a female character and even more to a dogmatic figure. In this case, Ca and S likely refer to the ground layer already studied, and as much Ca, as Fe and Sr, to the terracotta underneath. The decreased intensity

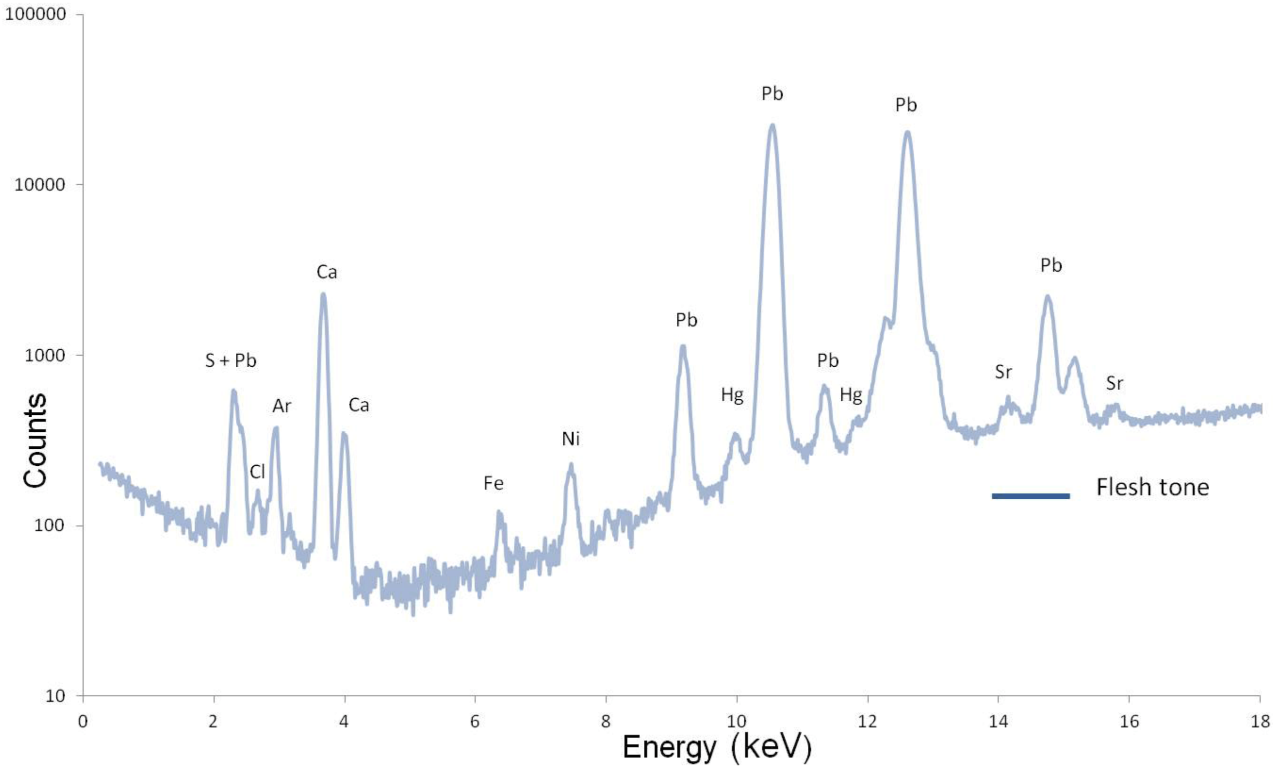

Figure 8. EDXRF spectrum of the flesh tone observed on the *Virgin*'s right hand.

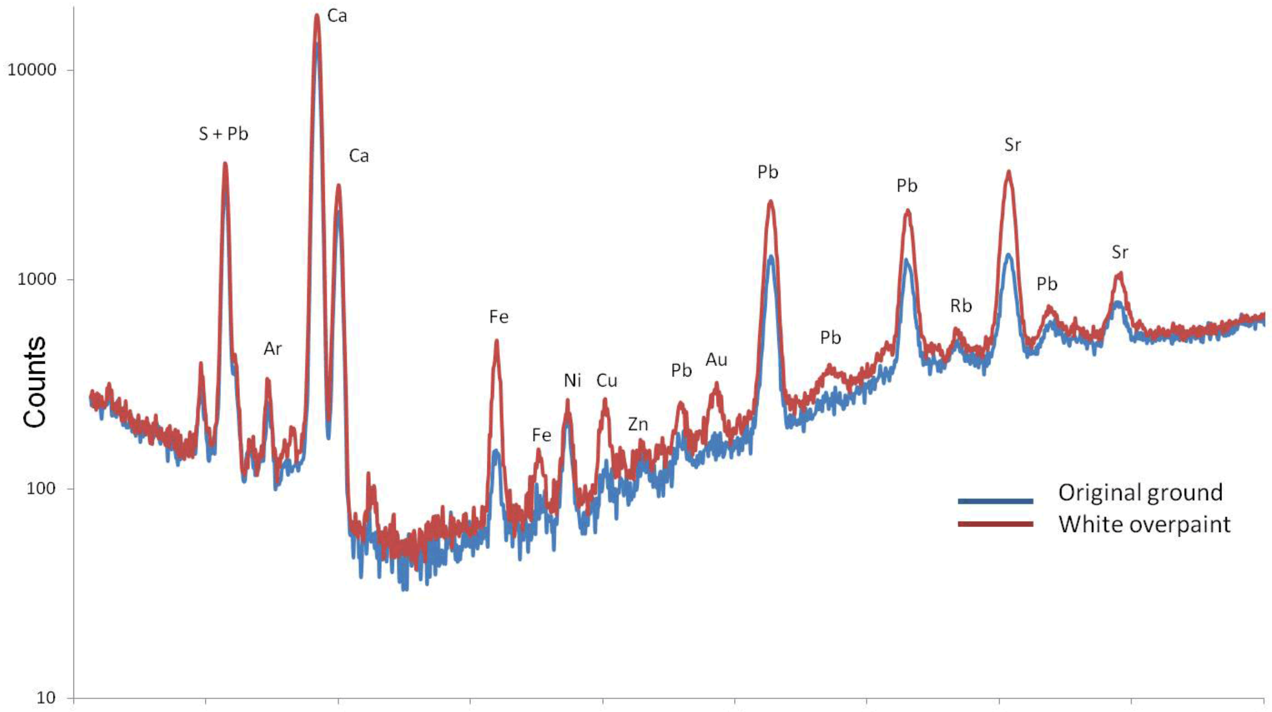

Figure 9. Comparison between the EDXRF spectra of the Baroque original ground and the Neoclassic white overpaint observed on the *Virgin*'s statue.

of these three elements relates to the attenuation effect of the superposed layers. Again, the element Pb may be also considered as being part of the intervention performed afterwards, as described below.

White overpaint

Figure 9 shows the spectrum of the latest intervention of a Neoclassic style applied to the statue (red line) with the spectrum of the original ground layer applied at the Baroque time (blue line). Thanks to this comparison, the detection of the element Pb from the Neoclassic overpaint appears clearly, the other elements belonging to the different layers underneath. Because of the color white analyzed on the surface, white lead is obviously the main constituent expected, even though it is not possible to assess the lead phases – the more basic carbonate plumbonacrite ($Pb_5O(OH)_2(CO_3)_3$) [35], hydrocerussite ($2PbCO_3{\cdot}Pb(OH)_2$) [36] or/and cerussite ($PbCO_3$) — in which *alvaiade* was employed, and the specific conditions in which the pigment was produced [37-39]. On the basis of the readings only, it proves also difficult to be definite on whether a ground layer specific to the monochrome overpaint was applied or not. The detection of both S and Ca may refer either to the original priming or a new gesso ground, and eventually to a *gesso-cré* preparation (supposedly a mixture of both gypsum and chalk, available as a marketed product in Portugal from 1780 onwards [12]), given that the layer build-up and the sate of conservation of the earlier coatings, which remain hidden, are unpredictable.

Apostle 2

On the selected sculpture depicting an *Apostle*, losses within the color paint of the bust are very few or difficult of access for the EDXRF equipment (Figure 10). That is why the measurements were carried out at the very surface of the bust in only five areas: the beard of a darker brown color, the face of a chalky aspect, the cloak of a light blue shade, the tunic of a mauve color and the flowers painted over this latter tone.

Dark brown beard

Although the color of the beard of a darker brown hue seems to have not changed over time on the Apostle, a parallelism between the spectrum of an earlier paint layer still visible in a loss (Figure 11, blue line) and that of an overpaint (Figure 11, red line) readily shows the main differences between what may be assumed as two different coatings: the high intensity of the elements K, Mn, Fe and Hg for the earlier polychromy, and the clear detection of the element Ba and Zn in the overpaint, besides the more significant intensity for the elements S and Sr in this latter intervention.

Figure 10. Top section of the statue of the *Apostle 2*, dated from the 17th century. The lower quality of certain paint layers observed at the very surface let suppose that the statue and the set to which it belongs were overpainted afterwards. Photo: Sónia Tavares.

Beard earlier coating

In the earlier coating (Figure 11, blue line), Mn is probably related with manganese-containing raw or burnt umber (MnO_2), Hg with vermilion (HgS) and Fe with earth pigments like ochers composed of oxides and hydroxides of iron. Among those, the registration of four pigments was recurring in the account books of the Tibães Monastery [12]: two varieties of goethite with the formula FeOOH, of a light and a darker yellow shade labeled *ocre claro* and *ocar escura* respectively; red iron oxide with the formula Fe_2O_3, labeled *almagre*; Cologne earth, a brownish black pigment composed of humic matters, fine clay and hematite Fe_2O_3, compared or equated to Vandyke brown [40] and labeled *sombra de colónia*. It may be assumed that these pigments, amongst the cheapest, were also in usage in the Alcobaça Monastery. The additional use of a black pigment, which could have remained under the limit of detection, is not excluded.

Beard overpaint

In the latter coating (Figure 11, red line), Ba may refer to the synthetic barium sulfate with the formula $BaSO_4$, used as a pigment (commonly called *blanc fixe* or constant white, and barium white) and extender; and Zn, to zinc(II) oxide with the formula ZnO, also manufactured as a white pigment called zinc white or Chinese white. Noteworthy is the fact that both pigments were materials processed at the end of the 18th century (barium white has been invented in 1780 and zinc white was already claimed as the best replacement for white lead in 1782) but were only truly established as marketed products to be used as watercolour and in oil by the 1830s [13]. It should be

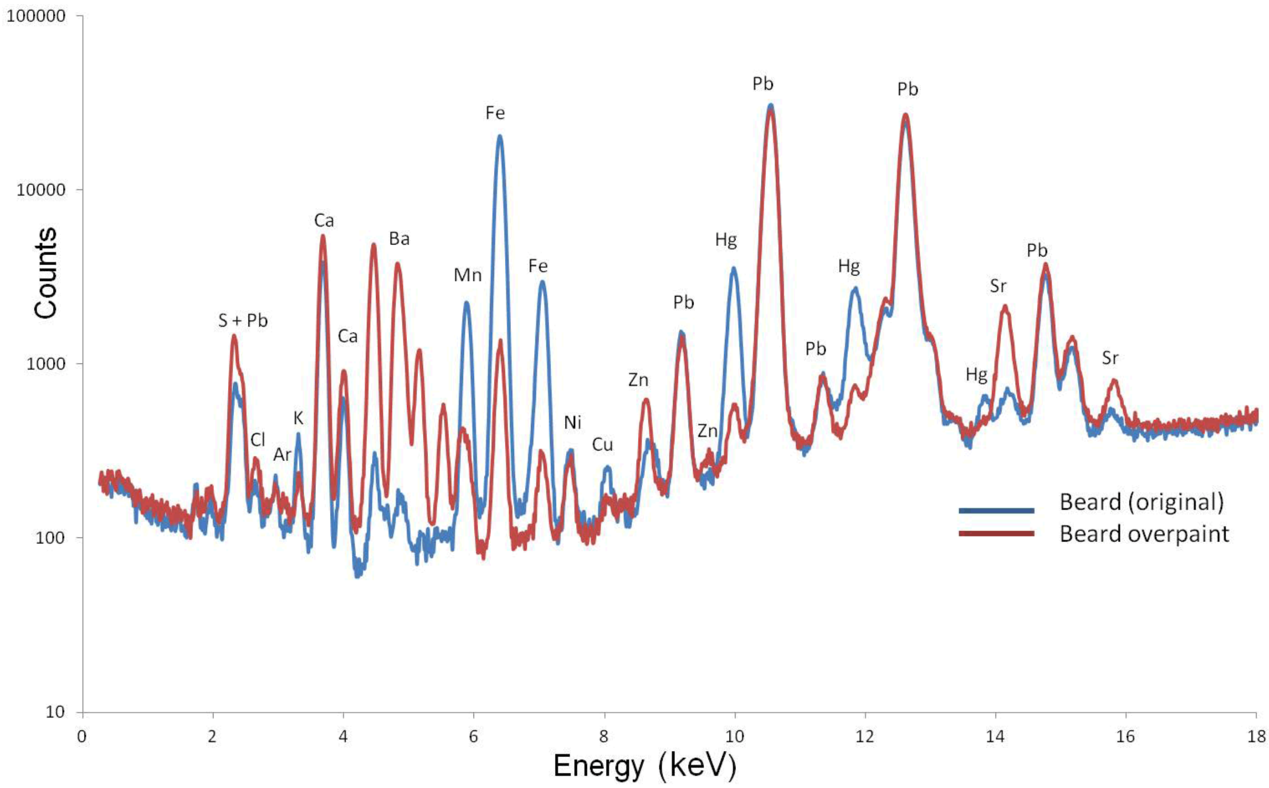

Figure 11. Comparison between the EDXRF spectra of the earlier coating and the subsequent intervention observed on the *Apostle*'s beard.

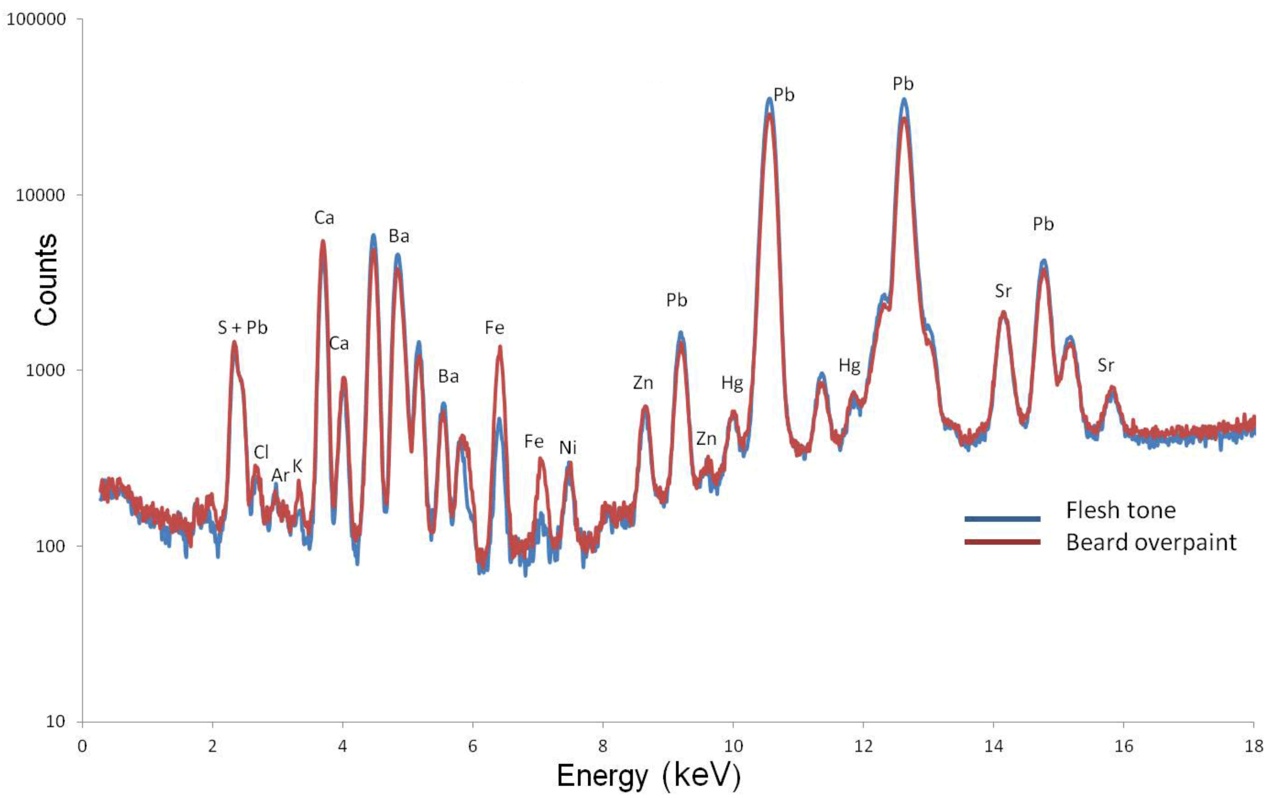

Figure 12. Comparison between the EDXRF spectra of the *Apostle*'s beard overpaint and the flesh tone observed in the adjacent area, on his face.

Tabela 2
Apostle 2 — Potential interpretation of the overall data obtained by EDXRF

EDXRF spectra	Detected elements	Interpretation
All spectra (priming)	Ca / S (?)	Chalk / Calcite: $CaCO_3$ One or more phases of calcium sulfate: Anhydrite / *Gesso grosso*: $CaSO_4$ Dihydrate or synthetic gypsum / *Gesso mate*: $CaSO_4{\cdot}2H_2O$
16 - Mauve cloth 22 - Original flesh tone	Pb	One or more phases of lead white: Plumbonacrite: $Pb_5O(OH)_2(CO_3)_3$ Hydrocerussite: $2PbCO_3{\cdot}Pb(OH)_2$ Cerussite: $PbCO_3$
21 - Original beard 23 - Beard overpaint	Pb	Red lead: Pb_3O_4
All spectra (with *estofo*)	Fe	Bole / Kaolinite / Fine clays + iron oxide (II): $Al_2Si_2O_5(OH)_4 + FeO$
21 - Original beard 22 - Original flesh tone 23 - Beard overpaint 24 - Flesh tone overpaint	Fe	Hematite: Fe_2O_3 Goethite / Ocher – Earth pigments containing Fe: FeO(OH) Cologne earth: humic matters + fine clay + hematite Fe_2O_3
22 - Original flesh tone 21 - Original beard 23 - Beard overpaint	Hg	Vermilion: HgS
21 - Original beard	Mn	Manganese dioxide (IV): MnO_2
21 - Original beard 23 - Beard overpaint		Carbon black: C Bone black (containing hydroxiapatite): $C + Ca_5(OH)(PO_4)_3$
16 - Mauve cloth 17 - Blue flowers 18 - Blue cloth	Ca	Indigo – blue organic dyestuff Precipitated over calcite?
16 - Mauve cloth 17 - Blue flowers 18 - Blue cloth	Au	Gold leaf – precious metal Gold alloy or pure gold? The composition should be analyzed by other methods
17 - Blue flowers 18 - Blue cloth	Fe	Azul da Prússia (from 18th century onwards): $Fe_4[Fe(CN)_6]3{\cdot}xH_2O$
23 - Beard overpaint 24 - Flesh tone overpaint	Zn	Zinc white / Permanent white / Chinese white (from 18-19th century onwards): ZnO
23 - Beard overpaint 24 - Flesh tone overpaint	Ba / S	Barium sulfate: $BaSO_4$

stressed that Barium sulfate also occurs as a component phase in various co-precipitated pigments, such as the compound known as lithopone, a synthetic pigment formed through co-precipitation of zinc sulfide and barium sulfate. Lithopone is said to have been discovered by G. F. de Doubet around 1850 and first produced on a large scale by J. B. Orr in 1874, hence its alternative name of Orr's zinc white [13]. Whatever the compound(s) employed, it appears that their widespread use during the 19th century objectively constitutes a *terminus post quem* and can assist dating the outermost coating, the application of which has definitely not occurred on the *Apostle* in the 18th century. With regard to the elements S, Ca, Pb and Sr, they may be related with the terracotta substrate and a ground layer, according to the layer build-up existing in the measured area. The importance Sr assumes in this spectrum may rely on two explanations: on one hand, high Sr levels can be associated with Ba minerals, e.g., barite and witherite, due to preferential substitution for the larger Ba^{2+} ion; on the other hand, it may fit the white pigment strontium sulfate, with the formula $SrSO_4$ [13].

Anyway, none of the white matters already referred can explain the dark color of the beard under study. Pigments ranging from yellow to black were certainly part of the palette. Those most commonly used in the paint trades since earlier times were the aforementioned ochers and carbon-based pigments. However, other pigments of a yellow, red and brown shade were manufactured in the 19th century, the formula of which could give rise to the results gathered by EDXRF. Their elemental composition could also reveal the presence of Fe (such as the Mars pigments [13] and Prussian brown [41]), or Ca and Pb (such as brown calcium plumbate Ca_2PbO_4 or lead brown composed of PbO_2), and even K or P (such as permanganate of potassium $KMnO_4$, or brown iron phosphate with the formula $(NH_4)_6{\cdot}Fe(P_2O_7)_2{\cdot}2H_2O{\cdot}Fe_2O_3$, containing also zinc yellow [41]).

Flesh tone

The analysis of the two coatings existing on the beard (Figure 11) allowed a better reading of the flesh tone actually visible on the *Apostle*'s face. In Figure 12, it appears clearly that this superficial layer (blue line) of a dull chalky aspect, more beige than pink, is contemporaneous of the brown overpaint already identified on the beard (red line), since Ba and Zn have been also detected on the face. Given the high intensity of Fe, the barium and zinc-based compounds were perhaps associated to ochers, or some of the already referred nineteenth-century yellow or brown pigments. On the other hand, it seems that the elements Pb and Hg go on related with the expected white lead and vermilion used to imitate a skin of a warmer tone; unless these elements were part of an underlaying flesh layer, this one counterfeiting the brighter and transfigurated pink completion expected for a saint.

Mauve and blue garments

The *Apostle*'s garments are well differentiated. The tunic is of a mauve color and the cloak, of a light blue one. Both paint layers were applied over water gilding. The colors are even, only decorated from place to place with two different floral patterns. The larger one was obtained by stripping off the colored layers for golden flowers to take shape through the gilding underneath. The smaller design was painted over the colored coating, of an intense blue shade on the tunic and of a very light shade (quite white) on the cloak.

Once again, the comparison between the gathered results of theses layers (Figure 13) shows that the blue coating of the cloak (blue line) is part of the barium-containing latter intervention, while the mauve coating of the tunic (red line) seems of an earlier period and to have remained untouched, for its elemental composition is not including Ba peaks.

Because previous measurements of the layers beneath the superficial colors were not performed, the further interpretation of the spectra showed in Figure 13 is far from being straightforward. Most of the detected elements may refer to the terracotta support, a gesso ground layer, an iron-rich bole layer and gilding as well, as already stressed regarding the *Virgin*'s polychromy.

Mauve paint layer

With regard to the mauve paint layer (Figure 13, red line), it is expected to have been obtained by mixing

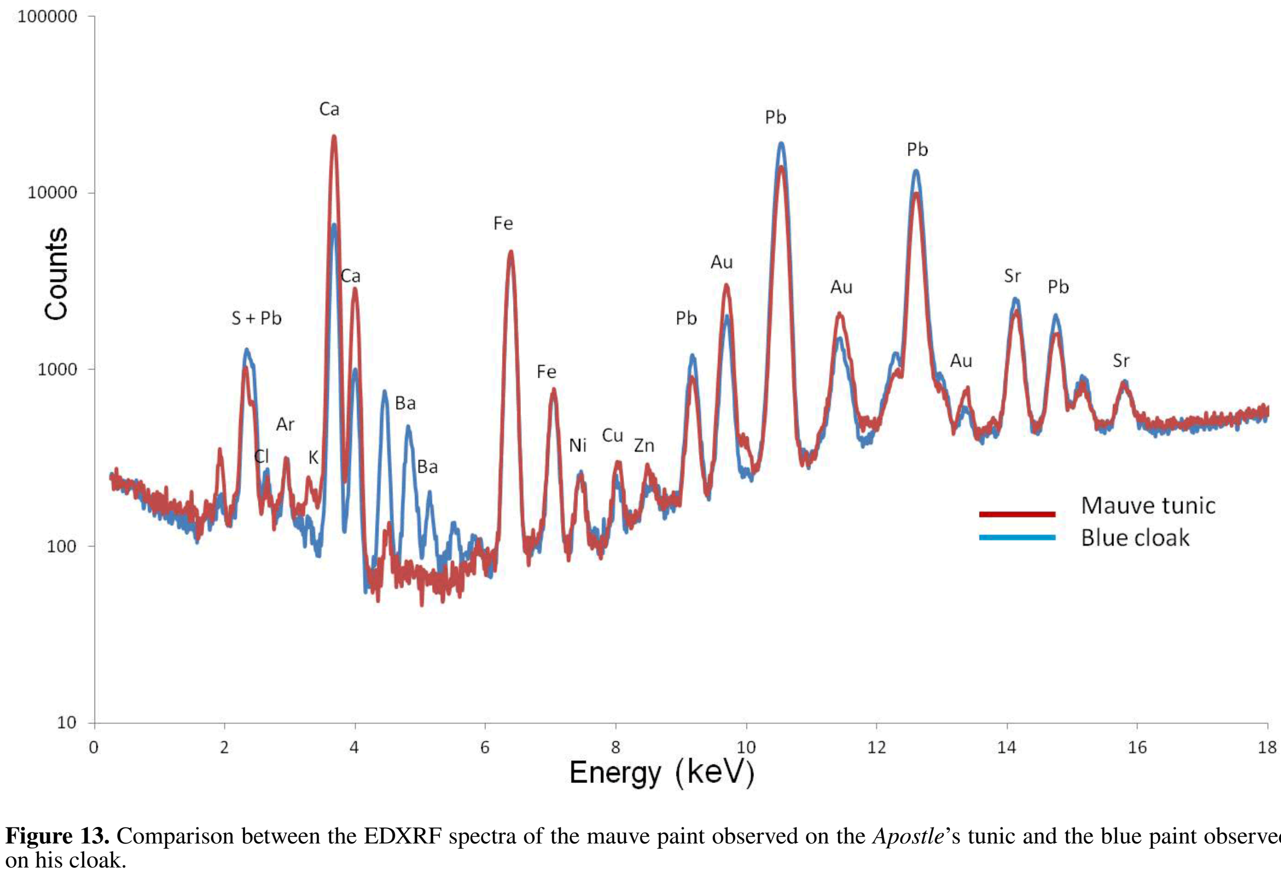

Figure 13. Comparison between the EDXRF spectra of the mauve paint observed on the *Apostle*'s tunic and the blue paint observed on his cloak.

white, blue and red pigments. White lead may obviously be assumed since it was the only white pigment available in the 17th century. Among the red pigments then in usage, red lead and hematite could make sense, except vermilion since no mercury-based pigment has been detected. Although the organic nature of other red colorants prevents to detect them by EDXRF, they may also be considered, taking into consideration the increase intensity of Ca in the spectrum. Indeed, calcium carbonate-based substances were, alone or in admixture with white lead, among the mineral substrates used to precipitate the extract of dyestuffs [42-46]. Many were the red dyes available since earlier times [42-48] and in Portugal in particular [48-50], but without proper analysis, it is impossible to determine whether one of them was employed and if so, which one. Regarding the blue pigments, used either to produce the mauve color or the blue floral design painted above, the spectrum shows that Cu was hardly detected, casting doubt on the use of azurite. The amount of azurite could be quite low or not used at all. In case azurite was not part of the color palette, only indigo as an organic coloring matter can be envisaged on the sculpture during the 17th century. The intensity of Ca in the spectrum may, again, justify the use of a blue dyestuff. The account books of the Tibães Monastery showed that several grade of indigo, called *anil*, could be purchased during the 17h and 18th century, allowing the creation of a very wide range of quality paint layers and blue shades [12].

Blue paint layer

As far as the blue color is concerned in the cloak paint layer (Figure 13, blue line), the question of which coloring matter was used is harder to solve only on the basis of the EDXRF measurement. The spectrum of this layer presents a similar elemental composition than that of the mauve layer, hence the similar considerations that should be drawn for both of them regarding azurite and indigo. However, for a coating dated from the 19th century, thanks to the detection of a barium-based substance in it (either in the color itself or a previous priming), it is more than legitimate to ponder the use of Prussian blue in the overpaint: because of the presence of Fe in its formula, and for being a pigment discovered between 1704 and 1707 and widely employed in Europe since the midst-18th century onwards [7-9, 18, 52]. Prussian blue is an umbrella term for the blue hexacyanoferrate(II) pigments (compounds based around $[Fe(II)(CN)_6]^{4-}$) which also contain Fe(III), and have different composition, method of production and adulteration. To such a point that Prussian blue can contain alumina, chalk, starch, sulfate of lime and baryta, magnesia, zinc oxide, etc. [13]. Noteworthy is the fact that the composition of these adulterants, namely of the inorganic chemical compounds, may also be consistent with the elements detected in the current spectrum, which sets strong limits of identification by the EDXRF technique alone.

Conclusion

The EDXRF technique was useful to have a first non destructive and non invasive approach on the materials potentially used over time on the sculptures of the Alcobaça Monastery. However, the technique itself is limited because several elements are not detectable or have very high detection limits, such as C, Al, Si, Na; and because each spectrum presents the information obtained from superposed layers (terracotta included). In such condition, it proves difficult to relate the elemental composition to the specific constituents of each layer. Furthermore, spectrum interpretation may also be hindered by the overlapping of characteristic peaks, escape peaks and sum peaks, or peaks originating from materials used in the experimental setup.

Anyway, the elements detected in the coatings supposedly applied in the 17th century to the two selected statues seem consistent with the pigments used at that time [53]. These coatings are very alike from a technical and artistic perspective regarding the range of tones and design. However, by comparing the obtained results, namely with regard to the color blue employed in each statue, it appears that the painter-gilders made different material choices and sought to diversify the final effects. These options seem to be consistent with the specific iconography and worship of each figure.

Thanks to the detection of Ba and Zn on the *Apostle*, the EDXRF technique allowed the latter intervention on the grouping depicting the *Delivery of the Keys* to be dated from the 19th century. With regard to the *Virgin Mary* and, by analogy, to the *Angel Gabriel* with which it forms a pair, only white lead was found on the outermost coating. Taking into account that this pigment was not replaced by white zinc, which was used as an alternative to the toxic white lead from the 1780s onwards, the Neoclassic monochromy applied to the *Annunciation* can be still dated from the 18th century.

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