STUDY OF BAROQUE ARTWORKS BY NON-DESTRUCTIVE TECHNIQUES

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Baroque artworks from (XVI-XVII c), i.e. canvases, mirrors, metals artefacts and wall paintings, were studied by different methods, to solve technical historical problems to deduce the original appearance and to establish the chemical and physical conditions of restoration and conservation. Several methods such as optical microscopy (OM); Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), X-ray energy dispersive spectrometry (EDX), X-ray diffraction (XRD) with Goebel mirror, Grazing angle and synchrotron radiation (SR) μXRD were used.

Baroque canvases

The famous baroque painter *Pedro Atanasio Bocanegra* was an outstanding student of *Alonso Cano* and painted a very special collection of the large format canvases about the life of *San Ignacio* (Herrera et al. 2005). The aim of this study on six paintings is analytical examination of paint samples taken from different points of the canvas dating from the 1600 AD (Figure 1). It was carried out using XRD, SEM observation as well as EDX spectrometry and FTIR (both in reflection and transmission mode). This resulted in the identification of materials to solve art technical historical questions, the deduction of the original appearance and the establishment of the chemical and physical condition for restoration and conservation.

The present research is focused on chemical description of the organic and inorganic components, particularly in the stratigraphy sequence, the pigments and binders, the superficial varnishes, etc. In order to elucidate the painting technique, the state of preservation, the process of decay and the cleaning tools for the design and execution of an appropriate restoration intervention a broad testing program was development.

Figure 1. Some of the *Bocanegra* paintings

The six paintings are composed of heterogeneous mixtures of organic and inorganic compounds with an often complex multi-layered build-up.

Macroscopic and microscopic studies are carried out on paint samples derived from the canvas. These samples are unique and in limited supply. Assuming that they are representative for an area under study, valuable general information about the painting can be deduced, which is described bellow.

Small samples were collected from zones near to areas already damaged of the six paintings. Twenty samples were analyzed, extracted from different representative zones of the six paintings. These samples were prepared as cylinder moulds and were embedded in epoxy resin as follows: the paint sample was placed on top of the hardened block and carefully covered with resin and then it was cast and left curing for 24 h at room temperature. After that, the sample was cut to expose a face showing the cross sections of paint layer, finally the surface was carefully polished on a rotating disc covered with abrasive SiC-papers characterized by various grade (800-1200) and finished with a cloth (Herrera et al. 2006).

These different cross-sections have been investigated by OM and SEM, which are established techniques in painting studies. Separate layers, pigment particles and organic constituents can be visualized well in paint cross sections. EDX results in a semi-quantitative spectrum of the elements in the paint cross-section. For the study by XRD of the paintings, the conventional Bragg-Brentano parafocussing geometry (θ-2θ coupled) was used. FTIR enables to define the composition of organic materials. The surface of the cross section must be perfectly planar in order to obtain good reflections.

In this work, we identify some pigments present in the different six-canvases of *Pedro Bocanegra.* Observation by optical microscope of the cross sections reveals in that the paintings on canvas consist at least of six different layers. The second layer on the canvases in twenty samples is composed of gypsum, argillaceous earth, iron oxides and animal glue mixed in different proportions. Gypsum and animal glue have been confirmed by FTIR spectroscopy. The white pigment is attributed to lead white and calcium carbonate, and the XRD diffraction patterns of the powder sample confirmed the presence of cerussite, hydrocerussite and calcium carbonate. EDX analyses of the red pigment identify Hg, and S and XRD diffraction patterns of the powder samples confirmed the presence of cinnabar. Some samples contain yellow pigment in the pictorial layer; EDX analyses identify Pb and Sn. The elemental composition and the distinctive particle morphology lead to the conclusion that the yellow pigment is the lead-tin yellow (Pb_2SnO_4). The blue pigment was examined using SEM/EDX and show that the blue pigment contains potassium, calcium, iron, cobalt, silicon and arsenic. In the semi-quantitative analysis the percentage of potassium decreases, this indicated that the blue pigment is degraded. The green pigment is composed of particles with high Cu content.

Compositional depth profiling of amalgam of two ancient Spanish mirrors

The glass mirrors backed with a tin-mercury amalgam, called commonly the amalgam mirror, were studied as produce between the sixteenth century until the beginning of the twentieth (Morser 1961). The Venetian mirror industry dominated the market until the middle of the seventeenth century (Hadsund 1993). This research is focused on mirrors (XVII century) found in significant artworks and considered as representative of the Spanish Cultural Heritage. They became opaque due to the environmental effects. The central question of this work is whether it is possible to explain the state of the amalgam layer of the ancient mirror measuring the change in diffraction profiles along the thickness of the amalgam. This study was carried out in two mirrors from XVIIth century one from ornament of the *Santo Domingo* church of Granada and the other one from ornamenting of *Cristo del Llano* church of Jaen.

In this work, a qualitative analysis of the crystalline phases of the amalgam surface of ancient mirrors was done based on the grazing incidence X-ray diffraction technique. With this technique, one can perform a depth profile of the sample obtained by varying the incidence angle of the X-ray beam with respect to the sample surface. The efficiency of this technique is well established in the field of thin layers and multilayers. The morphology of amalgam layer was studied by scanning electron microscopy (SEM), and the elemental analysis of the amalgam was done by energy dispersive X-ray spectrometry (EDX). X-ray photoelectron spectroscopy (XPS) was used to characterize the atomic composition.

SEM / EDX results show that the amalgam layer is composed of tin and mercury. This study supplies information on the variability in the chemical composition of the amalgam surface of the mirror. Also with this technique the identification of morphologic structure of tin oxides was done. Cassiterite (SnO_2) and romarchite (SnO) were found in the surfaces of both mirrors but in different proportions in the surface (Figure 2).

For the study by X-Ray Diffraction (XRD) of the most external layers of the amalgam the conventional Bragg-Brentano parafocussing geometry (θ-2θ coupled) is not useful. Due to the penetration of the X-ray beam, the diffracted intensity of the most external layers is very weak and the crystalline composition cannot be measured. For that reason the grazing angle technique was used, in which the X-ray beam impinges on the sample at a small angle (θ between 1° and 5°) (Figure 3), and stays fixed during the detector scan. By the small incidence angle, only X-ray signals

of the sample surface are registered. Variation of the incidence angle enables detection of a depth profile of the different layers in the altered amalgam.

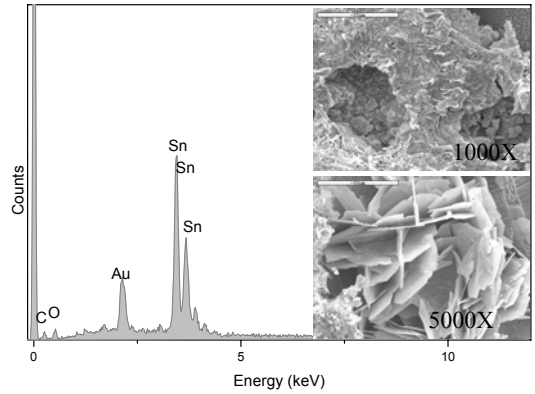

Figure 2. EDX spectrum of chemical composition of tin oxides and their morphological structure.

All the data were collected on a Siemens D-5000 θ-2θ Kristalloflex diffractometer equipped with grazing incidence attachment (θ fixed and 2θ scan), which consists of a long soller slit with a 0.4º divergence and LiF (100) monochromator crystal in parallel mode configuration. Classical coupled θ-2θ scans diffraction were used when it was necessary (Herrera et al. 2007).

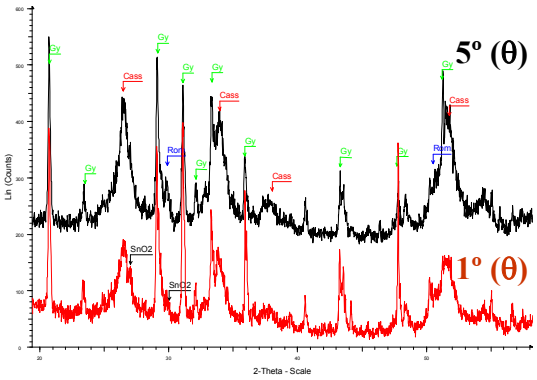

Figure 3. XRD patterns of the reflecting layer of the Granada mirror under incidence angles 1° (θ) and 5° (θ).

The mirror from Granada presents an extreme degree of alteration, as the reflecting layer (SnHg amalgam and metallic Sn) has disappeared; this alteration layer is only constituted of cassiterite (SnO_2), with a small proportion of romarchite (SnO). In the Granada mirror gypsum was found in the surface layer, touching the wall which is covered with plaster (gypsum) supporting the mirror.

In conclusion, the combined use of SEM/EDX, XPS and XRD provide a good insight into the surface chemical structure of two ancient baroque mirrors. Finally, from methodological point of view, grazing incidence X-ray diffraction technique was necessary to be used in the non-destructive depth profiling study of amalgam mirrors

Study of the external surface of metal artefacts by non destructive analysis using Goebel mirror

The study of external surfaces of materials coming from Cultural Heritage gives information about its degradation processes. This knowledge allows us the election of appropriate methods to carry out the restoration of historical artefacts. X-ray diffraction with Goebel mirror is a non-destructive technique to characterize directly the present compounds on the surface of materials without the need of sampling.

Graded multilayer optics creates a highly parallel incident beam while suppressing Kβ-radiation. By capturing a large solid angle, the mirror turns unusable radiation into a useful parallel beam (Figure 4). The Goebel mirror enables the investigation of irregularly shaped sample surfaces and reduces the requirement for the exact sample positioning. These characteristics are very important in the study of samples belonging to the Cultural Heritage, especially the archaeological ones, since in most of the cases samples cannot be taken to be studied by the conventional method of powder diffractometry (Duran et al. 2007).

Figure 4. Non destructive XRD analyses: Bragg-Brentano diffractometer with a Goebel mirror.

Using this technique we analyzed the upper layer of two Roman samples, one is a metallic Roman arrow point that is composed of iron. By means of Goebel mirror, it was possible to identify that the upper layer of the sample contained calcite and quartz, deposited during the burial in the soil. Also vesuvianite traces were found, possibly due to reaction between the soil components and the iron. (Figure 5).

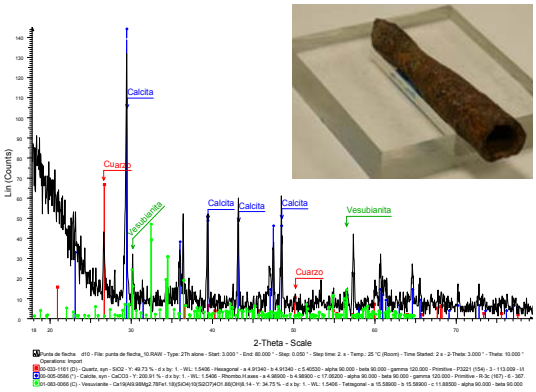

Figure 5. XRD pattern of the metallic Roman arrow point in Bragg-Brentano geometry with a Goebel mirror.

The other Roman sample is a button composed of bronze. The XRD pattern using Goebel mirror allowed to characterize only the external layer and the diffractogram showed that the surface contained calcite, quartz and feldspar that were deposited from the soil where the sample was found. (Figure 6).

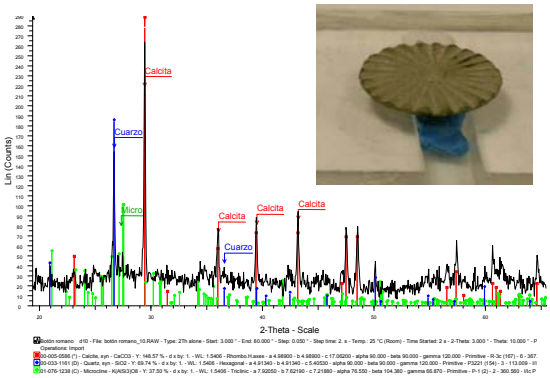

Figure 6. XRD pattern of the Roman button in Bragg-Brentano geometry with a Goebel mirror.

Characterization of iron oxide pigments by means of micro X-Ray diffraction experiments

The use of synchrotron radiation (SR) sources by materials scientists for Cultural Heritage studies is still comparatively new. Synchrotron radiation sources dedicated to the study of materials have been in existence for about 20 years. Synchrotron is a source of intense, bright light of variable wavelength mostly in the hard and soft X-rays; the principal properties of synchrotron radiation are as follows: High flux and brilliance, able to produce a fast data collection and the possibility to use small sample size (small beam footprint 2D and 3D studies to sub-mm/micro length scale). Possibility of wavelength tunability and choice of energy region to suit the problem.

Synchrotron techniques are particularly suited for non-destructive study or to the micro characterization of different materials including organic and inorganic ones, either amorphous or crystalline. New developments in synchrotron radiation techniques result in a significant advance to study the samples at micrometer size scale through the combination of different non-destructive techniques (Pantos 2005). The most employed till now have been synchrotron X-ray fluorescence and diffraction and, to a lesser extent, small angle scattering (on wood, bone and hair) 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. Table 1 shows several Cultural Heritage materials and their properties that can be studied by SR (Bertrand et al. 2006).

Earthy pigments varying from dull yellow to red and brown are commonly called ochre in paintings. The colour is given by the presence of different iron oxyhydroxides and oxides. High mineralogical variability can be demonstrated when natural ochres are compared.

Table.-1 Artworks studied by Synchrotron radiation techniques

Metal	Corrosion Composition Metallurgy
Ceramics	Technology Luster of varnished materials Use
Glass	Provenance Technology Deterioration
Paintings	Pigment identification 3D stratigraphy Conservation and restoration
Manuscripts and drawings	Ink analysis Ageing progression
Wood	Conservation Fossilization
Textiles and hair	Trace elements Identification

The natural ochres are composed of iron oxyhydroxides and oxides mixed with clay minerals (kaolinite, illite, smectites, etc.). The characterization of the phases present in ochre pigments by X-ray diffraction is difficult because the analysis is performed in micro-samples (cross-sections). The pigments are present in a narrow layer its percentage being very low and its reflecting power being weak in comparison with other phases present in the sample. Other techniques used in the identification of ochre pigments are optical

microscopy, scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) and infrared spectroscopy (FTIR). In the case of samples from Cultural Heritage, due to the small quantity of material and the mixture with other different compounds, it is necessary to perform the microanalysis using micro X-Ray diffraction.

Experimental work was done on sample embedded in a resin to prepare thin cross-sections. At least three cuts of the same sample were analyzed and averaged. Several thicknesses were tested and it turned out that 4-5 μm was the most appropriate thickness. The physico-chemical signatures of the pigments, preparation layers and binding media are necessarily related with relevant practices and know-how of the artists.

Trace elements in iron pigments were analyzed. The thin cross sections were analysed to identify their trace element signature. A focused X-ray micro-beam was successively tuned at 28 keV for global experiment. The X-ray fluorescence signal integrated over each single layer was detected against the X-ray micro-diffraction pattern collected in transmission with a bi-dimensional detector. From this signature, in the first layer or the painting it could be possible to identify some trace of monazite. We note the variability in the compositions of oxyhydroxides into the pictorial layer. This work reports on SR μ-XRD data collected at the beamline ID18F in the European Synchrotron Radiation Facility in Grenoble from two samples of earth-based pigment extracted from mural paintings from of Church of *San Agustin in Cordoba*. The identification of these phases was recorded with high resolution (15 μm ×-15 μm).

Acknowledgements

This work was supported by the European Commission, Marie Curie Action MEST-CT2004-513915.

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Back to index

VIBRATIONAL SPECTROSCOPY AS AN ANALYTICAL TOOL IN THE IDENTIFICATION AND CHARACTERIZATION OF NATURAL DYES EMPLOYED IN THE CULTURAL HERITAGE

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Introduction

The identification of dyes used in works of art is essential for dating, restoring and conserving artwork and for studying art history in general. There is a wide range of works focused on the analysis of inorganic pigments (Chen et al. 2006). In contrast, organic dyes have been less studied although natural pigments have been used as coloring materials in Cultural Heritage artworks throughout the history. Their analysis remains still extremely difficult, because they are very fluorescent, susceptible to being degraded at certain conditions and usually present at trace concentrations or highly dispersed in very complex objects. In fact, a milestone task in the Cultural Heritage study is the finding of suitable and sensitive analytical non-destructive techniques which could allow their study *in situ* without a sample removal (Wyplosz 2003).

Vibrational spectroscopy (Raman and infrared) provides very useful fingerprint spectra for the identification of natural organic dyes. Particularly, Raman spectroscopy has been firmly established as an invaluable technique for the identification of materials found in works of art and the Cultural Heritage (Smith and Clark 2001, Burgio et al. 2001, Smith and Clark 2004). It affords important molecular