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this issue.

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A PANEL PAINTING BY THE MASTER OF FEMALE HALF-LENGTHS ANALYSED BY PORTABLE XRF

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Abstract

A panel painting representing *The Pietà* by an anonymous author known as The master of Female Half-Lengths was analysed by a non-destructive XRF technique. *The Pietà* forms an important part of the permanent exposition of the Fine Arts Museum of Seville. An unusual brownish tonality of the painting led to a research on pigments and their possible changes during the centuries. Portable XRF equipment was used directly "in situ" in the exhibition room. The results showed the use of pigments, commonly applied in that century, lead white, lead-tin yellow, yellow and red ochre, cinnabar or vermilion, some copper based green pigment, azurite and smalt, as well as some organic red and black pigment. The chemical alteration of smalt, whose blue colour is not observed by the naked eye anymore, led to a brownish aspect of the painting. Also several retouches by modern pigments were found, which were first examined by UV light. The comparison to other Flemish paintings held in the permanent Museum's collection was also carried out.

Keywords Panel Painting, Flemish Art, Pigments, Chemical Changes, X-Ray Fluorescence



Research Aims

The Pietà presents an unusual brownish appearance, which called the attention of the restorers of the Fine Arts Museum in Seville, which holds the painting as a part of its permanent exhibition. This appearance led to a research on pigments used by the Master of the Female Half-Lengths. Any possible chemical changes of applied pigments, which would cause to the present state of the panel painting, as well as the original palette of the Master, were principal objectives of this research. Also the identification of later interventions was of interest, some of which can be observed already by the naked eye. Previously, some other Flemish paintings in the Museum's collection have been analysed, so the results would form part of the data base on Flemish painters from the 15th and 16th centuries in the Seville's Museum.

Introduction

An anonymous Flemish painter known as The Master of the Female Half-Lengths (Maestro de las Medias Figuras) was active in the first half of the 16th century. His auxiliary name was chosen on the bases of numerous women portraits he carried out, which present richly dressed ladies in half-lengths. The elegance of his models and the poetical elements which inspired some of his works show that he might have been active in Mechlin, in the highly cultured circle around Margaret of Austria, who lived in Netherlands from 1518 to 1530. The Master of the Female Half-Lengths was probably trained in the studio of Bernard van Orley, a painter who was very close to Margaret; nevertheless his later style is closer to Ambrosius Benson and Adriaen Isenbrandt. Among his works are not only female portraits, but also religious scenes, interspersed in picturesque landscapes in which the influence of Joachim Patinier is clearly seen. This situates the anonymous master also in Antwerp between 1527 and 1540 (Valdivieso González 1993).



Figure 1. *The Pietà* by The Master of the Female Half-Lengths (towards 1550).

Experimental procedures

The Pietà is part of the permanent collection and was not in a restoration process at the time of this research, so no micro-samples were extracted. For this reasons, the non-destructive portable X-Ray Fluorescence was considered the most suitable technique for the selected objectives. This technique is very useful in the non-destructive study of materials, especially in art. It allows the first

exam of an artwork, identifying inorganic pigments and helping to discover possible later interventions. XRF gives elemental results, revealing chemical elements present in a radiated point. By this technique it is not possible to identify molecular compositions nor organic pigments, because usual XRF systems do not detect elements with Z lower than 13 or 14 (Gómez 2000, Volpin and Appolonia 2002, Seccaroni and Moiola 2004, Deming Glinsman 2004).



Figure 2. Analysis *in situ* of the panel painting by portable X-Ray Fluorescence.

Our portable equipment uses an X-ray generator RX38 with W Anode from EIS Company and a silicon drift detector (SDD) with energy resolution of 140 eV. An Al filter of 1mm was coupled to the tube to suppress the W peaks from the anode in the X-ray spectra obtained during the radiation. The diameter of the radiated spot was 3mm. The analyses were carried out *in situ* during the days that the museum is closed to the public (Figure 2). The panel painting was radiated in 125 different points, selecting different colours, tonalities, shadows and highlights. All measurements were done under the same fixed conditions: 80 μ A of cathode current, 29.5 kV of applied high voltage and 300s of preset live time. This permitted a comparison of the spectra among them and also supported semi-quantitative results. The pigments were identified according to the characteristic energy (keV) of the X-ray peaks in each obtained spectrum, which correspond to specific chemical elements (Seccaroni and Moiola 2004, Deming Glinsman 2004, Matteini and Moles 2004). The spectra were compared with a pigment database that was elaborated at CNA, analysing commercial pure pigments from old traditional recipes. Also the wide bibliography on pigments was consulted

(Wehlte 1967, West Fitzhugh et al. 1987-2007, Knoepfli et al. 1990, Montagna 1993, Schram and Herling 1995, Brachert 2001, Eastaugh et al. 2004).

Results and discussion

In general, the most important chemical elements detected in the panel painting are Ca, Mn, Fe, Cu, Hg and Pb, however, in some areas also Mg, Al, Si, Co, Ni and As were found. Their presence as well as their individual net peak area count numbers (or cps) in a spectrum vary according to the pigment applied. Consecutively, this information also shows their relative quantity in the radiated point in comparison to other chemical elements in the same point. This allows us, in some cases, to estimate, if a certain pigment belongs to the superficial layer (higher net peak areas) or it can be found in one of the lower layers (lower net peak areas) of the painting.

Lead and calcium compounds

A presence of Pb was discovered in all analysed points, however in very different count numbers responding to Pb L α net peak areas, which go from 6 cps on the rocks of the background up to 927 cps in white Mary's wimple. In general, the highest count-rates can be found on white colour and highlighted areas of the painting, while the lowest ones in the darker parts, as expected. The presence of lead all over the painting shows an important role of some lead compound, that could be lead white (basic lead carbonate), yellow litharge or massicot (lead oxide) or orange-red minium (lead oxide). With XRF technique it is not possible to distinguish between these different compounds (West Fitzhugh et al. 1987-2007, Seccaroni and Moiola 2004). However, the colour of the analysed area can, in some cases, help with the identification of the pigment applied. In *The Pietà* panel, mostly lead white must have been used, first in the preparation layer, and secondly also as white pigment for white draperies, carnations and highlights. One of these Pb compounds, probably lead white or litharge, could have been applied also as a dryer for other pigments. High Pb peaks in some red draperies as the St. John Evangelist's coat show also a possible use of minium in this painting. On the other hand, low Sn peaks in some highlighted yellow areas reveal presence of lead-tin yellow, normally used to recall gold.

The other chemical element that is richly presented in almost all spectra is Ca, whose K α count numbers go from 1 cps in St. Mary Magdalene's white drapery to 23 cps in the Christ's hair. In most cases, it is difficult to find out to which chemical compound it belongs, but in panel paintings calcium can be basically found in gypsum or calcite preparation and in animal glue, used in preparations or as the binding media for pigments (Wehlte 1967, Knoepfli et al. 1990, Brachert 2001, Matteini and Moles 2004). It can also belong to some earth pigments or organic black pigments. The variations of Ca content are mostly due to the thickness or to the composition of the preparatory layers and not to the concentration of this element in a certain area (Seccaroni and Moiola 2004).

Pigments

(a) White colour

The palette of The Master of Female Half-Lengths was composed by pigments, commonly applied by the painters in that period of time (Wehlte 1967, West Fitzhugh et al. 1987-2007, Knoepfli et al. 1990, Montagna 1993, Schram and Herling 1995, Brachert 2001). The results can be seen in Table 1. The white pigment, as said above, is lead white, revealed by high Pb peaks in spectra obtained from the radiation of white areas, as white draperies or highlights. Its major concentration can be observed on wider white areas, where count numbers of Pb L α net peak areas go from 343 cps on the shadow of Christ's white shroud to 927 cps in white Mary's wimple.

(b) Carnations

Lead white was used also as the principal pigment for carnations, where its concentration varies depending on a lighter or darker skin tone. Count numbers of Pb L α peaks in carnations go from 90 cps up to 670 cps. The painter mixed lead white with a red colour, obtained, according to the analysis, by different pigments – cinnabar/vermillion, red ochre or hematite and maybe even an organic red lake.

(c) Red colour

The major red pigment in this painting is cinnabar or vermillion. They are both mercury sulphides, but the first one is natural, obtained from the mineral, while the second one is a synthetic reproduction of the mineral (Eastaugh et al. 2004). Both of them were

well known and used in the 16th century, when this panel painting was made. They can be distinguished by PLM technique, but not by XRF. Cinnabar/vermillion was applied, as said, already in the colour of carnation. On lighter areas its concentration is lower (Hg L α : 4 cps), while on reddish parts like cheeks or hands and legs the concentration decreases (Hg L α : 27 cps), which shows that the painter added more of this pigment. A very intense colour was used for lips, where the major concentration was detected on the female saint next to the cross (Hg L α : 41 cps). Differently, red Christ lips were modelled by blue azurite, as shown respectively by Hg and Cu peaks in the spectrum from this area. This blue colour also creates the aspect of the dead Christ's body. Cinnabar/vermillion was used in its purest form for red draperies. The highest Hg peaks can be observed on St. John Evangelist's tunic (Hg L α : 155 cps). On the other hand, the analysis of his red coat gives much lower Hg count numbers (Hg L α : 10 cps), so, probably, the colour layer is thinner or the pigment is more diluted. The same red pigment was found in high concentration as well on the cross in the background, in small figures in the left corner and in some other elements of the background.

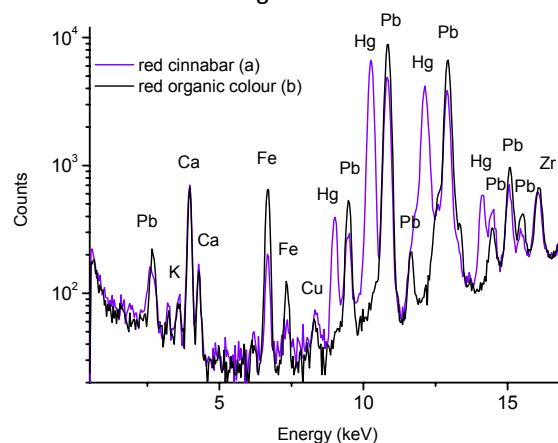


Figure 3. Comparison of two XRF spectra showing cinnabar red (Hg) from St. John Evangelist's coat (a) and an organic red colourant (no characteristic chemical elements) from St. Mary Magdalene's dress (b). In both spectra also the presence of red ochre can be seen (Fe).

In all red areas where cinnabar/vermillion was detected, also Fe peaks appear (Fe K α : 2 cps), showing that this pigment was mixed with red ochre or hematite, which was a normal procedure (Wehlte 1967, West Fitzhugh et al. 1987-2007, Knoepfli et al. 1990, Brachert 2001). Natural red ochre and hematite are both iron oxides, the second one is a mineral, while the first one is a clay material which

contains hematite. The presence of silicates can help to distinguish between both of them, however with XRF technique this is not possible (Eastaugh et al. 2004).

The XRF sensitivity for Si is too low to detect it, especially in mixed materials. The distinction therefore can not be made, so further on we will refer to the pigment as red ochre, being a wider term. Fe peaks are much higher on darker red areas (Fe K α : 13 cps), revealing that shadows were carried out by red ochre, to which also smalt was added (Co, Ni, As, Bi peaks). The analysis of the upper part of St. Mary Magdalene's dress show no Hg peaks, only Fe ones (Fe K α : 10 cps). The painter has used only red ochre, which he again mixed with smalt. According to the dark colour it is also possible, that in some areas of carnations or draperies the Master applied an organic red lake, which can not be confirmed by XRF (Figure 3). However, relatively high Ca peaks (Ca K α : 9 cps) could suggest that calcium was used as a substrate for an organic red lake, maybe carmine, and as such applied on the painting. High Pb peaks (Pb L α : 700 cps) in the red coat of the female saint standing next to the cross show towards the possibility of the use of minium, but we can not be sure, as explained above.

(d) Violet colour

Spectra of violet colour identify Ca, Fe, Co, Ni and Cu peaks, showing that the colour is a mixture of red ochre (Fe), smalt (Co, Ni), azurite (Cu) and maybe an organic red lake, as suggested by relatively high Ca peaks.

(e) Yellow colour

Yellow pigment is natural or burned yellow ochre, identified by lower or higher Fe peaks in the spectra, depending on the lighter or darker colour. It could have been applied also for darker carnations, where low Fe peaks appear. However, with XRF technique it is not possible to distinguish between yellow and red ochres, having only Fe K α peaks as the relevant information. Only in areas which are visibly yellow as hair of several figures (Fe K α : 4 cps) or the drapery of kneeling St. Mary Magdalene (Fe K α : 12 cps) the earth pigment can be identified as yellow ochre. On the other hand, in some spectra of highlighted yellow coloured areas low, not always well defined peaks of Sn can be observed (Sn K α : 1 cps). The presence of Pb and Sn together reveal the use of tin-lead yellow, as said before. There

are two types of lead-tin yellow, type I and type II. They are both lead-tin oxides, however the type II may contain free tin oxide and additional silicon (West Fitzhugh et al. 1987-2007, Montagna 1993, Eastaugh et al. 2004). In order to distinguish them, the presence of Si should be confirmed, which is not possible by XRF due to the low sensitivity for chemical elements under Z=13. Also the ratio between Pb and Sn could give some answers. But in *The Pietà* lead is present in every analysed point of the panel in high concentrations and it is impossible to know which part of Pb belongs to the yellow pigment and which to the preparation or dryer, so the ratio between Pb and Sn can not be calculated. The use of lead-tin yellow can be observed in the ochre skirt of St. Mary Magdalene, on the figure in yellow in the background, on some architectural elements, on the cross and maybe even in some carnations.

(f) Blue colour

Blue colour was obtained by two different pigments, azurite and smalt. Azurite, identified by Cu peaks was applied in smaller areas as blue lips of the dead Christ, shadows on white and violet draperies, in several areas of the architecture in the background, while low peaks can be detected also in the colour of the carnation of the dead Christ. Count numbers of Cu K α net peak areas vary from 1 cps in carnations to 95 cps in the violet tunic of a female saint on the right, depending on the analysed area. However, the prime blue pigment in the painting is smalt, which was applied for wider surfaces as Virgin Mary's coat, architecture in the background, the mountains and the sky that cover the upper part of the panel. It was also used, together with red ochre, for shadows of red draperies and, mixed with azurite, for shadows on some white clothes. In all these areas high peaks of Co, Ni, As and Bi can be observed, chemical elements characteristic for this blue pigment.

However, by the naked eye no blue colour can be observed in most of these areas and its presence was revealed only by XRF analysis. The pigments must have overcome some chemical changes during the centuries. Smalt has an intense blue colour at the beginning, but tends to lose its strength and can become totally transparent or it can turn brownish (West Fitzhugh et al. 1987-2007, Knoepfli et al. 1990). There can be several reasons for this chemical change of the

pigment: it can be influenced by discoloration of the paint medium or by saponification products, which are normally result of cobalt ions or excised potassium that comes in contact with the oil (Eastaugh et al. 2004). In the case of *The Pietà* panel it could not be determined which process led to the discoloration of the smalt. Nevertheless, due to this chemical change the painting has today the brownish aspect. Different tonalities of brownish-greyish colour correspond to relatively higher (Co K α : 35 cps) or lower (Co K α : 3) amount of the pigment, in the mixture with lead white (Figure 4).

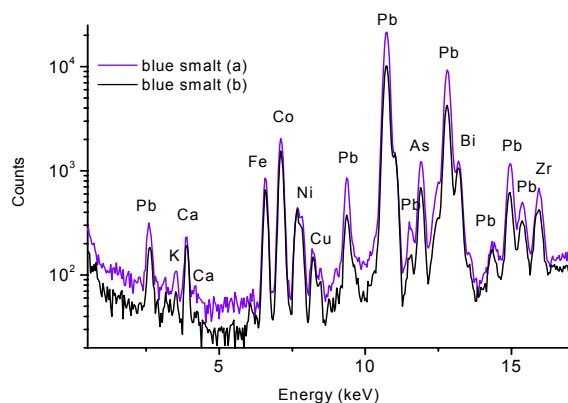


Figure 4. Comparison of two XRF spectra, showing blue smalt (Co, Ni, As, Bi) on the Virgin Mary's dress, in lighter (a) and darker (b) tonality, with more/ less Pb white added.

(g) Green colour

High Cu peaks in green areas (some parts of vestments, trees and grass) reveal the use of some copper based green pigment. Its highest quantity can be found in the green tunic of the female saint on the right border (Cu K α : 332 cps), while less pigment was applied on trees or grass (Cu K α : 130 cps). The palette of copper based green pigments is very wide, but with XRF it can not be identified more precisely, because it does not give the molecular composition of the pigment. Among the most used in the 16th century Flemish painting were malachite, verdigris and copper resinate (Wehlte 1967, Knoepfli et al. 1990, Montagna 1993), so the Master of the Female Half-Lengths probably used one of those. Different tonalities were obtained by adding lead white or some natural or burned ochre to the green colour. This mixture was used above all for the brownish floor of the scene. Low Mn peaks (Mn K α : 2 cps) observed together with Fe peaks on some spectra obtained from rocks and floor show that also natural or burned brown umbra was applied, especially for the darker tones. The black pigment, used

above all for details, fine lines and some shadows, is of organic origin and can not be identified by XRF.

Interventions, retouches

In various areas of the panel painting the presence of chemical elements Ti, Zn and Ba was observed already by the naked eye and then confirmed by the inspection under the UV light. They reveal the use of modern pigments titanium and zinc white, which appeared not before the middle of the 19th century, but entered in regular use only at the beginning of the 20th century (Wehlte 1967, West Fitzhugh et al. 1987-2007, Knoepfli et al. 1990, Montagna 1993, Eastaugh et al. 2004). Therefore can not form part of the original painter's palette and belong to later interventions, which are not documented.

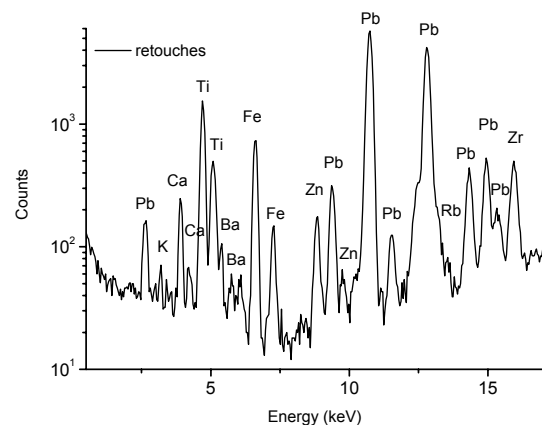


Figure 5. The XRF spectrum of the Christ's leg, showing important retouches, made by Ti-Zn white, mixed with some ochre.

The presence of low Ba peaks could identify the use of barium sulphate, which can be found as the pigment base in Ti white or together with Zn sulphur in lithopone, also applied in 20th century retouches. Net peak areas of Ti, Zn and Ba are extremely variable, in some cases can not even be determined, while in the others can get up to 78 cps or even 600 cps as in the case of Zn K α peak on the Christ's body. These pigments were mixed with others, mostly ochres, to obtain the appropriate colour of the retouched area. Where Zn peaks are very high, normally also Fe peaks are strong.

In some cases, retouches can be seen by the naked eye, especially on the junctions between the panels. As the wood was drying, the panels were separating. The gaps between the junctions were restored and overpainted, but these interventions help us see where

these junctions are, without having to take the painting off the wall. Among the figures in the painting, the dead body of Christ has many retouches with Ti-Zn white (Figure 5), an important intervention was discovered also in St. John Evangelist's face and in some saint's vestments, while many small retouches can be found all over the painting (Figure 6).

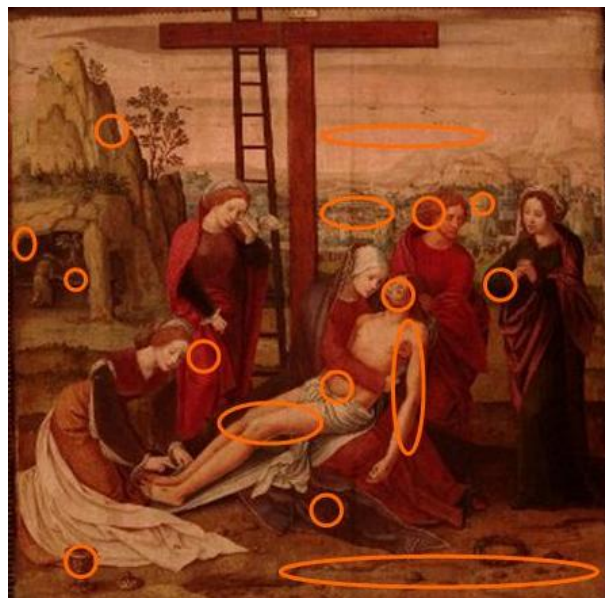


Figure 6. *The Pietà* by The Master of the Female Half-Lengths. Several retouched areas with Ti-Zn white.

Table 1. The pigments applied on *The Pietà* panel painting, according, to colour and chemical elements. Elements given in red type are present in high concentration, while (tr) indicates trace amount

Colour	Chemical elements	Pigments
White pigment	Ca, Fe, Cu (tr), Pb	Lead white
Carnations	Ca, Mn (tr), Fe, Cu (tr), Hg, Pb	Lead white + cinnabar/vermilion + red or yellow ochre + red lake (?)
Yellow pigment	Ca, Fe , Pb , Sn (tr)	Yellow ochre + lead-tin yellow
Red pigment	Ca, Mn (tr), Fe , Hg , Cu (tr), Pb	Cinnabar/vermilion + red ochre + red lake (?)
Blue pigment	Ca, Fe, Co , Ni, Cu , Pb , As (tr), Bi (tr)	Smalt + azurite
Green pigment	Ca, Mn (tr), Fe, Cu , Pb	Copper based green pigment
Brown pigment	Ca, Mn, Fe , Cu, Pb	Burned yellow ochre + umbra
Black pigment	/	Organic black pigment
Interventions	Ca, Ba, Ti, Zn , Fe	Titanium white + zinc white + barium sulphate (lithopone?)

Conclusions

The panel painting *The Pietà*, made by the anonymous Master of the Female Half-Lengths

towards 1550, belongs to the permanent collection of the Fine Arts Museum in Seville. Because of its unusual brownish tonality it was analysed by the portable non-destructive X-Ray Fluorescence technique, directly *in situ*. The original palette of the Master as well as possible alterations of pigments applied were the main object of this research. The painting was analysed in 125 points, always under the same measurement conditions. The pigments applied are common in the 16th century, lead white, yellow and red ochre, cinnabar, azurite, smalt and some copper based green pigment. Also a possible presence of lead-tin yellow and minium was detected, while some results led to the conclusion about the use of some organic red lakes and black pigments, which can not be identified by XRF. The brownish tonality of the painting is a result of chemical alterations of blue pigment smalt which lost its blue colour and turned brownish and transparent. This is why the sky, the mountains and the vestments that should be blue, appear brown, like in other Flemish paintings in the Museum's collection. On the other hand, a lot of retouches were found, made by modern pigments Ti and Zn white, especially in the junctions of the wood panels and in the Christ's figure, but also many small ones were detected (Table 1). There are no informations about earlier interventions; this is why these results are of special interest for restorers and conservators.

Acknowledgements

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References

- Brachert, T. (2001). *Lexikon historischer Maltechniken: Quellen – Handwerk – Technologie – Alchemie*. München: Callwey Verlag.
- Deming Glinsman, L. (2004). *The Application of X-Ray Fluorescence Spectrometry to the Study of Museum Objects*. Amsterdam: University of Amsterdam.
- Eastaugh, N., Walsh, V., Chaplin, T., Siddall, R. (2004). *Pigment Compendium: A Dictionary of Historical Pigments*. Burlington: Elsevier.
- Gómez, M.L. (2000). *Exámen científico aplicado a la conservación de obras de arte*. Madrid: Cátedra Instituto del patrimonio histórico español.
- Knoepfli, A., Emmenegger, O., Koller, M., Meyer, A. (eds.) (1990). *Reclams Handbuch der künstlerischen Techniken*. Stuttgart: Philipp Reclam jun.
- Matteini, M., Moles, A. (2004). *La chimica nel restauro: I materiali dell'arte pittorica*. Firenze: Nardini editore.
- Montagna, G. (1993). *I pigmenti: Prontuario per l'arte e il restauro*. Firenze: Nardini editore.
- Schram, H.P., Herling, B. (1995). *Historische Malmaterialien und ihre Identifizierung*. Stuttgart: Ravensburg Buchverlag.
- Seccaroni, C., Moiola, P. (2004). *Fluorescenza X: Prontuario per l'analisi XRF portatile applicata a superfici policrome*. Firenze: Nardini editore.

Valdivieso González, E. (1993). *La pintura en el Museo de Bellas Artes de Sevilla*. Sevilla: Edición Galve.

Volpin, S., Appolonia, L. (2002). *Le análisis di laboratorio aplicata ai beni artistici policromi*. Padova: Il Prato.

Wehlte, K. (1967). *Werkstoffe und Techniken der Malerei*. Ravensburg: Otto Maier Verlag.

West Fitzhugh, E., Feller, R.L., Roy, A., Berrie B. (eds.) (1987-2007). *Artists' pigments: A Handbook of their history and characterisation*. Washington, New York, Oxford: National Gallery of Art/Oxford University Press.



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TECHNOLOGIES FOR THE CONSERVATION AND VALORIZATION OF CULTURAL HERITAGE (CSD-TCP): SPAIN SHOWS ITS PRIORITIES THROUGH A NEW CONSOLIDER RESEARCH PROGRAM

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In December 2007 the Ministry of Science and Innovation (MiCInn) placed its wager on cultural heritage. It approved the project called *Research programme on technologies for the conservation and valorization of cultural heritage* (TCP), designed to create a strong cluster of research groups around the theme of applying technology to the study, protection and valorization of cultural heritage. This cluster, once consolidated, should be able to compete with similar networks on an international level. The funding necessary was provided by the new Consolider-Ingenio 2010 program, designed for large-scale support of scientifically competitive networks.

Due to different administrative problems the CSD-TCP project has not entered full functioning mode until 2009, which has not impeded the streamlining of cooperation between the partners. These include 15 research groups (Figures 1-3) from different institutes of the Consejo Superior de Investigaciones Científicas (CSIC) and the universities of Jaén (UJa), Politécnica de Madrid (UPM), País Vasco (UPV-EHU) and Santiago de Compostela (USC), as well as one private company (NECO). These partners enjoy funding up to 5 million € in 5 years, which has helped continued research, contracting of experts and other service providers and,

generally, ensuring the highest quality in heritage research available on the market. The team members and their affiliations are detailed in Table 1. This large team includes some of the best Spanish specialists in cultural heritage studies from the diverse disciplines involved in studying and protecting this valuable social asset. The team uses current trends in the field, availing itself of top of the line resources and technologies. Collaboration between the teams is the main objective so that a solid network can be created for the future. This cooperation stems from the previous experience of the teams involved, which has only grown tighter as the program has advanced.

Table 1. Member groups of the CSD-TCP team

Member	Coordinator	Institution
ArqBio	M. Moreno	CCHS, CSIC
ArqueoMetal	A. Perea	CCHS, CSIC
CERVITRUM	M.A. Villegas	CCHS, CSIC
EST-AP	I. Sastre	CCHS, CSIC
GIPSE	J. Vicent	CCHS, CSIC
GFYT	S. Ormeño	UPM
CAAI	A. Ruiz	UJa
EPEC	A. Martínez Cortizas	USC
SINCRISIS	M.V. García Quintela	USC
GPAC	A. Azkarate	UPV-EHU
LANAPAC	M. Castillejo	IQFR, CSIC
LaPa	F. Criado Boado	IEGPS, CSIC
MICROPATH	C. Saiz-Jimenez	IRNAS, CSIC
PAP	R. Fort	UCM-IGE, CSIC
PATRYMAT	M.T. Blanco-Varela	ICCET, CSIC
NECO	C.A. González	NECO Information Technologies

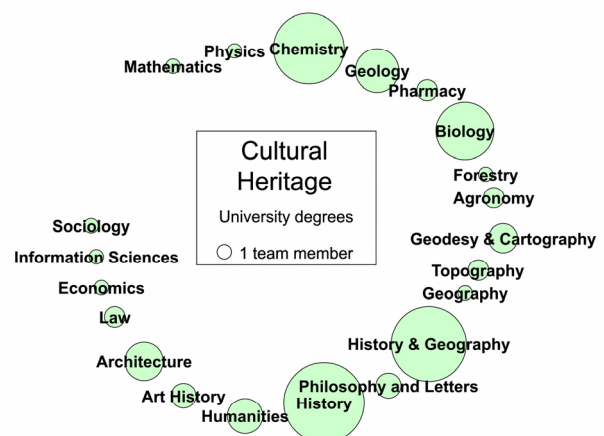


Figure 1. Team composition (I)

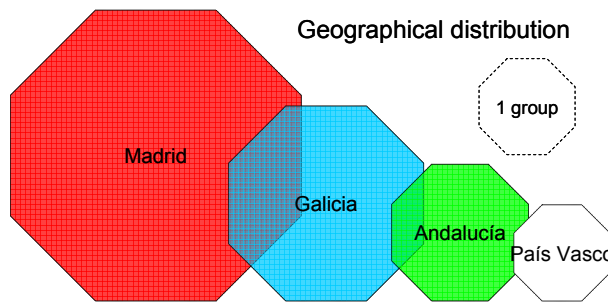


Figure 2. Team composition (II)

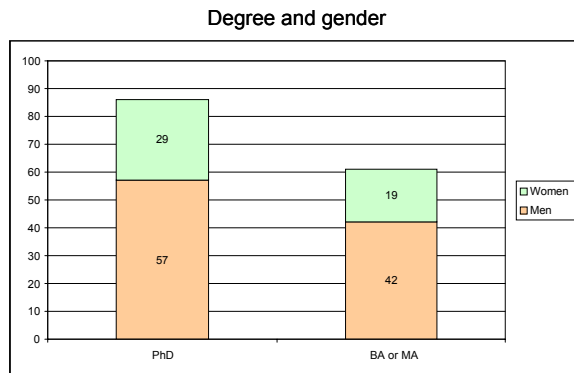


Figure 3. Team composition (III)

Coordination is based on a simple structure. At the head, the LaPa team (IEGPS, CSIC), headed by Felipe Criado Boado, is in charge of overall coordination. As vice-coordinators, Almudena Orejas Saco del Valle (CCHS, CSIC) and Cesareo Saiz-Jimenez (IRNAS, CSIC) coordinate two of the three nodes which subdivide the team, the last node being coordinated by LaPa as well. These nodes are fairly balanced in composition among each other, both in number of researchers and teams. The vice-coordinators are interlocutors with the PIs of each group, relaying information. Through core group meetings, the node leaders also establish overall coordination policy, thereby improving disciplinary balance.

The CSD-TCP project was organized along different axes centered on demonstration projects and transversal activities. The first were on-the-ground heritage which was to serve as test-cases for CSD-TCP teamwork. The second were other activities aimed at establishing methodological protocols for a variety of challenges and approaches in studying cultural heritage.

The development of the project, however, has far outgrown this plan, incorporating different dimensions of the scientific process.

Therefore, the current structure of the project can be outlined in three parts:

Demonstration projects

These include those that were proposed originally, plus a few others. They include on-site heritage which, though it has been studied since before the program, the application of CSD-TCP as a team has greatly expanded the scientific and social potential of these sites. Below are a few examples of the most active demonstration projects.

Vitoria-Gasteiz: This city unknowingly held within it the remains of an ancient wall, over 300 meters in length and up to 10 meters in height: the 11th century Pre-foundational City Wall, which lay hidden in back yards and degraded plots. The restoration features coherent language and imagery throughout, educating citizens by facilitating the recovery of their collective memory regarding these “forgotten architectures”, while favoring the social integration of the neighborhood through their identification with the cultural heritage they possess (and which they were not aware of before). This task has been undertaken resolutely by regional institutions (the Department of Culture of the Basque Government) and local ones (the Council of Vitoria-Gasteiz and the Agency for the Integral Revitalization of the Historic Centre), who have jointly financed approximately 5.5 million €, which is estimated to be the final cost of the project.



Figure 4. The Time of the Iberians comes to life through heritage valorization.

Voyage to the time of the Iberians: the development of the Iberian culture in the province of Jaén between the 7th and 1st Centuries BC left a strong imprint that we can appreciate even now. We still have

archaeological evidences from this period such as the fortified cities (*oppida*) of Cástulo, Giribaile and Puente Tablas, the burial chambers of Toya and Hornos, the burial mounds (*tumulus*) of Cerrillo Blanco and sanctuaries such as El Pajarillo or the one in Cueva de la Lobera. The proposed *Voyage to the time of the Iberians* (Figure 4) is a project ruled by the Andalusian Center of Iberian Archaeology headed for its execution by the County of Jaen and the Ministry of Tourism, in coordination with the various municipalities and with the collaboration of the Ministry of Culture. The project promotes the recovery and improvement of a number of archaeological sites and the creation of a network of visitor centers, museums and interpretive centers linked to the Iberian Museum, which is being promoted by the Department of Culture of Andalucía.

Santiago: the Landscape Archaeology Laboratory (LaPa) based in the Instituto de Estudios Galegos Padre Sarmiento (IEGPS, CSIC), has a fundamental role in the coordination of the Consolider team. Within it, it manages some projects aimed at advancing specific objectives of the CSD-TCP. One of the most attractive for the general public is the surveillance of the rehabilitation of historic buildings in the Old Town of Santiago de Compostela. Within it there is an analysis which includes archaeological control, historical and architectural evolution, conservation and preservation of each building. All the information generated by these studies is documented, analyzed and recorded in order not to lose sight of the heritage-related intervention which is being done. Following this line of integrated studies, the *Spatial* project is also being carried out, with the goal of developing a model definition which can express the spatial representation of heritage. In order to achieve that, elements with a structural-spatial dimension which constitute cultural heritage must be identified and characterized, as well as the existing relationships between them. An additional challenge is to test some methods for digital and geographical representation of that information.

Territory of Gijón: research on the archaeological heritage of the Asturian city and its surroundings has been a theme with an ample trajectory and well-publicized scientific results, both socially and in the academic

sphere. This research has been possible thanks to the collaboration of multiple institutions (Universidad Autónoma de Madrid, Ayuntamiento de Gijón, CSIC, Universidad de Oviedo) and specialists which have studied and preserved the built, moveable, landscape and environmental heritage. Many structures and ensembles have been studied, including production areas (fish-salting factory) and domestic spaces (in Cimadevilla). Several of them have, in fact, been made visitable and understood within their current contexts, like the Roman baths at Campo Valdés and the Late Roman city wall. In recent years, and in coordination with the Consolider TCP program, some studies of the Roman *villa* of Veranes have been carried out, with the aim of understanding and showing the architectural, social, productive and territorial aspects of a Roman rural centre, which became a rich complex towards the end of the Empire. Meanwhile, in downtown Gijón, the Tobacco Factory excavations have shed light on an ancient water deposit. The sedimentation of this structure has yielded exceptional inorganic and organic remains (seeds, pollen, branches, imprints, microfauna...), as well as tools of daily use. The possibility of incorporating this information and remains to the City Museum which will be built in this Factory opens the possibility of integrating this heritage into the museum exhibit.



Figure 5. In the territory of Gijón, the *villa* of Veranes has become a high-quality cultural resource.

Exploratory projects

Some of the transversal activities originally planned have become 'exploratory projects' due to their experimental or exploratory nature. Their objective is to test new methodologies and techniques, evaluating their potential as frontier science. Below are a few examples:

One of the main ground-breaking axes of the CSD-TCP has been the creation and development of Spatial Data Infrastructures (SDIs) based on heritage. This novel working tool integrates, through an internet interface, data and metadata of geographical, heritage or any other type of nature. It can be used either by scientists or the general public, thereby becoming a form of dissemination in itself. The IDEZAM (www.idezam.es), based on the Bierzo RVN (León) demonstration project, was the first to be created, in collaboration with the Fundación Las Médulas. Another demonstration project which is about to have its own SDI is the Pino del Oro Mining Zone (Zamora), through the IDEZOMIPO. The CSD-TCP is actively involved in developing other SDIs (e.g. www.casamontero.org/wui/index.html), and participating in the committees involved in the creation of the first protocols regarding cultural heritage and R + D-based infrastructures in general.

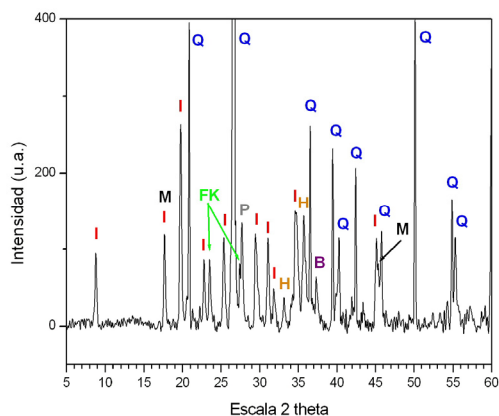


Figure 6. Analyzing the composition of portable heritage.

One of the main challenges facing the CSD-TCP team is the variety of laboratory work involved. The original transversal activities proposed included establishing common protocols useful in heritage study, analysis and protection (Figures 6 and 7). This difficult process has begun by establishing standardized policies for some laboratories such as the R+D facilities of the Archaeology and Social Processes research line at the CCHS. There, 11 different spaces with various infrastructure ranging from stereoscopic monitors to an Electron Beam Microscope, have come under single management and are in the process of achieving quality standards normally beyond the reach of research facilities.



Figure 7. Microscopic analysis of portable heritage.

These are but a couple of many exploratory projects undergone or in the process, in which we, as authors, have been involved more or less directly. This is by no means an objective or complete listing. By their very nature, these projects are proposed and performed following scientific challenges posed while in the process of analysis or experimentation, which renders any attempt to be thorough useless.

Training and transference activities

One of the main objectives of the program is to transfer its results to society in a variety of ways. The development of a training program which is currently underway, as well as the participation in diverse science policy networks, or active involvement in valorization and management of heritage have become fundamental activities.

Following this objective, we consider that one of the best ways for spreading the knowledge is creating a complete formation plan that can involve both, theoretical and practical classes. So we have designed a proposal which will include, first, a High Specialization Course

(HSP) with a duration of six months that will provide the theoretical basis and some laboratory practice time, second, some visits to the places where the demonstration projects are carried on, and third, two Summer Schools of strong practical schedule and a shorter duration. The HSC is related to Models of Intervention on Cultural Heritage, and will include six different modules with topics as socioeconomic impacts, mitigation and adaptation strategies, environmental impact assessment, risk evaluation, damage and diagnosis and new products, techniques and methods, not forgetting the real importance and significance of the cultural element per se.

The Summer Schools will last one week each. The first one is centered on the old agricultural processes, the wounds it left on the landscape and the study of cereals and other seeds. The second one is about ancient gold mining processes, how they were developed, and the ways we have now to detect them and assess their significance in the territory that is involved. With these summer schools we are trying to show how to put in practice the background acquired in the HSP, assuming them as a perfect complement, demonstrating that multiple scientific approaches can be done, and how combining all of them we can reach new conclusions and generate more knowledge.

That is the plan for 2011, but our aim is to gradually increase this training provision in the future, making new summer schools with different issues that could supply the new needs of the society.

The CSD-TCP has been very active in national and international policy regarding R+D and heritage. Members of the team have participated in developing the 2020 Strategy for the Spanish Government. The project leader is a member of the Joint Project Initiative committee regarding cultural heritage, to begin in 2011. The project vice-coordinator was a member of the standing committee behind the development of the ESF Science Policy Briefing regarding landscapes, presented in October 2010 to the European Commission. This is just a relevant selection of international committees where team members are involved.

It is the firm belief of the CSD-TCP team that science must be strongly involved both in policy making and in transferring scientific results to society, both through direct exploitation and increasing the visibility to society as a whole. Thus, many activities have been directly aimed at explaining our research to the general population, in seminars, publications and workshops.



Figure 8. Valorizing the cultural heritage of Pino del Oro.

For similar reasons, valorizing and managing cultural heritage is one of the fundamental pillars of the CSD-TCP. In this way, local populations are benefited with new social and cultural resources. In the Pino del Oro Mining Zone demonstration project, itineraries, brochures, guides and other materials have been created, always in tune with the natural protection which they enjoy being inside a Park, and in coordination with local and regional authorities (Figure 8). More activities in this direction are planned, including a web page, better signaling, and a visitor center.

Heritage management activities have been continuous in the Bierzo RVN demonstration project, including participation in the preparation of public policy documents dealing with territorial ordering on a local level. Collaboration with the Fundación Las Médulas has allowed the CSD-TCP to actively participate in science-to-society activities dealing with that World Heritage Site.

The CSD-TCP is making every effort to publicize its activity. In the AR&PA Innovation 2010 fair in Valladolid it had its own stand. We were present in the Innovation area, and displayed the multiple scientific approaches of the team and the demonstration projects in which this new way of working on Cultural Heritage is carried on. In order to let visitors take information home with them, we did a leaflet with general project information.

Moreover, in this moment when Internet relays information around the world, we are working on a new web page (www.proyectos.cchs.csic/csd-tcp) that could become the place where all the news of the team will be made public, the projects that are active, information including new courses, related links and other data that could be of interest to visitors.



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SYNCHROTRON RADIATION EXPERIMENTS IN SPANISH CULTURAL HERITAGE BAROQUE MATERIALS: AN OVERVIEW

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The field of Cultural Heritage has been actively studied by several research groups in different parts of the world. Within the sixth and seventh Framework Program of the EU, the EU ARTECH project (*Access, Research and Technology for the conservation of the European Cultural Heritage*) [1], and its successor CHARISMA (*Cultural Heritage Advanced Research Infrastructures: Synergy for a Multidisciplinary Approach to Conservation /Restoration*) [2], a consortium among 13 internationally distinguished European infrastructures devoted to artwork conservation, offer a coherent set of possibilities to access to the most advanced scientific instrumentations and knowledge on the field of cultural heritage studies.

In Spain, particularly in Andalusia, over the past decade, multi-disciplinary research has been carried out in the interface between art, archaeology, biology and solid state science. The Andalusian Government has become involved; they promoted different programs with the aim to support new advances in this area. The Institute for Natural Resources and Agrobiology of Seville, the Fine Arts Schools of the University of Seville, and the University of Malaga are involved in obtaining and developing this interface using new strategies to support the field of cultural heritage.

The Cultural Heritage Group at the Materials Science Institute of Seville has an extensive expertise in the advancement of conservation science and the characterisation of materials and alteration processes. A strong effort has been made in the last few years to develop innovative methodologies and techniques using synchrotron radiation sources. These advancements have contributed to the knowledge of cultural heritage and conservation science.

This work reviews some practical cases for the use of synchrotron radiation (SR) in the study of different materials which are representative of Spanish Cultural Heritage. All of these ornamental elements are characteristic of the Andalusian Baroque period of art.

Synchrotron radiation is an increasingly important tool for research in cultural heritage. In Europe the most important SR infrastructures are: *ESRF* (European Synchrotron Radiation Facility) in Grenoble, *SOLEIL* Synchrotron in Paris, *BESSY* in Berlin and *Diamond Light Source* in Oxford. The unique properties of synchrotron radiation have enabled the growth of techniques that would not have been feasible in a laboratory situation.



Figure 1. (a) Spanish baroque organ from Baeza, Jaen, (Anonymous, c.a.1785) (b) detailed view of the "flue pipe". (c) tongue and shallot from the reed pipes.

A Synchrotron radiation source consists of a storage ring where charge particles, usually electrons circulating in a vacuum vessel of a high-energy particle accelerator and travelling at velocities close to that of light. The synchrotron radiation is produced either in the bending magnets needed to keep the electrons in a closed orbit or in insertion devices such as wigglers or undulators situated in the straight sections of the storage ring. In the insertion devices, an alternating magnetic field forces the electrons to follow oscillating paths rather than moving in a straight line; as a result, a narrow cone is emitted, which constitutes the synchrotron radiation. The beam lines are placed tangentially to the storage ring when dealing with a bending magnet and parallel to the straight section of the storage ring when dealing with an insertion device. Several aspects of an X-ray source determine the quality of the X-ray beam that it produces.

The principal property of synchrotron radiation is brilliance rather than flux. Brilliance is determined by the number of X-ray quanta per area of the source, per solid angle, per second, and often per spectral interval. Such a quantity allows the researcher to compare the quality of the X-ray beam from different sources. It should be noted that the maximum brilliance from third generation undulators is about 10 orders of magnitude higher than that from a rotating anode (Creagh 2007, Baruchel et al. 2008).

High flux and brilliance, ability to produce a fast data collection and the possibility to use small sample size, small beam footprint enables to obtain area mapping 2D and 3D studies at millimetre to micron length-scale. The wavelength tunability and the energy region can be selected to suit the problem at hand (Herrera 2009, Herrera et al. 2009a). The most employed techniques till now have been synchrotron X-ray fluorescence analysis (XRF); X-ray diffraction (XRD); micro-X-ray diffraction (μ XRD), grazing incidence X-ray diffraction (GID) techniques, X-ray absorption spectrometry (XAS) and infrared microscopy. The synchrotron beam can be focused in sub micrometric spots, allowing the examination of very small samples. The list of artwork studied by using SR is made up of a large variety of materials (Bertrand et al. 2006, Cotte et al. 2008, Duran et al. 2010).

The research work included in this paper is related with cultural heritage studies of our own research focused on the characterization of three different materials: organ pipes, tin mercury mirrors, and multi-layered canvas paintings which are representative of Spanish Cultural Heritage.

Identification of trace elements present in the flue and reed pipes of a Spanish baroque organ

A comparative study of the composition and microstructure of different flue pipes (tin and lead spotted metals) and reed pipes with a moving tongue (Cu and Zn alloys) from a Spanish baroque organ (Figure 1a) are presented on this overview. The experiments were carried out using a combination of laboratory techniques as well as microanalytical methods at the *ESRF*. μ X-ray fluorescence (μ XRF) at high and low energies is employed for elemental and chemical

imaging distribution at the sub-micrometer scale.

Flue pipes

The percentage of tin and lead changes the properties, and thus, the function of the pipes within the organ. Lead has been the standard material of organ pipes for a very long time. Moreover, its high density and softness make it easy to work with, and allows lead to dampen unwanted resonance (Lewis 1974).

Modern lead from 20th century has a low strength/weight ratio which makes it

particularly prone to fail; this is probably a consequence of its high purity. To compensate for this, during the casting process many modern organ builders add the trace elements removed during the modern refining process. These trace elements present in ancient organs generally consist of small amounts of antimony, bismuth, copper, and silver. It has been suggested that the trace elements in 17th century lead, made the pipes sturdy enough to stand for many years, that is, the trace elements produced the desired stiffness (Herrera et al. 2009b).

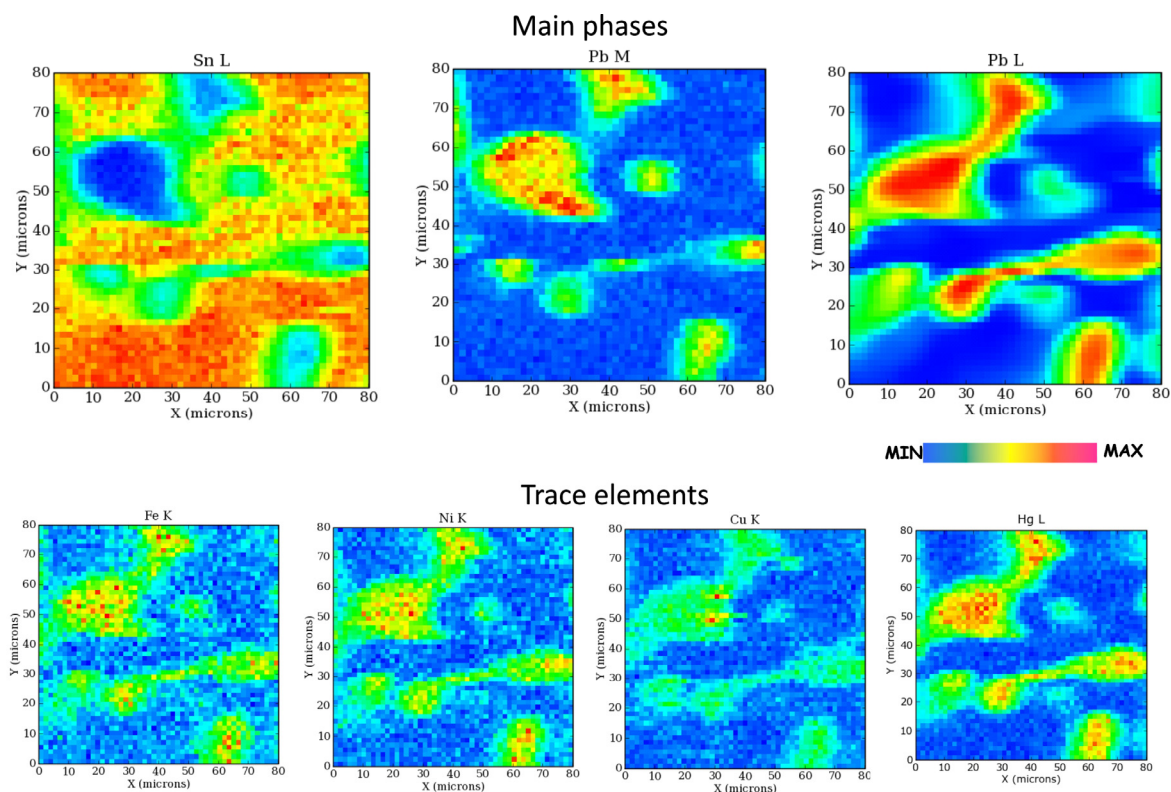


Figure 2. Distribution of major and trace elements of the flue pipe cross-section sample.

Pipes manufactured with tin-rich alloys have a bright sound and typically look shinier than pipes manufactured with lead-rich alloys. In order to study the distribution and correlation of the trace elements presence in Pb and Sn phases it was necessary to quantify their concentration in the bulk and their distribution within *major* phases; one sample from a flue pipe of an ancient Baroque organ was chosen (Figure 1b). μ XRF analysis was carried out using synchrotron radiation microbeams as excitation source. This type of species and multi-elemental densities can be detected at the micrometer scale. A quantitative analysis using PyMCA code (Solé et al. 2007) was

computed based on the assumption that the incidence of the monochromatic beam on the flat sample occurred without secondary excitation (Figure 2).

These experiments reveal the different trace elements and their localization in the Pb and Sn segregated phases using μ XRF. The fits yielded an elemental concentration around 85% [Sn] and 15% [Pb] for the major elements. Values ranging from 0.05% [Hg], 0.02% [Ni], 0.016% [Fe], and 0.01% [Cu] were found for these trace elements. For the remaining elements, the quantification derived very low concentrations (below to 0.01%)

that were within the detection limits of the ID18F station. All elements exhibited an inhomogeneous distribution with spatial colocalization consistent with Pb incorporation.

The study of the distribution of the elements shows that the organ pipes are spotted metals. These results are important for the new organ builders because today's lead is totally pure. Adding trace elements may reproduce antique technology to make better pipe organs. Based on these results, builders should try to create pipes with trace elements that were present in the past.

Reed pipes

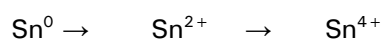
Reed pipes contain an additional vibrating part, the Cu-based alloy tongue that vibrates on the shallot. The tongue crucially influences and produces sounds (Kob 2000, Nederveen and Dalmont 2004) (Figure 1c). In most cases, both tongues and shallots are made of brass (a copper–zinc alloy). Important finding of these results was the confirmation of the role of metallic lead in the final microstructure of the tongue. The results indicate that the old historical brass tongue has a fitted elemental concentration yield of around 64%Cu and 34% Zn for the main elements. 2D mapping highlighted the presence of traces of Pb, Ni, Fe, and Sn in the bulk of the sample. Pb is segregated from Cu and dissolves As and Bi (Herrera 2009, Herrera et al. 2009b, Muñoz-Paez et al. 2011).

Study of alteration process of ancient mirrors using micro diffraction techniques

Characterization of diverse amalgam surfaces, with different alteration degrees from Andalusian historical mirrors, has been studied by XRD using synchrotron radiation in a grazing incidence mode (GID) and other spectroscopic techniques X-ray photoelectron spectroscopy (XPS), and reflection electron energy-loss spectroscopy (REELS) were used (Herrera et al. 2008).

According to previous publications in which we presented an analytical approach, synchrotron radiation-based x-ray diffraction (SR-XRD) allowed us to clarify the formation of different corrosion processes involved in the alteration of the mirrors. The mercury evaporation is closely related to the corrosion of the amalgam. In order to reveal the relationship between the mercury release and the tin oxides formed on the most external

layer it is necessary to determine the composition and the chemical state of the components of the amalgam surface. Tin oxide layer formed on the amalgam surface avoids the mercury evaporation. The XRD information of one of the samples showed that the phases present between 0.25 μ m and 1.17 μ m thick are tin dioxide (Sn⁴⁺) and tin monoxide (Sn²⁺). The original amalgam was constituted by Sn⁰. Therefore corroded mirrors show a similar corrosion process, that is, the oxidation of tin in the following way:



The mercury-rich liquid phase present in the amalgam accelerates the corrosion of the tin-rich solid phase through may be also attributed to the galvanic action.

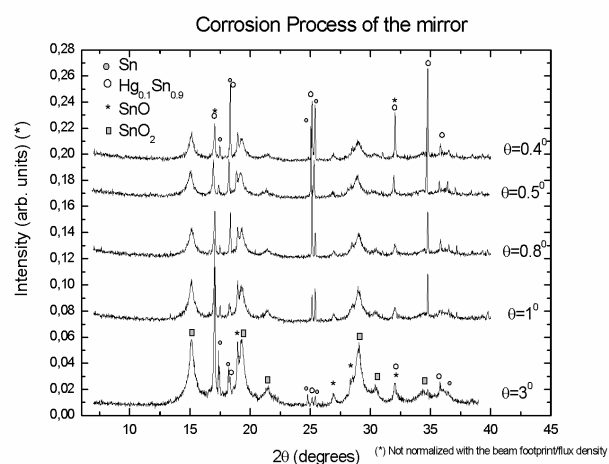


Figure 3. SR-XRD patterns of the small dark area outside the undamaged amalgam layer.

Tin corroded preferentially over mercury; However when the amalgam is corroded, mercury is released as tin oxidizes, thus, two phases are present and galvanic corrosion can take place. The tin-rich solid phase would be expected to oxidize with the release of mercury, causing the softening of the amalgam in the corroded area. Within the corrosion process defined on top, SnO, which is formed first, is thermodynamically unstable, and further oxidizes very slowly to SnO₂ (Figure 3). The two tin oxides are usual products due to atmospheric corrosion and correspond to the reported ones of tin exposed indoors (Kossolapv and Twilley 1994), and the long time elapsed from the mirrors manufacture (XVII Century). The use of a large beam with a high angle resolution provides an accurate means for semi-quantitative analysis and the use of a sub-mm

beam opens a way for separating the dark corroded and uncorroded part of the amalgam. The alteration processes of the ancient mirrors suggest a gradual increase of tin degradation along the outer layers of the amalgam.

Here, one would expect oxidation of the surface of the metal to form a passive tin dioxide film which would protect the metal from further corrosion. However, the mercury is volatile and slowly disappears from the tin-mercury compound leaving finely divided particles of tin that are oxidized forming nanocrystals (Herrera et al. 2009c).

Combination of X-ray microprobes for study of multi-layered canvas paintings

There is a great deal of interest in copper minerals formed in several environmental situations. Two of the copper carbonate minerals, azurite [$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})$] and malachite [$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$], are important pigments. This example focuses on the use of these copper carbonates as pigments during the Spanish Baroque period of art. The copper pigments are usually detected by scanning electron microscopy (SEM)/ energy dispersion X ray analysis (EDX) (Herrera et al. 2007). XRD has been proven to be a valuable tool for the clear identification of inorganic pigments. However, with conventional XRD, it is rather difficult to acquire all of the information from multi-layer samples due to the thinness of the colour layers, which are in the range of several tens of microns. Furthermore, the contributions of the small quantities of the copper pigments to the total sample are very low.

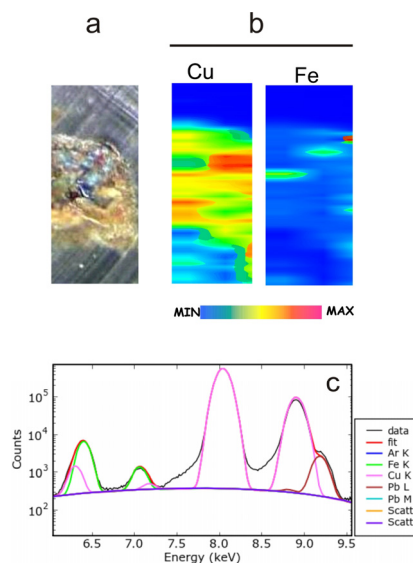


Figure 4. (a) Thin cross-section of the multi-layered canvas painting authored by Bocanegra (XVII) (b) SR- μ XRF elemental maps of Cu and Fe grains (c) XRF spectra at high excitation energy.

To solve the difficulties involving the characterization of different pigments coexisting in the same color layer, experiments using μ XRF/ μ XRD microprobe on the thin cross sections of this sample were conducted. They illustrate the potential of the combination of these techniques. Two-dimensional mapping was performed with the simultaneous acquisition of diffraction patterns (in transmission) and fluorescence spectra (at 90° from the incoming beam, in the horizontal plane) at each pixel of a 2D-array. Figure 4 shows the sample that was selected due to the complexity of the pictorial layer containing the different pigmented colors (red, blue and green).

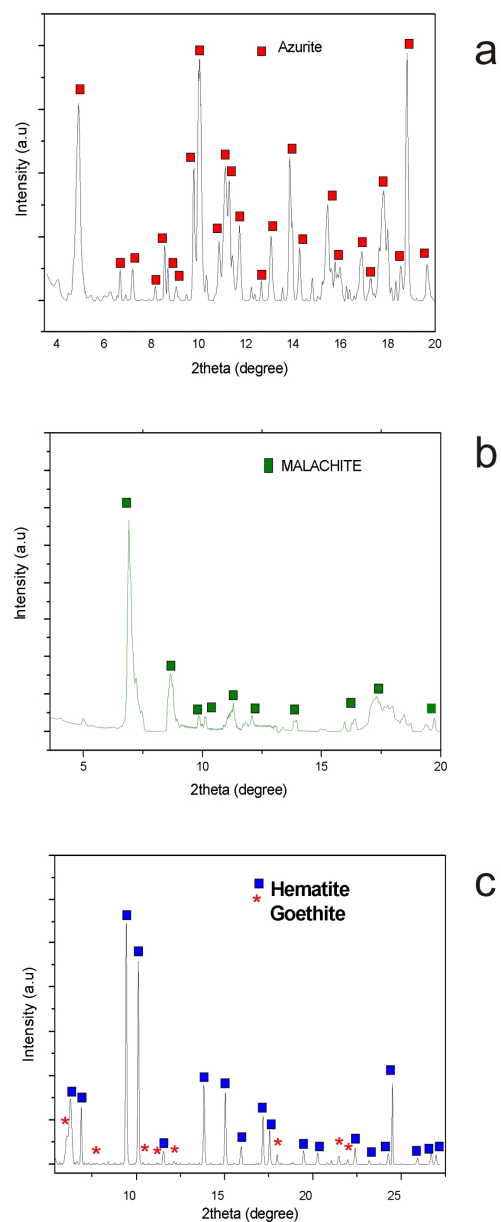


Figure 5. SR- μ XRD pattern of (a) blue, (b) green and (c) red grains obtained in the pictorial layer.

There is clear redundancy in analyzing the parallel elemental and structure information provided by XRF and XRD (Figure 5). An μ XRF spectrum shows the K lines for Cu and Fe. The thin cross section is superimposed on some of the elemental mapping (Cu and Fe).

Concluding Remarks

Synchrotron-based X-ray microprobes are particularly useful for non-destructive studies as well as for the micro-characterisation of different materials present in multi-layered paintings and sub micrometric samples. These studies demonstrated that synchrotron radiation micro-imaging techniques can be used to analyse pictorial layers (including grains) at the micrometer scale. μ -XRD is very useful for the identification of phases that are present in low proportions in multilayer samples.

Using μ -XRF microprobe at a Synchrotron Radiation source with its high brightness, low divergence and highly linear polarization it was possible to obtain additional information, such as detecting trace elements as well as its spatial distribution, a type of information usually not readily obtained within the laboratory framework.

Acknowledgements

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References

- Adriaens, A. and Dowsett, M. (2010). The coordinated use of synchrotron spectro-electrochemistry for corrosion studies on heritage metals. *Acc. Chem. Res* 43: 927-935.
- Baruchel, J., Bleuet, P., Bravin, A., Coan, P., Lima, E., Madsen, A., Ludwig, W., Pernot P. and Susini J. (2008). Advances in synchrotron hard X-ray based imaging. *C.R. Physique* 9: 624-641.
- Bertrand, L., Vantelon, D. and Pantos, E. (2006). Novel interface for cultural heritage at SOLEIL. *Applied Physics A* 83: 225-228.
- Cotte, M., Susini, J., Solé, V.A., Taniguchi, T., Chillida, J., Chécroun, E. and Walter P. (2008). Applications of synchrotron-based micro-imaging techniques to the chemical analysis of ancient paintings. *J. Anal. At. Spectrom.* 23:820-828.
- Creagh, D.C. (2007). Radiation in art and archaeometry. In D.C. Creagh and D.A. Bradley (eds.) *Physical Techniques in the Study of Art, Archaeology and Cultural Heritage*: 1-95. Amsterdam: Elsevier Science,
- Duran, A., Jimenez- De Haro, M.C., Perez-Rodriguez, J.L., Franquelo, M.L., Herrera L.K. and Justo A. (2010). Determination of pigments and binders in Pompeian wall paintings using synchrotron radiation - High-resolution X-ray powder diffraction and conventional spectroscopy - chromatography. *Archaeometry* 52: 286-307.
- Herrera, L.K., Justo, A., Perez Rodriguez, J.L. and Duran, A. (2007) internal technical report (ICMSE-CSIC).
- Herrera, L.K., Duran, A., Franquelo, M.L., González-Elipe, A.R., Espinós, J.P., Rubio-Zuazo, J., Castro, C.R., Justo, A., Perez-Rodriguez, J.L. (2008). Study by grazing incident diffraction

and surface spectroscopy of amalgam from cultural heritage ancient mirrors. *Central European Journal of Chemistry* 7: 47-53.

- Herrera, L.K. (2009). *Physico-Chemical Research of Cultural Heritage Materials Using Microanalytical Methods*. PhD Thesis, Seville University.
- Herrera, L.K., Montalbani, S., Chiavari, G., Cotte, M., Solé, V.A., Bueno, J., Duran, A., Justo, A. and Perez-Rodriguez, J.L. (2009a) Advanced combined application of μ X-ray diffraction/ μ -X-ray fluorescence with conventional techniques for the identification of pictorial materials from Baroque Andalusia paintings. *Talanta* 80:71-83.
- Herrera, L.K., Justo, A., Munoz-Paez A., Sans, J.A. and Martinez-Criado G. (2009b). Study of metallic components of historical organ pipes using synchrotron radiation X-ray microfluorescence imaging and grazing incidence X-ray diffraction. *Anal. Bioanal. Chem* 395:1969-1975.
- Herrera, L.K., Justo, A. and Perez-Rodriguez, J.L. (2009c). Study of nanocrystalline SnO₂ particles formed during the corrosion processes of ancient amalgam mirrors. *Journal of nano research* 8: 99-107.
- Kob, M. (2000). Influence of wall vibrations on the transient sound of flue organ pipes. *Acta Acoust.* 86: 642-648.
- Kossolapv, A. and Twilley, J. (1994). A decorative Chinese dagger: evidence for ancient amalgam tinning. *Studies in Conservation* 39: 257-264.
- Lewis, W.R. (1974). The metallurgy of tin lead alloys for organ pipes. *ISO information.* 767-768
- Muñoz-Paez, A., Herrera, L.K., Justo A., Sans J.A. and Martinez-Criado, G. (2011). Study of metallic pieces from the Andalusian baroque period with micro X-ray diffraction and micro X-ray fluorescence. *Diamond Light Source Proceedings SRMS-7* 1:1-3.
- Nederveen CJ, Dalmont J-P (2004) Pitch and level changes in organ pipes due to wall resonances. *J. Sound Vib.* 271: 227-239.
- Solé, V.A., Papillon, E., Cotte, M., Walter, PH. and Susini, J. (2007). A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra. *Spectrochim. Acta Part B* 62: 63-68.

Web sites

- [1] <http://www.charismaproject.eu>
[2] <http://www.eu-artech.org>



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NETWORK ON SCIENCE AND TECHNOLOGY FOR THE CONSERVATION OF CULTURAL HERITAGE

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Coalition editors

A new Network on Science and Technology for the Conservation of the Cultural Heritage will be launched on March 1, 2011. This will be supported by the Spanish Ministry of Science and Innovation through project HAR2010-11432-E.

This Network was founded by 65 research groups from the Spanish Council for Scientific Research (CSIC) and Spanish universities, cultural institutions and sector's enterprises.

Its wide spectrum and the high number of researchers (up to 450) from areas such as archaeology, architecture, engineering, chemistry, materials science, physics, geology, biology, etc. constitute the best value to this proposal. The diversity of institutions and research profiles involved in the Network is crucial to afford an interdisciplinary issue as is the conservation of Cultural Heritage.

The main goal of this collaborative research is to promote national and international joint initiatives among the science-technology-enterprise system agents.

The activities of this Network will:

1. Give a boost to the research and work groups by means of the coordination of the activities, currently scattered in different scientific areas.

2. Give institutional recognition to the activities and promotion of the member groups by means of priority actions.

3. Foster the collaboration among the research groups in order to create a critical mass by means of their association to similar European networks and to facilitate the access to consortia and projects.

The composition of the Network is presented in Table 1.

Table 1. Members of the Network on Science and Technology for the Conservation of Cultural Heritage

CSIC Research Groups		
Group name	Coordinator(s)	Institution
Corrosion and metal protection for building and Cultural Heritage	Emilio Cano	CENIM
Conservation of historical and monumental glass and ceramic materials (CERVITRUM)	María Ángeles Villegas	CCHS
Decorative rocks: physicochemical processes	Adolfo Iñigo, Eloy Molina	IRNASA
Geoenvironmental analysis in hypogean environments	Sergio Sánchez Moral	MNCN
Study on materials and techniques employed in artworks	Ángel Justo Erbez	ICMSE
Microbial ecology and geomicrobiology - ECOGEO	Carmen Ascaso Ciria	CCMA
Petrology applied to Cultural Heritage conservation	Rafael Fort González	IGE
Multidisciplinary research group on ceramic and vitreous materials and archaeometry of Cultural Heritage (MATERARCERVID)	Pedro J. Sánchez Soto	ICMSE
Lasers and nanotechnologies for Cultural Heritage (LANAPAC)	Marta Castillejo Striano	IQFR
Ceramic and Glass Heritage ICV	Carmen Pascual	ICV
Application of non-destructive nuclear analysis techniques to Cultural Heritage	Miguel Ángel Respaldiza Galisteo	CNA
Social structure and territory – Landscape Archaeology	F.-Javier Sánchez-Palencia	CCHS IETCC
Materials science applied to Cultural Heritage - CEMAPA	M ^a Teresa Blanco Varela	IEGPS
Heritage Laboratory - LaPa	Felipe Criado Boado	IRNASE
Microbiology and Cultural Heritage	Cesáreo Sáiz Jiménez	IRNASE

University Research Groups

Group name	Coordinator(s)	Institution
Technology and conservation of Archaeological Heritage	Joaquín Barrio	Universidad Autónoma de Madrid
Analytical characterization, recording, conservation and restoring of Cultural Heritage	Margarita San Andrés	Universidad Complutense de Madrid
Research group for the protection and study of Architectural and Archaeological Heritage	Virginia Galván Martínez	IE Universidad/Instituto de Empresa
Research group on Architectural Heritage and Sustainability (GIPAS)	Gonzalo Barluenga Badiola	Universidad de Alcalá de Henares
Group of environmental studies applied to Cultural Heritage of Santiago de Compostela University	Benita Silva Hermo	Universidad de Santiago de Compostela
Laboratory of applied Petrology	Juan Carlos Cañaveras	Universidad de Alicante
Science and written culture	Teresa Espejo	Universidad de Granada
Bioengineering and Materials (BIO-MAT)	Diego A. Moreno	Universidad Politécnica de Madrid
MATERIAYARTE	María Arjonilla Álvarez	Universidad de Sevilla
FEMTOUSAL	Pablo Moreno	Universidad de Salamanca
Geomaterials	Rosario García Jiménez	Universidad Autónoma de Madrid
Ion Beam Analysis at CMAM UAM for Cultural Heritage	Alessandro Zucchiatti	Universidad Autónoma de Madrid
Material characterization of Cultural Heritage assets	José Francisco García Martínez	Universidad de Barcelona
Materials and building	Fco. Javier Alejandro Sánchez	Universidad de Sevilla
Group of Analysis and mechanic-structural restoration	Mario Solís Muñiz, José Domínguez Abascal	Universidad de Sevilla
Metallurgy and Materials engineering	José María Gallardo Fuentes	Universidad de Sevilla
Cultural landscapes in southern Spain	Francisca Chaves Tristán	Universidad de Sevilla
Study and conservation of Architectural Heritage building materials	Eduardo Sebastián Pardo	Universidad de Granada
Studies on alteration and conservation of building materials	José Francisco Vale Parapar	Universidad de Sevilla
Group on geomorphological and environmental research (GIXA)	Ramón Blanco Chao	Universidad de Santiago de Compostela
Petrology and Geochemistry applied to Cultural Heritage - PGPA	M ^a Pilar Lapuente Mercadal	Universidad de Zaragoza
Research group on chriptogames	Antonio Gómez Bolea	Universidad de Barcelona
Polimeric materials and Cultural Heritage	Massimo Lazzari	Universidad de Santiago de Compostela
Research group on built Heritage (GPAC)	Agustín Azkarate Garai-Olaun	Universidad del País Vasco
Andalusian Centre for Iberian Archaeology	Arturo Ruíz Rodríguez	Universidad de Jaén
AIPA. Analysis and intervention of Architectural Heritage	Juan Monjo Carrió	Universidad Politécnica de Madrid
Photosynthetic biofilms	Mariona Hernández Mariné	Universidad de Barcelona
Archaeometry Unit of University of Valencia Materials Science Institute (ICMV)	Clodoaldo Roldán García	Universidad de Valencia

Mural coverings and architectural finishings	Víctor J. Medina Flórez	Universidad de Granada
IBea -Ikerkuntza eta Berrikuntza Analitikoa (Analytical Research and Innovation)	Juan Manuel Madariaga	Universidad del País Vasco
Group of Mechanical Technology and Archaeometallurgy	Antonio José Criado Portal	Universidad Complutense de Madrid

Cultural Institutions

Institution	Responsible person(s)
Institute of Spanish Cultural Heritage	Alfonso Muñoz
Centre for conservation and restoration of cultural assets of Castilla y León	Milagros Burón Álvarez
Museum of Altamira	José Antonio Lasheras Corruchaga
Research and technologic development Group of Valencian Institute for Conservation and Restoration of Cultural Assets (IVC + R)	Juan Pérez Miralles, Carmen Pérez García
National Roman Art Museum of Mérida	Rafael Sabio González
Foundation National Glass Centre	Cristina Gil Puente
National Museum Art Centre Queen Sofía	Jorge García Gómez-Tejedor
El Prado National Museum	María Dolores Gayo
Las Médulas Foundation	María Ruiz del Árbol
Andalusian Institute of Cultural Heritage (IAPH)	Román Fernández-Baca Casares
Guggenheim-Bilbao Museum Foundation	Ainhoa Sanz

SMEs

Company	Responsible person(s)
SIT Transportes Internacionales, S.L.	Ana Tabuena, Guillermo Andrade
Restauración de edificios, artesanados y retablos Alonso, S.A. (REARASA)	Carlos Javier Alonso Arribas
Geomnia Natural Resources SLNE	Enrique Sanz Rubio
Arqueoestudio	Lorenzo Galindo Sanjosé
Cerámica y Vidrio "Della Robbia". Consorcio-Escuela de Artes y Artesanos de Gelves	Juan José Lupión Álvarez
Arte Conservación y Restauración, S.L. (ARTYCO S.L.)	Fernando Guerra-Librero Fernández
Sika, S.A.U.	Luz Granizo
Biología y Medio Ambiente (BMA)	Xavier Ariño Vila

Coalition Newsletter will be the official dissemination vehicle of the Network, which will continue fostering multidisciplinary

rendezvous of scientists and agents involved in the scientific study of Cultural Heritage.



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