9th International Conference on NDT of Art, Jerusalem Israel, 25-30 May 2008
For more papers of this publication click: www.ndt.net/search/docs.php3?MainSource=65

NON-DESTRUCTIVE XRF ANALYSIS OF PIGMENTS IN A 15TH CENTURY PANEL PAINTING

A. Križnar[2], M.V. Muñoz[1], F. de la Paz[1], M. A. Respaldiza[2], M. Vega[1]
[1] Museo de Bellas Artes, Plaza del Museo 9, 41001 Seville, Spain
[2] Centro Nacional de Aceleradores (CNA) -University of Seville
Avda. Thomas A. Edison 9, Parque tecnológico Cartuja '93, 41092 Seville, Spain
Corresponding Author: akriznar@us.es

ABSTRACT

The Retable of the Passion of Christ (towards 1415) forms part of the permanent exposition of the Museum of Fine Arts of Seville. It was painted by an anonymous author, who shows stylistic influences of Juan Sánchez de Castro, the most significant artistic figure in the Seville's painting of the 15th century. The retable is composed by a main scene, "The Christ carrying the cross", and two smaller scenes at each lateral side. On the left side above there is "The Agony in the Garden", below "The Flagellation", at the right side the "Crucifixion" and below it "The Pietà". The panel was analyzed by the non-destructive XRF technique directly in situ in the exposition room, using portable equipment with X-ray tube of 30 kV, anode of W and one SDD detector with energy resolution of 140 eV. The goal of this research was to know which pigments were applied in this artwork. The analysis revealed that the white pigment is lead white, maybe mixed with small amount of calcium white. The red pigment is cinnabar (characteristic Hg peaks), applied also in the carnations together with lead white. Some red ochre and some organic red pigment were added, as well. The blue pigment is azurite, identified by high peaks of Cu. High copper peaks were found also in the green pigment, which is probably verdigris (according to its intensive colour). The brown colour was obtained by natural or burned yellow ochre (Ca, Fe) and umbra (Mn, Fe). The black pigment is of organic origin, not possible to identify by XRF. The aureoles are gilded (Au), under gold there is red bole (Fe). Spectra of some analysed points show peaks of Zn and Ba, revealing the use of modern material lithopone and therefore some later restoration. This is confirmed also by low Cd peaks in some red areas, showing the use of modern cadmium red.

INTRODUCTION

The Retable of the Passion of Christ (Fig. 1) was painted by an anonymous author, who shows stylistic influences of Juan Sánchez de Castro, the most significant artistic figure in the Seville's painting of the 15th century. The origins of the Seville school go back to the 13th century, after the reconquest of the town by Ferdinand III in 1248. The first testimonies preserved until today date in the 14th century, but the first signed works made by recognized authors were painted not early than in the 15th century. In the first half of this century the local artistic language predominated, although enriched with extern European influences. So, in the work of Juan Sánchez de Castro the search for new artistic expression can be observed, the one that was flourishing in the Italian and Flemish painting of the second half of the 15th century. The Museum of fine Arts in Seville does not posses paintings made directly by his hand, but there are several artworks that show his artistic influences. One of them is the anonymous author of the Passion retable exposed in the first museums' hall. Although the master is not known, we can appreciate a high quality of the execution of this set of tables in the marvelous framework.

Fig. 1. The Retable of the Passion of the Christ, by an anonymous author (ca. 1415).

The retable is composed of five scenes. The central and the most important one represents *The Christ carrying the cross*, situated in a profound scenery with architecture and multiple personalities, according to the Flemish painting of the time. On each lateral side of the central scene there are two smaller tables showing the sequence of the most important stops in the Passion of Christ. On the left upper side there is *The Agony in the Garden* with an angel and three apostles. Below is situated *The Flagellation*, where the main scene is accompanied by the *Annunciation* taking place in the small room that opens on the left. On the right upper side of the central table there is *The Crucifixion* with John Evangelist supporting Virgin Mary who faint, while below the composition of these two figures is repeated by the central *The Pietà*, accompanied by St. Francis. In both cases the scene opens towards the nature on the horizon, a characteristic Flemish contribution to the painting of the period.

OBJECTIVES AND EXPERIMENTAL PROCEDURES

The Passion retable calls for an attention not only from the art historical point of view, but also from the technical aspect. It is characterized by vivid and still intense colours as well as by fine brushstroke that speak of the quality of the painter. It is known that the painting went through some restoration interventions in the past, the last one in 1992-93. At that time no analyses were done. In the Museum there was a strong interest to know which pigments were used by the master and how did he construct the colour layers. Since the retable was not in a restoration process, it was not considered convenient to extract any micro-samples. For this reason the non-destructive technique of X-Ray Fluorescence was chosen for the analysis of pigments.

The XRF technique is very important in the study of materials, especially in art. It offers the first exam of the artwork, without touching it or damaging it in any way. With portable equipments the tests can be run in situ (Fig. 2), without a necessity to move the peace of art from its original place. It is one of the gentlest ways to obtain information about the materials and technique applied by the artist. It also serves to discover possible later interventions, revealing modern materials where there should only be traditional ones. The retable was analysed in 59 points, trying to exam different colours and tonalities, shadows and lights. The pigments applied were recognized on the bases of characteristic chemical elements from the XRF spectra of analysed points. The elements are identified by the energies of their characteristic X-ray peaks. The comparison of the counts per second of the different elements in a particular point with regard to the background, gives us the possibility to asseverate the presence or not of a particular element in that analysed point. The spectra were also compared with a pigment database that was elaborated at CNA, analysing commercial pure pigments from old traditional recipes. It is not always possible to identify the precise pigment applied, because the XRF analysis offers the elemental and not the compositional results. There exist several pigments with the same characteristic chemical elements. In this case, it can not be distinguished between them only by this technique. XRF technique also does not serve to identify organic materials, because it does not detect elements with Z lower than 13 or 14. That is why organic pigments can not be detected by XRF.

Fig. 2. XRF análisis in situ.

The XRF equipment used to analyse the Retable of the Passion of the Christ has an X-ray tube of 30 kV with anode of W and one SDD detector with energy resolution of 140 eV. A 1 mm Al filter was coupled to the tube to suppress the characteristics W peaks of the anode. This instrument was used directly in situ, in the exhibition room (Fig. 2), during the days when the museum is closed to the public. Before each new measurement session, the XRF equipment was calibrated in energy, radiating the air and showing characteristic peaks of Ar from it and Zr peaks from an internal collimator of the detector, and analysing some single elements reference materials. All the measurements were done with fixed instrumental conditions (29.5 kV of applied high voltage, 80 μA of cathode current and 300 s of preset live time). A semi-quantitative analysis was done by using the areas of XRF peaks obtained in the multi-channel analyser. These areas can give us a semi-quantitative estimation of the element 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. However, a comparison of the concentrations between different elements can be only possible if a complete calculation (that is, making the corrections for X-ray production cross-sections, self-absorption, etc.) of the concentrations are made.

RESULTS

The pigments used originally are all commonly applied in the 15th century. They can be identified, as said above, on the basis of the characteristic chemical elements shown in single analysed point. If chemical elements reveal some modern material, they serve as a prove of an intervention and as a sign that the analysed pigment does not belong to the original palette. This one can consist only of so called historic pigments, used by the masters in the past. About historic pigments applied in painting a lot of literature has been published, which greatly helps scientists to deal with the painting patrimony. In the Passion retable a wide selection of historic pigments has been found, as well some interventions. The results are as follows.

White Pigment

The white colour was analysed on the Christ shroud. The predominant chemical element in all spectra is Pb, which reveals a white pigment as lead white. It was used not only for white parts, but also in a mixture with other pigments to lighten them and to obtain different tonalities. It is also a basic pigment for carnations, where it is mixed with other pigments, such as cinnabar and an organic red (see for instance fig. 9). This white pigment used widely in table and panel painting has a good cover potential and a brilliant white colour. That is why the painters liked to use it, although it was poisoning. It was applied also in the painting preparation, mostly mixed with calcium white or gypsum, and sometimes also as a dryer. For this reason, Pb uses to appear in all spectra of such a prepared painting. This is also the case in this retable, where the presence of Pb is detected everywhere, but in variable quantities, depending on the layer in which it was applied.

Red Pigment

The predominant chemical element in all spectra taken from different red vestments is Hg, which reveals that the red pigment applied is cinnabar (Fig. 3). The $K\alpha$ and $K\beta$ peaks of S, other characteristic element of this pigment, is covered by the $M\alpha$ and $M\beta$ peaks of Pb and therefore can not be seen. Low peaks of Fe show that the painter probably mixed cinnabar with small amount of red ochre. These two pigments were used also for the carnations, in higher or lower quantity, depending on the tonality of the skin that the painter wanted to obtain. The spectrum of red cherub in the *Pietá* shows no characteristic elements of any red inorganic pigment, which leads to the conclusion that the pigment applied must be of an organic origin and therefore it can not be identified by XRF (Fig. 3). It is not logical that the painter would use another pigment just for the small cherub figure, which means that this organic pigment could be possibly found also in the cinnabar and red ochre mixture. The red cinnabar (as well as probably also the organic red pigment) was used for the violet colour, obtained by mixing it with blue azurite.

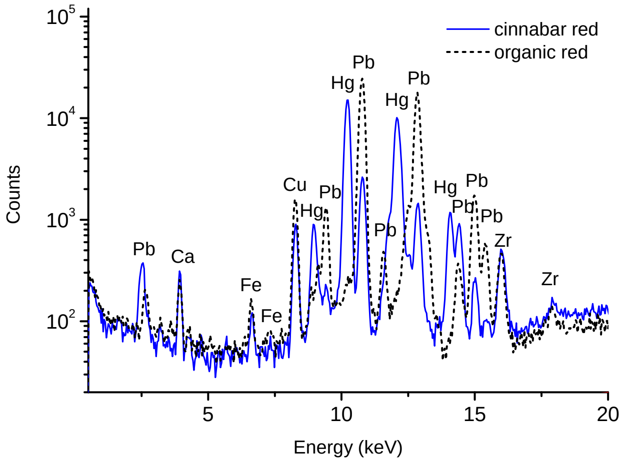

Fig. 3. Comparison of two XRF spectra a) cinnabar red on the coat of St. John Evangelist on Crucifixion (straight line) and b) not identified red organic pigment of the cherub on the Pietà (dot line).

Blue Pigment

On all five tables there are several different tonalities of blue colour that go from very light to very dark. The analysis of many points shows that in every spectrum there is an important presence of Cu, revealing that the blue pigment is azurite (Fig. 4). The count numbers vary greatly, depending on the tonality of the colour. In the dark areas such as drapery folds, the peaks of Cu are higher, while in the light areas such as the sky or the Christ tunic, the peaks are lower. In the light areas there is a higher presence of Pb, showing the use of lead white to lighten the basic blue colour. In the dark areas also higher peaks of Ca and Fe can be observed, revealing the use of an organic black pigment, based on Ca, and of burned ochre (Fe). Different tonalities of blue colour were obtained also by the underlayers, painted in grey or in dark brownish colour. They served as bases for the mineral pigment. The Christ tunic was painted on the grey bases and therefore gives a colder and lighter blue colour, while the vestments of Virgin Mary and other accompanying persons were painted on the dark preparation, which gives a dark, heavy blue tone.

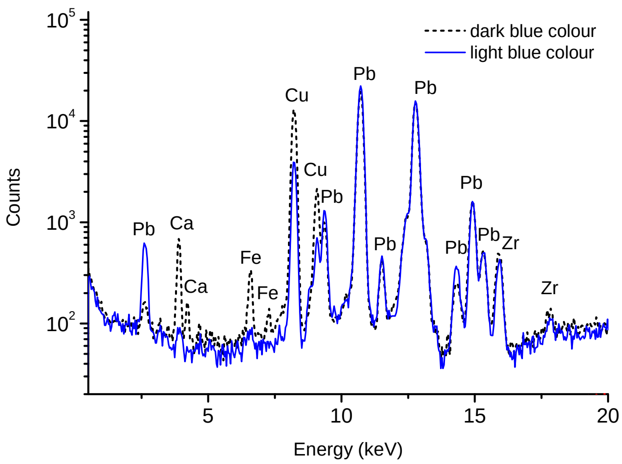

Fig. 4. Comparison of two XRF spectra a) light blue colour of the sky (straight line) and b) dark blue colour of the woman's dress (dot line), both from the central table.

Green Pigment

Also the green colour has many different tones, from light to dark. However, the spectra of all analysed points are quite similar. The most important element is Cu, showing that the colour was made by some copper based pigment (Fig. 5). With XRF technique it is not possible to distinguish between different green pigments, based on these chemical elements, since Cu is the only characteristic chemical element for a series of them. It is possible to narrow the possibilities by selecting only the historic pigments, among which the most used were malachite and verdigris. According to the colour observed in this retable, it is most likely that the painter applied verdigris, a greenish-bluish pigment, popular especially in the Flemish painting of the 14th and 15th centuries. It was often mixed with lead white or painted above it to get the transparency of the colour. In contact with the air and light it turns brownish (transformation of copper resinate to copper oxide), what can be observed in several areas of the painting. The count numbers of Cu vary according to the lighter or darker tone. In darker areas there is more Cu and less Pb, while vice versa in lighter areas. The higher peaks and therefore the densest and darkest colour can be found in the central table of *Christ carrying the cross*, in the trees and hills at the back of the scene. Also the presence of Fe, showing the use of natural or burnt ochre, is of interest. The painter used it to obatin darker tonalities and also for shadows. Where the peaks of Cu and Fe are higher, those of Pb are lower, meaning that lead white is situated in the underlayer. There are no peaks of Si or Mn to identify the Fe based pigment as green earth.

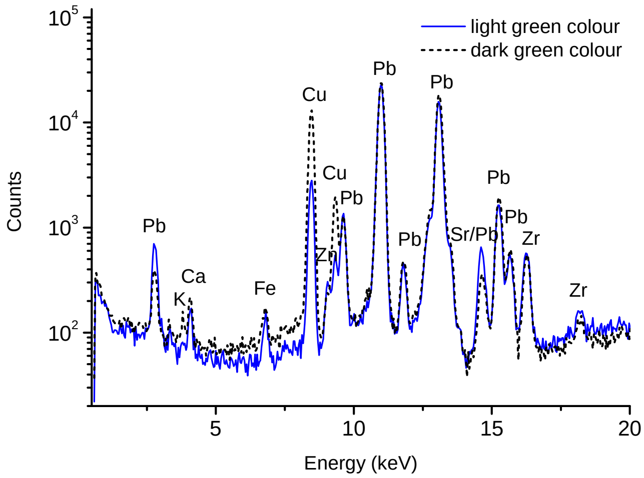

Fig. 5. Comparison of two XRF spectra a) light green colour and b) dark green colour from the hills at the back of the central table. In both cases a copper based pigment, probably vivianite, was used (Cu).

Ochre and Brown Pigments

The colours of different ochre and brown tonalities were analysed on the architecture, the cross, the Franciscan vestment, on hair of various figures. The predominant chemical element, besides Pb whose count numbers vary according to the darkness of the colour, is Fe. The dark brown colour makes us think that the possible pigment could be natural or burnet umbra, but the use of this pigment would reveal the existence of Mn and Fe together, which is not the case. This leads to the conclusion that the pigment applied is natural or burnt yellow ochre (Fig. 6). Lighter tones were obtained by adding lead white, while darker tones with mixing the basic earth pigment with an organic black (more Ca). Spectra show also low peaks of Cu, which in this case belong to the copper based green pigment applied in the under-layer. The presence of Hg reveals also the use of cinnabar, especially to obtain reddish tonalities of the architecture in the central table.

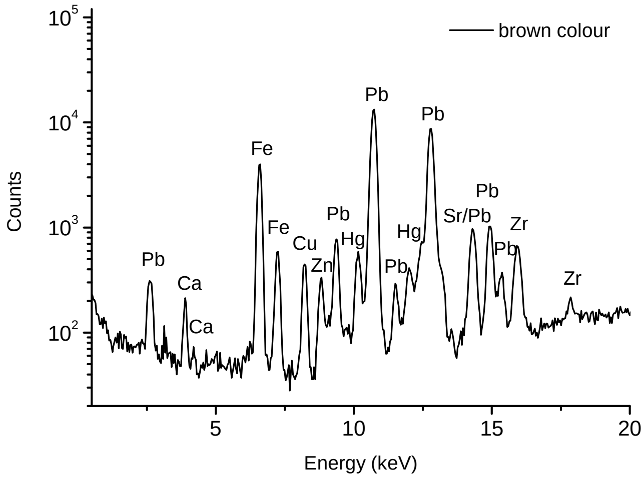

Fig. 6. XRF spectrum of the brown colour from the cross in the central table. Burned ochre (Ca, Fe) with cinnabar (Hg).

Black Pigment

The black colour was applied basically for details such as exterior borders of aureoles, or thin lines for black hair on the dark brownish basic colour. A wider black area is found on the column on the *Flagellation* scene, where it can be observed, as well, that the black layer was painted on top of a vivid green colour. The black pigment was used also for shadows and to obtain darker tonalities of other colours. The majority of these details are too tiny to analyse them by the X-ray whose diameter is wider, but the analysis of some shadows and of the column reveal a higher presence of Ca, that is, higher count numbers of this element. Calcium, in this case, belongs to the black pigment of an organic origin that can not be identified more precisely by XRF (Fig. 7).

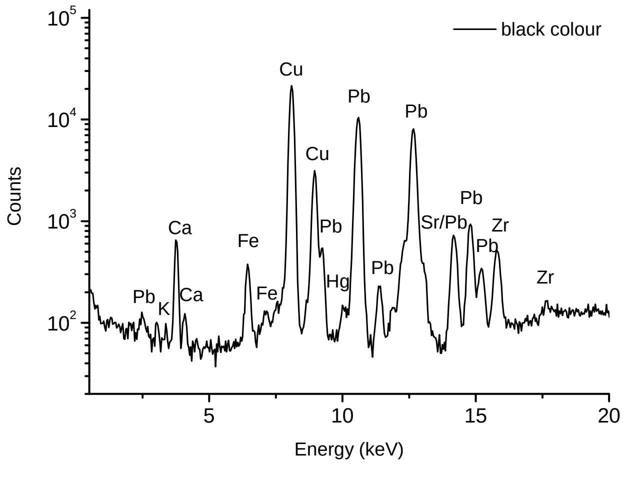

Fig. 7. XRF spectrum of a black colour from the column on the Flagellation scene. An organic black pigment, based on Ca, was used. High Cu peaks belong to the green underlayer.

Gold

Gold was confirmed by high Au peaks (Fig. 8) on all the aureoles and also on the framework. High peaks of Fe in all these spectra reveal the presence of bole, red iron oxide, used as the preparation for the gold, which was a common procedure.

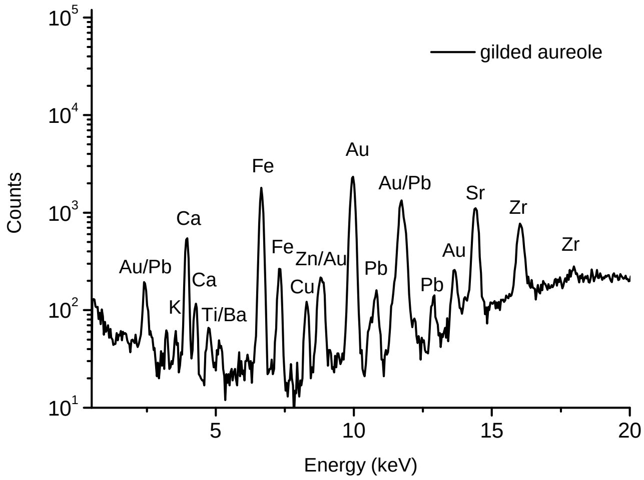

Fig. 8. XRF spectrum of the gilded Christ aureole from the central table. High Au peaks confirm the presence of gold, while the Ca and Fe peaks reveal the bole underlayer.

Interventions

The common presence of Ba and Zn in many areas of all five tables reveal the use of lithopone in some earlier restoration intervention (Fig. 9). It is a modern material, discovered in 1847 and used widely in restoration works. In most of the cases where this pigment was found, the spectra show also higher peaks of Ca and Fe, sometimes also Mn. These elements reveal the use of natural ochre or umbra, mixed with lithopone to obtain the desired colour. It seems that the central *Passion* table is the one with the majority of retouches, but also the four side tables have some small but important interventions. Some of them are seen by the naked eye, for example some carnations that have turned greyish. The analysis of these points has confirmed the use of lithopone. In some red vestments, painted with cinnabar and red earth, also the presence of Cd was discovered. Low peaks of this chemical element reveal the use of cadmium red for the retouches.

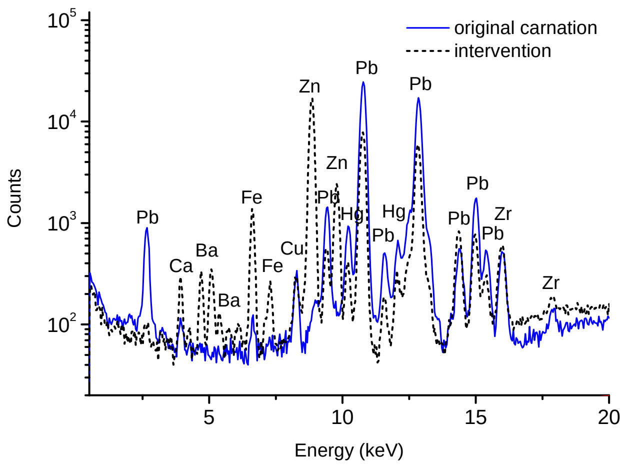

Fig. 9. Comparison of two XRF spectra a) the original carnation colour on St. John Evangelist's face, made of lead white (Pb) and cinnabar (Hg) (straight line) and b) the intervention on Simeon's face, based on lithopone (Ba, Zn) (dot line), both from the central table.

CONCLUSIONS

The *Retable of the Passion of Christ* by an anonymous painter forms part of the permanent collection of the Museum of fine Arts in Seville. The pigments applied in the painting were of interest, but it was not considered convenient to extract any micro-samples, since the painting was not in the restoration process. This is why a non-destructive technique of X-Ray Fluorescence was chosen for the analysis. Portable XRF equipment was used *in situ*, in the exposition room, which permitted an exam of the painting in 59 different points without the need to displace or damage it anyhow. The results are based on a semi-quantitative interpretation of the information, based on the elemental chemical identification of the pigments.

The white pigment is lead white, applied for white vestments as well as in carnations. The presence of Pb in every point of analysis reveals that in the preparation of the table lead white was used as well. The basic red pigment is cinnabar (Hg), mixed with smaller amount of red ochre (Fe) and probably also some red organic pigment (XRF can not identify any characteristic elements), found also on the cherub. Cinnabar, mixed with blue azurite, was used also for violet colour. Azurite is the blue pigment applied in many areas, presented from very light to very dark tones. These different tonalities are obtained also by a greyish or brownish underlayer. The green colour is made of some copper based green pigment, which is not possible to identify more precisely by XRF. According to its intense green colour and some changes to brown tonality, the most credible pigment is verdigris, very common in the Flemish painting of 14th and 15th centuries. Ochre and brown colours are of yellow ochre, used in its natural or burned form. The black pigment is of an organic origin, based on Ca, but not possible to identify precisely by this technique. Gold was confirmed on all aureoles and on the framework of the five tables, as well as the use of red bole for the preparation under it.

Count numbers of all characteristic chemical elements on which the pigment identification is based, change according to the density and darkness of the colour. Lights were obtained by adding lead white to the basic pigment, while the shadows by adding toasted ochre or an organic black pigment. In many areas also some posterior interventions can be found, identified by the presence of lithopone (Ba, Zn). Most retouches are found in the central table, some of them seen also by the naked eye. Low peaks of Cd in some red vestments reveal the use of cadmium red, a modern pigment applied in this case for retouching. The results provided in interesting and useful information about this specific peace of art that will help conservators and restorers in its future prevention.

ACKNOWLEDGEMENTS

We acknowledge the financial support from the Project of Excellence 2005/HUM-493 of Junta de Andalucia.

BIBLIOGRAPHY

1. Bassegoda i Hugas B. (ed.) 1990. Francisco Pacheco: El Arte de la Pintura. Madrid: Cátedra.
2. Calvo A. Conservación y Restauración, Materiales, técnicas y procedimientos, de la A a la Z. Edición del Serbal: Barcelona, 1997.
3. Dornheim S.D. & San Andrés Moya M. 2004. Litargirio y masicote. Terminología, propiedades y usos. Reproducción a escala de laboratorio de algunos de sus procesos de obtención. XV. Congreso de conservación y restauración de bienes culturales 2004, Actas, Vol. I: 533-546.

4. Gómez M. L. 2000. Examen científico aplicado a la conservación de obras de arte. Madrid: Cátedra, Instituto del patrimonio histórico español.
5. Knoepfli A., Emmenegger O., Koller M. & Meyer A. (eds) 1990. Reclams Handbuch der künstlerischen Techniken. Vol 1-3. Stuttgart: Philipp Reclam jun.
6. Montanga G. 1993. I pigmenti. Prontuario per l'arte e il restauro. Firenze: Nardini editore.
7. Moreno Mendoza A., Pareja López E., Sanz Serrano M. & Valdivieso Gonzáles E. 1991. Museo de Bellas Artes de Sevilla. Sevilla: Ediciones Gever, S.L.
8. Seccaroni C. & Moioli P. 2002. Fluorescenza X. Prontuario per l'analisi XRF portatile applicata a superfici policrome. Firenze: Nardini editore.
9. Serchi M. (ed) 1999. Cennino Cennini: Il Libro dell'Arte. Firenze: Felice Le Monnier.
10. Schram H.P. & Herling B. 1995 Historische Malmaterialen und ihre Identifizierung. Stuttgart: Ravensburg Buchverlag.
11. West Fitzhugh E., Feller R. & Roy A. (eds.) 1987-1997. Artists' pigments. A Handbook of their history and characterisation. New York, Oxford: National Gallery of Art: Washington, Oxford University Press.

Back to Top