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. Colaboration 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.

Back to index

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.

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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.

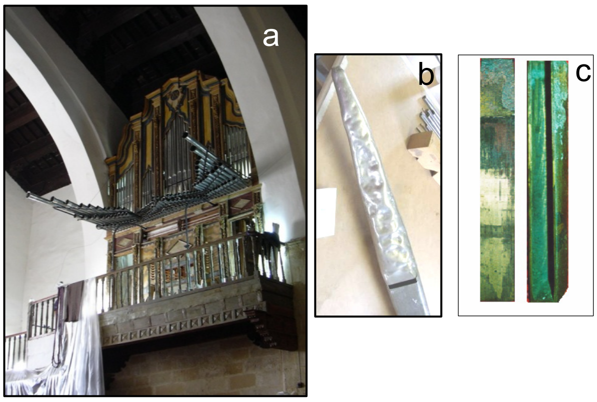

Figure 1. (a) Spanish baroque organ from Baeza, Jaen, (Anonymous, c.a.1785) (b) detailed view of the "flue pipe". (c) tongue and shallot from the reed pipes.

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 (μXRD), 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*. μX-ray fluorescence (μXRF) 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).

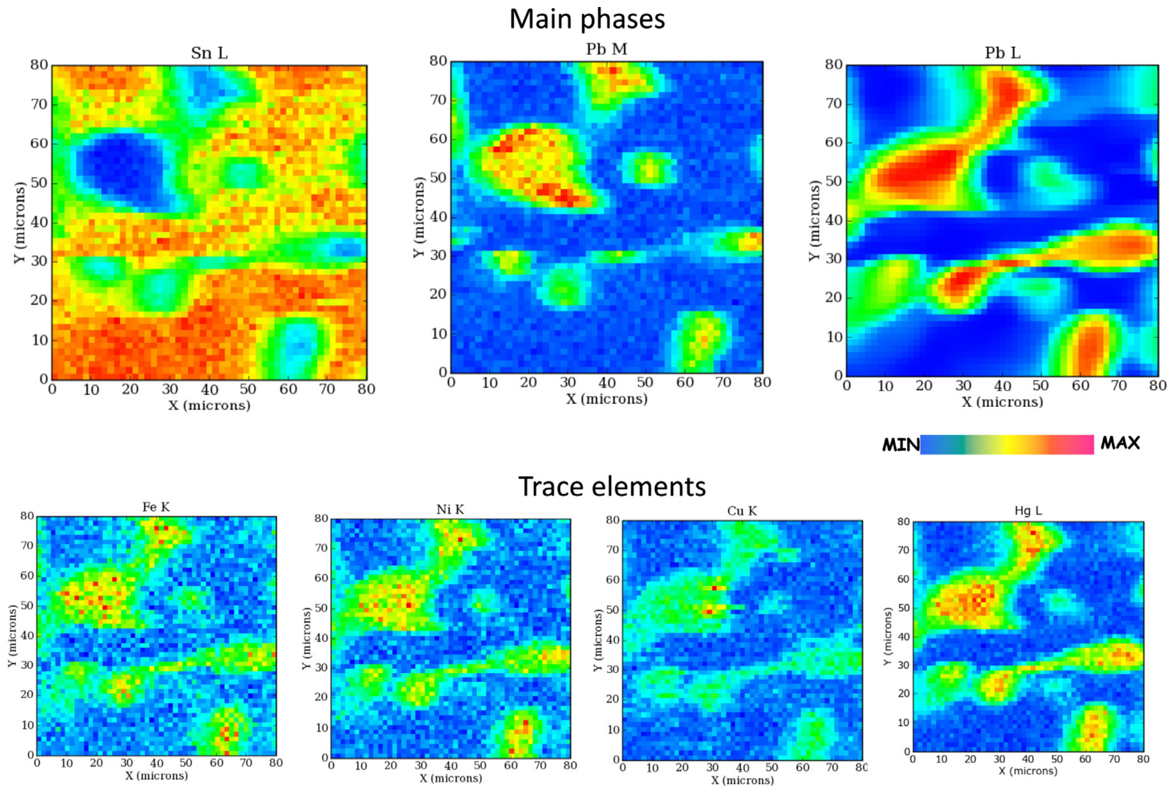

Figure 2. Distribution of major and trace elements of the flue pipe cross-section sample.

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 neccesary 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 (Figure1b). μXRF 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 μXRF. 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 co-localization 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 0.25μm and 1.17μm thick are tin dioxide (Sn^{4+}) and tin monoxide (Sn^{2+}). The original amalgam was constituted by Sn^0. Therefore corroded mirrors show a similar corrosion process, that is, the oxidation of tin in the following way:

$$Sn^0 \rightarrow \quad Sn^{2+} \quad \rightarrow \quad Sn^{4+}$$

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.

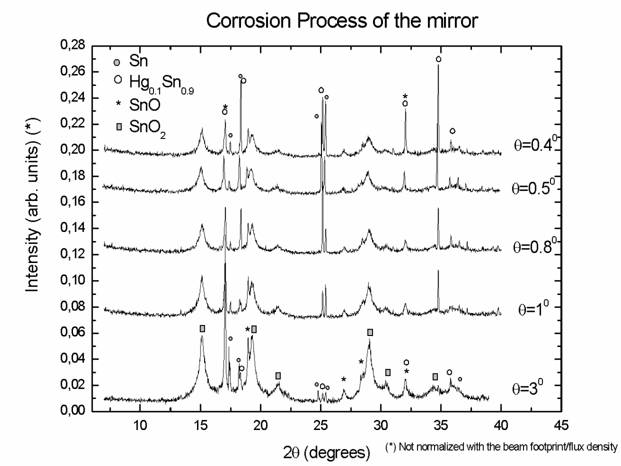

Figure 3. SR-XRD patterns of the small dark area outside the undamaged amalgam layer.

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 SnO_2 (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 [$2CuCO_3.Cu(OH)$] and malachite [$CuCO_3.Cu(OH)_2$], 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.

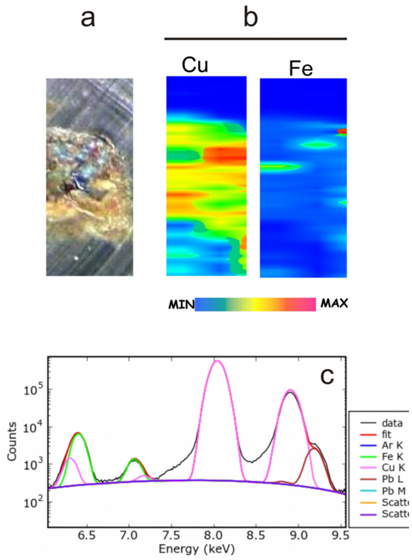

Figure 4. (a) Thin cross-section of the multi-layer canvas painting autored by Bocanegra (XVII) (b) SR-μXRF elemental maps of Cu and Fe grains (c) XRF spectra at high excitation energy.

To solve the difficulties involving the characterization of different pigments coexisting in the same color layer, experiments using μXRF/μXRD 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).

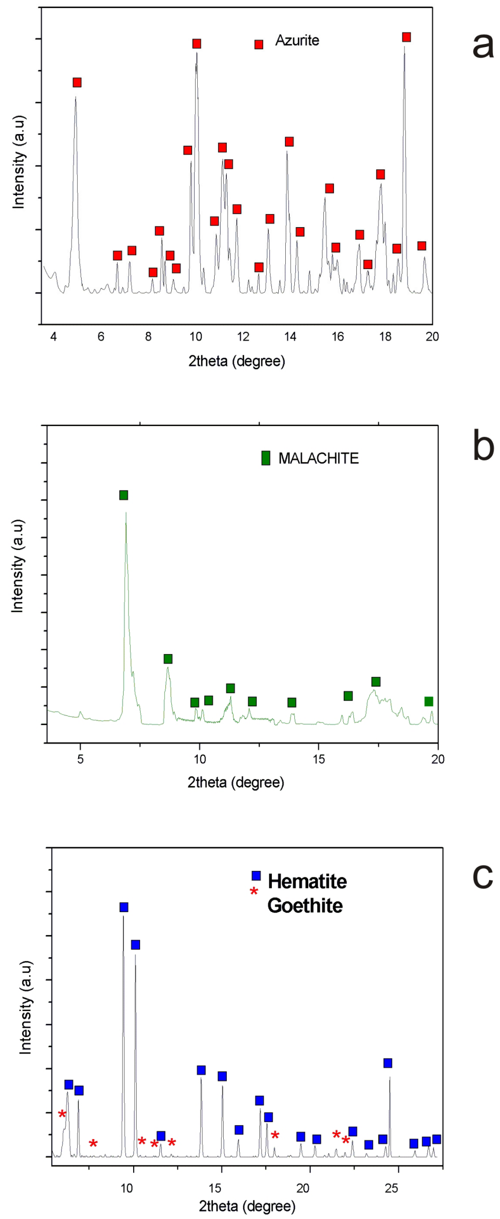

Figure 5. SR-μXRD pattern of (a) blue, (b) green and (c) red grains obtained in the pictorial layer.

There is clear redundancy in analyzing the parallel elemental and structure information provided by XRF and XRD (Figure 5). An μXRF 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., Checroun, 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 µX-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


Back to index

NETWORK ON SCIENCE AND TECHNOLOGY FOR THE CONSERVATION OF CULTURAL HERITAGE

Miguel A. Rogerio-Candelera and Cesareo Saiz-Jimenez

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.