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Lasers in the Conservation of Artworks

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Compositional depth profiles of gilded wood polychromes by means of LIBS

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ABSTRACT: Gilded wood polychromes are important artistic expressions in Galicia (NW Spain) during the baroque period. The variety of techniques applied in gilded ornamentation and the possible existence of products of previous interventions make difficult the restoration process of these artworks which frequently include the removal of a brass-based paint (purpurin) added to cover the lack of gold leaf. The aim of this work is the characterization by means of LIBS of the different layers in gilded wood polychromes. For this purpose small pieces taken from two baroque altarpieces were analyzed using a Nd:YAG laser source operating at the wavelength of 355 nm to obtain characteristic LIBS spectra and compositional depth profiles.

1 INTRODUCTION

During the baroque period, polychromes on wood were the most important forms of sculpture in Spain. One of the most genuine Spanish baroque creation was the "retablo" which is a large, architectural panel divided into compartments which contains religious statues. These artistic workpieces were frequently polychromed and decorated with gold. In Galicia (NW of Spain) the baroque style appeared in the first half of the 17th century and it lasted during the whole 18th century in a great number of "retablos" located in rural churches and chapels.

In polychromes the wood substrate is usually covered with different layers; ground, paint layers, gold leaf, varnish and so on. Characterization of the different layers becomes of great importance before any restoration work can be attempted.

Several studies have shown the capability of laser-induced breakdown spectroscopy (LIBS) to identify the elemental composition of pigments and to characterize the different layers in painted artworks (Anglos et al. 1997, Burgio et al. 2000, Castillejo et al. 2000, Castillejo et al. 2001, Melessanaki et al. 2001, Clark 2002, Oujja et al. 2005b, Kaminska et al. 2006). LIBS technique is based on the spectral analysis of the emission from the plasma produced during laser ablation. In this sense, when a pulsed laser beam is focused onto the sample surface, it induces not only the ejection and vaporization of material from the sample surface, but also the formation of a plasma plume which emits light at wavelengths characteristic of the elemental composition of the removed layer.

Therefore, the analysis of the emission spectra can provide detailed information about surface composition at each pulse, that is, the in-depth compositional profile of the sample.

On the other hand, in the last years, laser cleaning has been increasingly applied to artworks. The process must be controlled to avoid the damage of the substrate (gold leaf and paint layers in our case). In this context, LIBS appears as an adequate diagnostic tool (Gobernado-Mitre et al. 1997, Maravelaki et al. 1997, Tornari et al. 2000, Castillejo et al. 2002, Acquaviva et al. 2004, Colao et al. 2004, Oujja et al. 2005a, Acquaviva et al. 2005).

The aim of this work is to test the capability of LIBS for the characterization of the different layers in gilded wood polychromes and to obtain compositional depth profiles which can help, not only in the knowledge of the structure and composition of these materials, but also in a controlled laser cleaning of these artworks. For these purposes LIBS has been applied to the identification of the different layers in real samples of gilded wood polychromes taken from two baroque altarpieces: Antiguo Retablo de Santa María la Mayor (17th century), nowadays at the Museo de Pontevedra, and Retablo de la Capilla del Pazo de San José de Vistalegre (18th century) Tui, Pontevedra; both involved in restoration processes.

2 EXPERIMENTAL

The results reported here were obtained with a Q-switched Nd:YAG laser source (Quantel, model

Brilliant B) operating at the third harmonic, 355 nm. The samples were irradiated in air at room temperature and pressure. The laser beam was focused onto the sample surface by a plano-convex quartz lens with a focal length of 300 nm situated on a ruled rail that allowed to change the distance between the lens and the sample in a controlled way. X-Y translation stages and an alignment system consisting of two He-Ne lasers was used to help in sample positioning in terms of laser focal point situation and spectral collection. The emission of the plasma was collected and guided to the spectrograph (Oriel, model MS257) with a fiber optic. Light was dispersed by using the 600 grooves/mm grating of the spectrograph. An intensified coupled charge device, ICCD (Andor, model DH5H7-18F-03) detected the spectral resolved emission from the plasma.

The depths reached by the laser ranged from 40 to 60 μm, depending on the sample, with a typical etch per pulse of 5 μm and a crater area of around 0.2 mm^2. This procedure allows to distinguish by LIBS the different layers which constitute the polychrome without causing an important damage to the piece.

In addition to LIBS a stratigraphic analysis with the optical microscope was performed over a minuscule specimen taken with scalpel from the altarpiece and embedded in epoxy resin.

Figure 1. Natividad de la Virgen (153 x 76.5 cm^2). One of the five panels which constitute the altarpiece Antiguo Retablo de Santa María la Mayor (17th century), nowadays at the Museo de Pontevedra (Spain). The square in the upper right side indicates the white zone where LIBS analysis were performed.

3 RESULTS AND DISCUSSION

As it has been previously pointed out, the carved wooden substrate is covered with a series of layers in polychromes; the number and characteristics of each one depend on the artistic technique used. In the case of gilded work, there are many different techniques (González-Alonso 1997); in brief, the carved wooden substrate is usually covered with a white ground layer or *gesso* (generally a mixture of hide glue and chalk), a layer of red bole (a mixture of clay and glue), gold leaf and in some cases a paint layer above. The quality and characteristics of the gold leaf can be different; the gold usually is alloyed with Ag and Cu and even Pt or other metals.

3.1 *Antiguo Retablo de Santa María la Mayor*

The ancient altarpiece of Santa María la Mayor (Pontevedra) consists of five wooden panels showing important episodes of the life of The Virgin. They are bas-reliefs carved by Jácome de Prado (1623 - 1626) and stylistically could be classified as an early and popular baroque piece (Filgueira-Valverde 1991). In Figure 1 one of the panels corresponding to the "Natividad de La Virgen" is shown. The vestments and other parts of the panel were ornamented using the method of sgraffito on gold which consists in covering the gold leaf with a paint

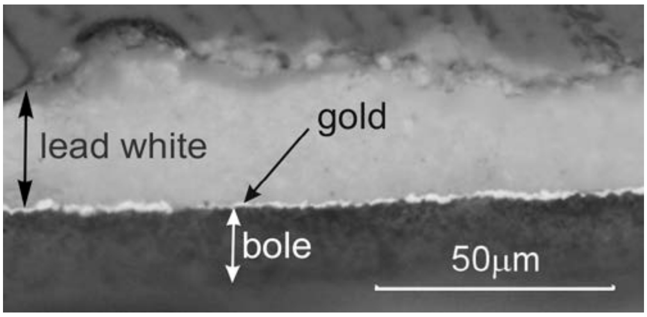

Figure 2. Embedded cross section of a small fragment removed from the altarpiece Antiguo Retablo de Santa María la Mayor. On the top, a layer of white pigment followed by a thin layer of gold leaf and a layer of red bole underneath, can be appreciated.

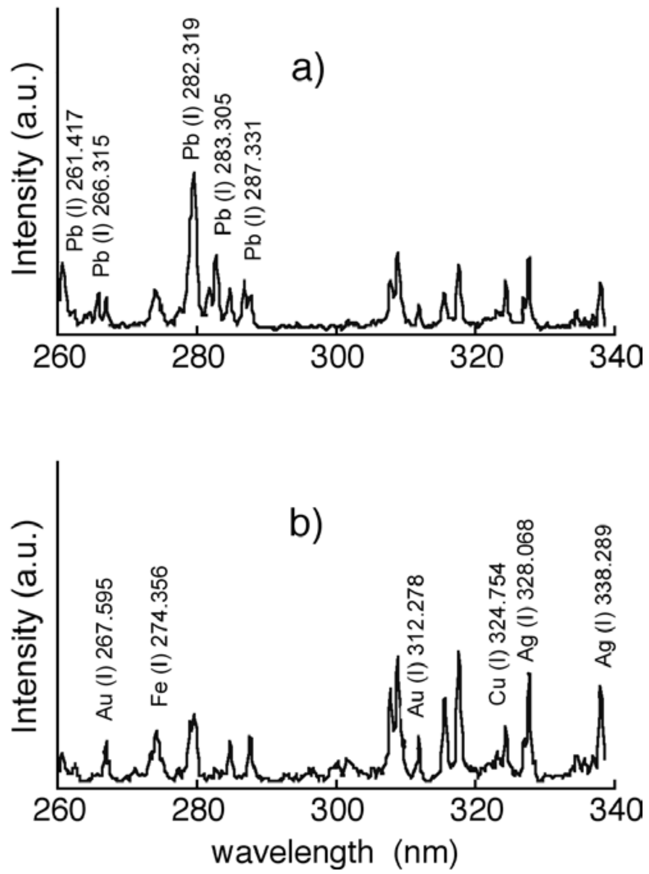

Figure 3. LIBS spectra corresponding to: a) 1st pulse and b) 3rd pulse of a series of ten laser shots delivered at the same point of the sample taken from the Antiguo Retablo de Santa María la Mayor.

layer which is incised or scratched through, to reveal the gold underneath.

Figure 2 depicts the optical micrography of a stratigraphic section (cross section) of a white-colored area of the polychrome. Different layers can be observed: on the top a white pigment layer (≈ 30 μm depth), underneath a thin layer of gold (2 – 3 μm) and finally the layer of red bole (25 – 30 μm), a mixture of red clay and glue.

LIBS depth profiles were carried out by subsequent ablation of the sample surface at the same irradiated spot. Figure 3 shows LIBS spectra obtained in the 1st and 3rd pulses of a series of ten laser shots. The first two laser pulses produced a spectrum in which emission lines due to lead can be distinguished (Fig. 3a) confirming the use of lead white pigment ($2PbCO_3 \cdot Pb(OH)_2$) in the external layer of the polychrome. The next two pulses result in an increase of the relative intensities of peaks attributed to Au, Cu and Ag (Fig. 3b) characteristics of a gold alloy.

The in-depth variation of the intensity of all the elements which appeared in successive LIBS spectra has been obtained after normalization of signals to take into account the decrease of the plasma signal

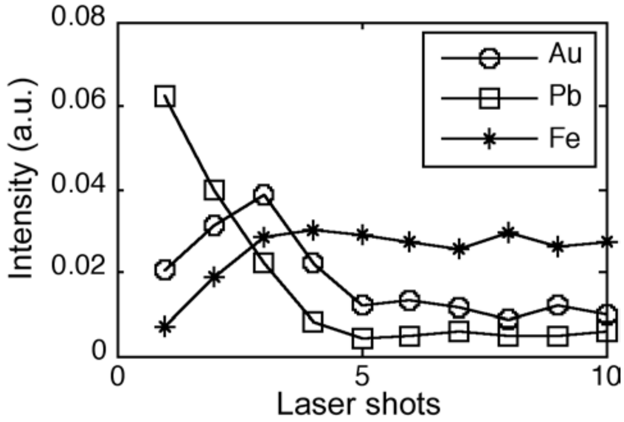

Figure 4. Variation of intensity of (❍) Au (I) 312.278, (☐) Pb (I) 282.319, and (∗) Fe (I) 274.356 lines as a function of the number of laser shot; i.e. sample depth in Antiguo Retablo de Santa María la Mayor. Lead is the characteristic element of the external layer (lead white), gold indicates the intermediate layer and finally iron content is characteristic of the red bole.

with depth (López et al. 2005). Figure 4 shows the variation of intensity as a function of the number of laser shots, i.e. sample depth, for the peaks Pb (I) 282.319, Au (I) 312.278 and Fe (I) 274.356, characteristics elements of each layer (lead white pigment, gold leaf and bole). Lead content decreases in the first four laser pulses whereas gold content increases, taking its higher value around the third pulse. The iron content, characteristic of the red bole, remains practically constant after the fourth pulse.

3.2 *Retablo del Pazo de San José de Vistalegre*

The altarpiece of the chapel in Pazo de San José de Vistalegre (Tui-Pontevedra) is shown in Figure 5. It was built in 18th century by an unknown author and represents an example of baroque altarpieces located in rural churches or chapels in Galicia (NW Spain). It was made of gilded and polychromed wood. The altarpiece presents a central niche with the image of San José surrounded by six small statues of other saints.

The process of restoration of this altarpiece included the removal of a brass-based paint (purpurin) probably added in previous interventions to cover the lack of gold leaf. Purpurin turned opaque due to the oxidation process of its constituents; furthermore, oxidation products increased the adhesion to the substrate making difficult the mechanical or chemical elimination of such substance. This problem is quite frequent for restorers because purpurin was used extensively throughout the last century to cover loss of gold leaf. In this case, the capability of LIBS as a control tool in a laser cleaning process focused on the elimination of purpurin in gilded polychromes was tested. Specifically, LIBS was used to distinguish between original materials (gold leaf) and purpurin added in previous interventions.

Figure 5. The altarpiece of the chapel in Pazo de San José de Vistalegre (Tui-Pontevedra), 18th century. Gilded and polychromed wood. The square in the bottom left side indicates the zone studied.

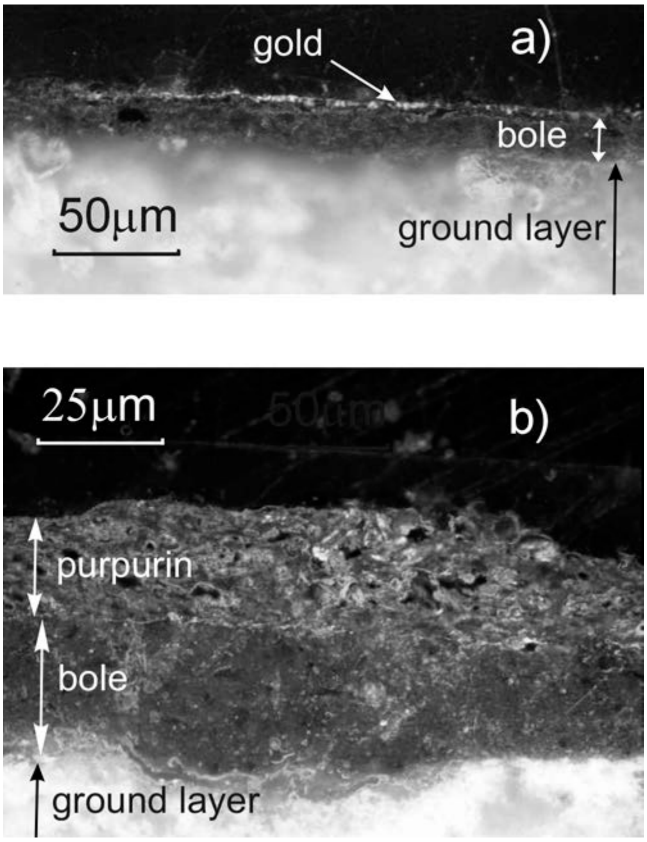

Figure 6. Two optical microscopy images of cross sections obtained at different points of the Retablo del Pazo de San José de Vistalegre. In (a) no purpurin was added. In (b) a thick pile of purpurin can be appreciated.

Figure 6 shows the cross sections obtained by means of optical microscopy of specimens taken from the altarpiece. Figure 6a corresponds to a sample free of purpurin showing a top layer of gold leaf $\approx 3\ \mu m$, a layer of bole $\approx 20\ \mu m$ and the layer of white ground $> 50\ \mu m$. Conversely, Figure 6b depicts a sample where purpurin was added. A thick and mat pile of purpurin over the layer of bole can be appreciated.

LIBS spectra, in the range 260 nm to 340 nm, of gold leaf and purpurin layers, respectively, are shown in Figure 7. As depicted in the plots, gold was alloyed with silver and copper and purpurin consists basically of copper and zinc.

Where purpurin was added (Fig. 8b), LIBS depth profiles show that copper (peak Cu (I) 327.396) characteristic of the purpurin and iron (peak Fe (I) 274.356) are present for the 8 first pulses, which, in addition to stratigraphy in Figure 6b, indicates that the purpurin is probably mixed with the bole. The intensity of Ca (II) 315.887 increases in the last two pulses indicating that the ground layer has been reached. These results confirm the structure of the polychromes obtained by means of optical microscopy and demonstrate the capability of LIBS, not only to give information about the structure and composition of the different layers in polychromes, but also to monitor the laser cleaning of these artistic materials; specifically, the elimination of purpurin added to cover the losses of gold leaf.

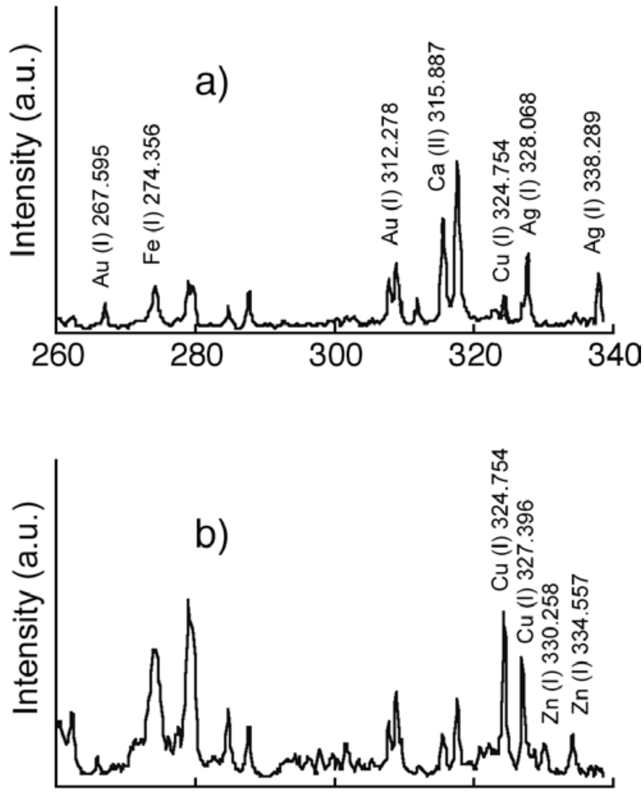

Figure 7. LIBS spectra of a) gold leaf and b) purpurin layers in the spectral window from 260 to 340 nm. Gold used was alloyed with Ag and Cu and purpurin is a brass based material.

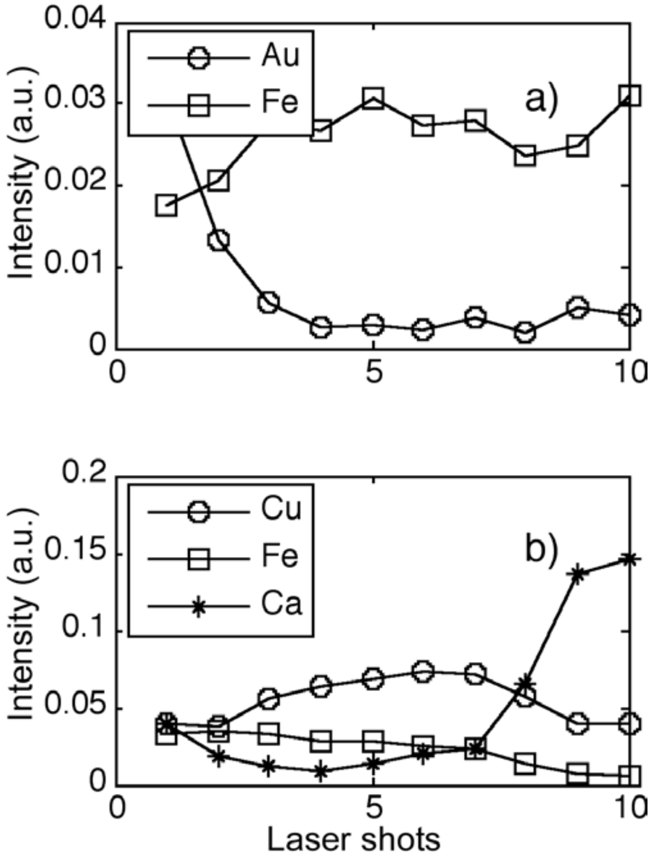

Figure 8. LIBS depth profiles obtained in areas of the altarpiece (a) free of purpurin and (b) with purpurin added. The intensity of the peaks Au (I) 274.356, Cu (I) 327.396, Fe (I) 274.356 and Ca (II) 315.887, which characterize the different layers in polycromed samples from the altarpiece of the chapel in Pazo de San José de Vistalegre, are shown as a function of the number of laser shots.

4 CONCLUSIONS

Laser Induced Breakdown Spectroscopy, LIBS, has allowed to perform the elemental characterization of the different layers in gilded wood polychromes and to obtain compositional in-depth profiles of real samples from two baroque altarpieces. Specifically LIBS has allowed to characterize the different layers in a polychrome decorated with the technique of sgraffito on gold and to distinguish added layers of purpurin, a brass based pigment, extensively used during the last century to cover the losses of gold leaf. For these reasons LIBS appears as an adequate technique not only for the knowledge of the structure and composition of gilded wood polychromes, but also as a control tool in the laser cleaning of these materials.

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