Laser-induced breakdown spectroscopy study of silversmith pieces: the case of a Spanish canopy of the nineteenth century

M. A. Go´mez-Moro´n[1] · P. Ortiz[2] · R. Ortiz[2] · J. M. Mart´ın[2] · M. P. Mateo[3] · G. Nicolás[3]

[1] Instituto Andaluz de Patrimonio Histo´rico (IAPH), Isla de la Cartuja, Camino de los Descubrimientos S/N, 41092 Seville, Spain

[2] Department of Physical, Chemical and Natural Systems, Universidad Pablo de Olavide, Carretera de Utrera Km 1, ES-41013 Sevilla, Espan˜a

[3] Laser Applications Laboratory, University of A Corun˜a, C/ Mendiza´bal s/n, 15403 Ferrol, Spain

Abstract Canopies of needlework velvet or silversmith pieces placed on twelve or more battens are widely employed in Spanish catholic ceremonies to cover the image of the virgin. In this paper, we focus our interest on those pieces made of silver. These silver crafts suffered a revolution in the nineteenth century with the development of an electrolyte system that can be applied over carved metal pieces, in order to obtain a silver layer by electrodeposition similar in appearance to the original sterling silver and cheaper. The aim of this research was the application of laser-induced breakdown spectroscopy (LIBS) to the study of a canopy of the nineteenth century in order to assess the techniques used for its manufacturing and the identification of replacement and restoration of original pieces. The LIBS depth profiles show the presence of a micron silver layer over an alloy of copper and zinc in most of the surfaces. Corrosion products, alloy missing, and the restoration with copper layers were detected. These results are consistent with those obtained by scanning electron microscopy with energy-dispersive of X-ray with the advantage that LIBS is a methodology that allows analysing metal pieces without sampling or preparation. In summary, LIBS is a technique that allows the study of silversmith pieces with electrochemical preparation according to the Ruolz technique, and it is also possible to detect subsequent restoration or corrosion zones.

1 Introduction

Laser-induced breakdown spectroscopy (LIBS) is an analytical technique that allows qualitative and quantitative analysis of works of artworks and monuments [1–14]. This laser spectroscopy method provides spatially resolved compositional information virtually instantaneously, without preparing the sample and with a minimum damage for the artworks. Its simplicity and speed facilitate the study of a large number of samples in a short period of time and the analysis of a greater number of areas in one piece without sampling.

LIBS has been widely applied to the analytical study of metal works [15–20], even in underwater conditions [21–24], and to control the cleaning of metal [25–27]. Firing the laser pulse repetitively on the same location, LIBS technique allows analysing not only the surface of the sample but also the inner layers, because at each pulse a small amount of material is ablated on a new fresh surface, and hence the spectral information is provided at different levels of depth. The advantage over usual methods which allow obtaining depth profiles is that no preparation of specimen is needed nor additional tool to remove material mass. Because the laser beam caused the ablation, depths of several hundreds of micrometers can be investigated easily by LIBS compared with the nanometric to micron range of vacuum techniques where an ion gun is employed for the sputtering. This last point can be an advantage or a drawback depending on the spatial resolution required to characterize suitably the possible different layers found on

a specimen surface. The in-depth capability of LIBS technique is of great interest for the characterization of metal artifacts when corrosion processes and restoration procedures need to be identified and characterized. For this reason, in the field of silversmith, LIBS can be the right procedure to investigate thicknesses of deposited or restored layers with minimum damage [28, 29].

This study examined five samples belonging to a silver canopy from Vera-Cruz Brotherhood at Aracena (Huelva, Spain). Historical review highlight that Macarena Brotherhood (Seville, Spain) bought the canopy to Isaura´s Workshop in 1871, and it was manufactured in Barcelona. Afterward, this canopy was transferred to the Brotherhood of Gypsies (Seville, Spain) and the Brotherhood of the Holy Burial of Alcala del R´ıo (Seville, Spain) before arriving to its current owners [30].

Francesc Isaura acquired the Ruolz patent to produce pieces with a silver layer in Spain in 1848. This technology revolutionized the silver industry to cut costs, so its use spread among the bourgeois everyday pieces as well as works of religious [31].

Ruolz Silver (patent of Henri de Ruolz, 1838.) is an industrial methodology based on the application of an electrolytic system on pieces of metal to obtain a silver layer by electrodeposition similar in appearance to an original silver artefact [32].

The process involves the transfer of metal ions from a silver anode to a metallic cathode, for instance brass, in a liquid medium (the electrolyte), composed mainly of metallic salts (AgCN and KCN). The battery power source is external to force electrochemical redox reaction to occur. After the processes of galvanic deposition, a piece with silver appearance, less cost, and better mechanical characteristics is obtained [33, 34].

In this study, LIBS technique is used for the chemical characterization of the Vera-Cruz Brotherhood´s silver canopy in order to assess the techniques used for its manufacturing and to identify the replacement and restoration of the original piece.

2 Materials and methods

In the experimental LIBS apparatus used in this work, a Nd:YAG laser was operated in the Q-switched mode, at 532 nm, delivering pulses of 200 mJ with 5-ns duration. The selection of 532 nm was preferred over the first harmonic 1064 nm because the resulting LIBS signal was suitable, and the laser mark generated on the pieces was minimized due to lower thermal effects in the visible range compared to infrared one. The laser pulse energy was also attenuated to some mJ to reduce heat affected zone produced by the laser spot on the specimens. The laser beam was focused by a planoconvex lens (f = 100 mm) onto the sample surface and the resulting laser spot was about 260 lm which resulted in a fluence of 17 J/cm^2. A lower laser spot could be obtained if required by the curators using a lens with a lower focal or with a more sophisticated focusing system.

The pieces were mounted on a motorized holder which did not produce any damage on their surface and provided new positions for LIBS signals acquisitions. The irradiation was made in air at atmospheric pressure without any previous sample preparation.

The LIBS signals were captured by imaging the induced plasma light onto the entrance of an Echelle spectrometer by means of an optical fiber and an intensified charge-coupled device (ICCD) was used for the photon detection. The LIBS measurements were carried out in the 200- to 800-nm spectral window with an acquisition gate of 10-ls duration delayed by 1 ls with respect to the beginning of the laser pulse.

Before beginning the measurements, standards of silver, copper, and zinc were studied to identify peaks and optimize conditions. The pieces were irradiated in both sides of their surface (front and rear sides) in areas of interest to check the composition homogeneity, as previous works indicated that the silver layer was only in the front sides to minimize the cost of artworks [35].

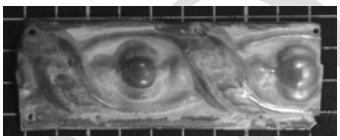
The laser ablation spots were assessed by a stereomicroscope Leica GZ6 and an optical microscopic with reflected light Leica JEOL JSM 5400LV.

Five silversmith pieces from the current canopy (Fig. 1) of the Vera-Cruz brotherhood were studied. The samples have an average thickness of 0.5 mm and different conservation degrees (Table 1).

Fig. 1 Photography of the silversmith canopy of the Vera-Cruz brotherhood

For the validation of LIBS results, small fragments (\5 mm^2) taken from the edges of the silver pieces have been examined parallel and perpendicular to the surface by SEM–EDS. The study parallel allows knowing the conservation degree and corrosion products on surface, while a transversal sample perpendicular to the surface allows knowing the alloy and corrosion layers in depth. These extracted samples, after the observation of surface, were embedding in a cold methyl methacrylate resin to obtain a stratigraphic section to know the layers. Sampling has followed the recommendations of the technical commission CNR-ICR NORMAL 3/80 [36]. The metallographic description and detailed analysis of the stratigraphies and surfaces of the samples were completed using a scanning electron microscope JEOL JSM-6460 LV model equipped with energy-dispersive analyzer of X-ray model INCA X-sight, Oxford Instruments.

Table 1 Description and conservation degree of silversmith pieces studied by LIBS

Sample	Shape and aspect	Image	Conservation degree
1	Rectangular carved piece with a glossy silver face and matte silver surface on the back. Spots where the base metal was discovered		Good conservation degree Blue-green and white corrosion products in very specific areas
2	Rectangular carved piece with a glossy silver face and matte silver surface on the back		Good conservation degree Blue-green corrosion products in very specific areas
3	Rectangular carved piece with a glossy silver face and matte silver surface on the back. Spots where the base metal was discovered		Good conservation degree Blue-green corrosion products in very specific areas
4	Rectangular carved piece where the base metal was discovered		Bad conservation degree Blue-green corrosion products extended over the surface
5	Shield-shaped carved piece with a glossy silver face and matte silver surface on the back		Good conservation degree

3 Results and discussion

LIBS analyses were performed in two modes:

(a) Superficial measurements, where only 2 or 3 pulses were applied to determine elements located on the surface and beneath it. The resulting laser spot was almost invisible, and hence the damage caused to the specimen was minimal. Indeed, only a magnified visual inspection could see the mark generated by laser irradiation. Analyses made on both sides of the specimens revealed the presence mainly of silver, copper, and zinc as it can be seen in a characteristic LIBS spectrum (Fig. 2). Main lines of interest were observed at 546.53 nm for Ag, at 521.84 nm for Cu, and at 472.23 nm for Zn. Rest of peaks corresponded to other elements such as Ca, Al, Si and Fe.

(b) In-depth profiling where a higher number of pulses were required to follow the evolution of elements of interest (i.e., Ag, Cu and Zn) inside the specimen.

When depth profiling is performed using LIBS, experimental conditions need to be optimized to remove a minimal mass at each analysis while keeping an adequate level of spectral signal. In particular, pulse energy and resulting fluence are the critical parameters to consider. An excess of fluence is, in general, not detrimental for common LIBS analyzes, but for depth profiling, this excess could lead to removal of one or more layers of interest simultaneously in one laser shot. In the depth profiling mode, the mark generated was more visible due to the application of a higher number of pulses (20 compared to 2 or 3), but in any case, a mark of 200–300 μm diameter (Fig. 3) could be assumed negligible for the curator taking into account the information provided in this kind of analyses.

On the other hand, LIBS signals obtained with low fluences can be not suitable to be exploited. For this reason, fluences over threshold ablation are required. In our case, because the thickness of interest was about 0.5 μm, pulse energy was chosen about 4.5 mJ with a corresponding fluence of 17 J/cm^2 as already mentioned. In these conditions, a maximum of 20 pulses were required to draw a profile and differentiate regions into the specimens.

LIBS measurements, confirmed by those obtained with SEM–EDS, showed that the five specimens under study can be classified in three different types: original silversmith pieces (samples 1, 2 and 4), original silversmith pieces with restoration (sample 3), and replaced silversmith pieces (sample 5). This classification can be made following the type, number, and thickness of layers located above brass.

LIBS in-depth profiles correspond to a LIBS intensity signal of one element versus number of pulses delivered in the same position. The significance of this parameter is relative because the ablation rate (the depth analyzed per laser pulse) depends on pulse energy and subsequent fluence, and therefore, the number of pulses required to remove a layer of a certain thickness will depend on the experimental conditions of the analysis. Hence, this parameter is usually converted to distance which illustrates clearly the intensity of the element as a function of depth. For this conversion, it is necessary to know the ablation rate that is calculated from the number of pulses necessary to ablate a layer and the depth of that layer measured by other method. In this study, the thickness of each layer was determined by SEM measurements on a cross section of the specimen. Of course, if we need to prepare a cross section of the specimen for the thickness estimation, the LIBS procedure loses part of its interest. However, this step can

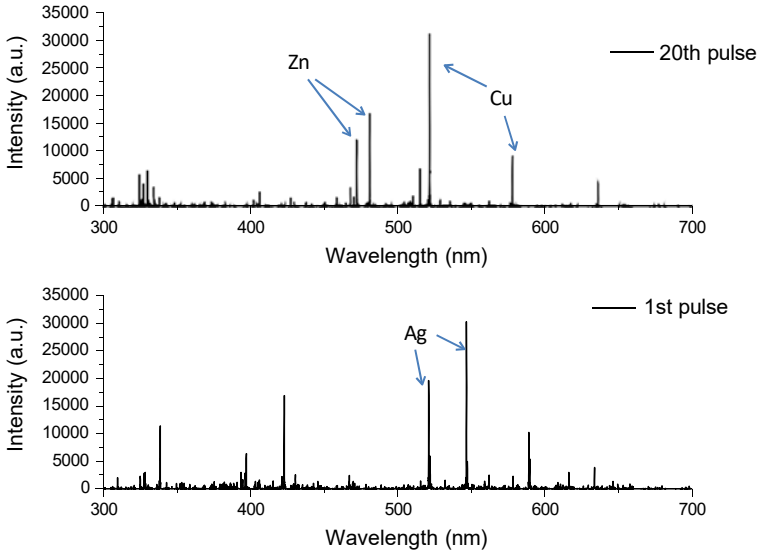


Fig. 2 LIBS spectra from sample 1 showing selected lines of interest: 546.53 nm for Ag, 521.84 nm for Cu and 472.23 nm for Zn

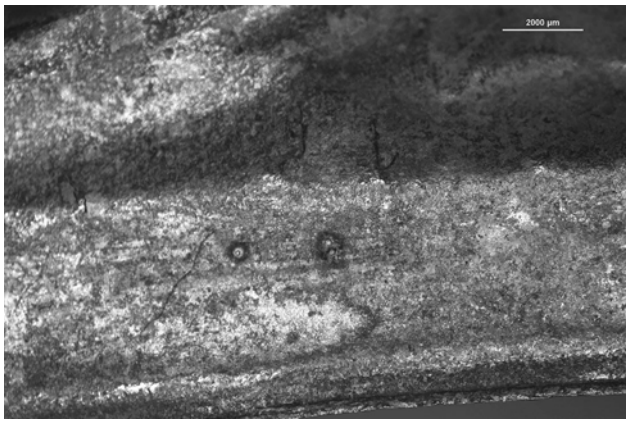


Fig. 3 Mark on silver sample 1 after ablation by LIBS

be avoided if we calculate the ablation rate of the material investigated measuring crater depth by optical means (for example by microscope or by laser sensor). In our irradiation conditions, silver and copper layers were removed with an ablation rate of 0.75 and 1.50 lm/pulse, respectively. As the knowledge of the thickness of the silver layer in the pieces is of interest in this study, the ablation rate corresponding to silver, 0.75 lm/pulse, was used for the conversion of ''number of pulses'' to ''depth'' in the LIBS intensity profiles for a more accurate estimation of silver layer thickness.

While LIBS measurements were made in a static position on both faces of pieces, EDS ones were obtained by line scanning of elements on the cross sections of pieces.

Both techniques showed the use of electrochemical deposition over both faces and on each sample, in contrast to the first hypothesis of Bethencourt and Go´mez [35] who supposed a sealed on the XIX pieces to avoid the cost of silver.

Once, we have demonstrated that both sides where silvered the study has been centered on the front side as it is the face that it is exposed to the public and with a high artistic value.

3.1 Original silversmith pieces

Three of the samples analyzed were in this group (samples 1, 2, and 4) which corresponds to brass pieces (Cu/Zn 60:40 alloy) with a thin layer of silver, following the Ruolz methodology. In this type of pieces, silver was present in the first LIBS spectra of the samples and disappeared after 1–3 pulses corresponding to its removal of surface. Figure 4a shows a LIBS profile where silver decreased drastically to zero after the first pulse while copper and zinc has the opposite behavior. Hence, a thin layer of silver was found on the top surface of the brass. In this case of samples, only five laser pulses could be employed instead

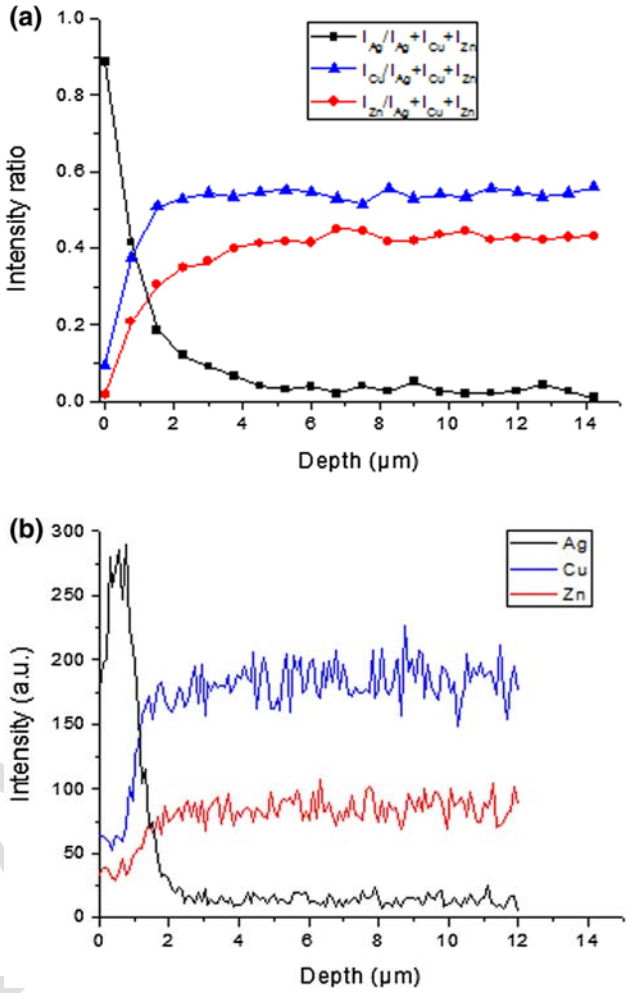


Fig. 4 LIBS and EDS profiles performed on original silversmith piece 1, showing an Ag top superficial layer on brass

of 20 for the characterization of the piece in order to reduce the damage occasioned by the analysis.

Figure 4b exhibits a similar behavior as Fig. 4a and corresponds to an EDS profile analysis of a cross section of the sample, where the silver layer can be evidenced. The thickness of this layer measured by SEM was about 1.5 lm, while LIBS provided values between 0.7 and 2 lm depending on the area of measurement. The differences between these two methods can be assumed negligible, taking into account irregularities in the silver layer in terms of thickness along the piece and the wear generated with the passing of the years. The silver is even lost in some parts of the pieces due to the surface erosion of the canopy and corrosion of brass (Fig. 5).

A remarkable benefit in using LIBS technique is that spectroscopic data allow the possibility of estimating the presence of alloy missing phenomena or corrosion described by Bethencourt and Gómez [35], and in these cases an increase in concentration of copper on surface or under

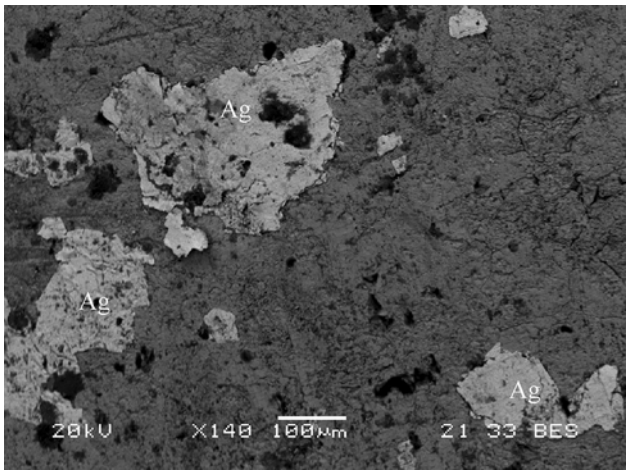


Fig. 5 SEM micrograph of a fragment extracted from sample 2 surface, where silver layer is lost in some parts and appears on surface brass

silver layer is detected by SEM-EDX (Fig. 6). This layer could be characterized by zones where copper content is higher than in matrix, with the consequent decrease in Zn concentration (dezincification). This behavior where Cu and Zn contents are inversed indicates the presence of an alloy missing phenomenon or corrosion. This phenomenon, known as dealloying, has been observed by LIBS (Fig. 7) and corresponds to an increase in concentration of copper respect to zinc on the surface. LIBS do not allow appreciating the discontinuity or loss of adhesion between the different layers that could be observed by SEM (Fig. 6) but provides a way to evidence dealloying without preparation or examination of the specimen.

3.2 Original silversmith piece with restoration

One of the samples (sample 3) can be classified as original piece but with a restoration process (due to a degradation of its surface). In this case, four layers were distinguished (Fig. 8): (1) a silver-rich surface layer with thickness of about 1.5–2 1m where no other elements can be appreciated, (2) a copper layer of 3–4 1m where Ag is also detected probably due to upper layer, (3) a second layer of Ag with thickness of 2–3 1m, and (4) a core of brass, e.g., Cu and Zn alloy.

3.3 Replaced silversmith piece

One of the samples (sample 5) belongs to this group and corresponds also to a brass piece (Cu/Zn 60:40 alloy) but with a thicker layer of silver, obtained again by the Ruolz

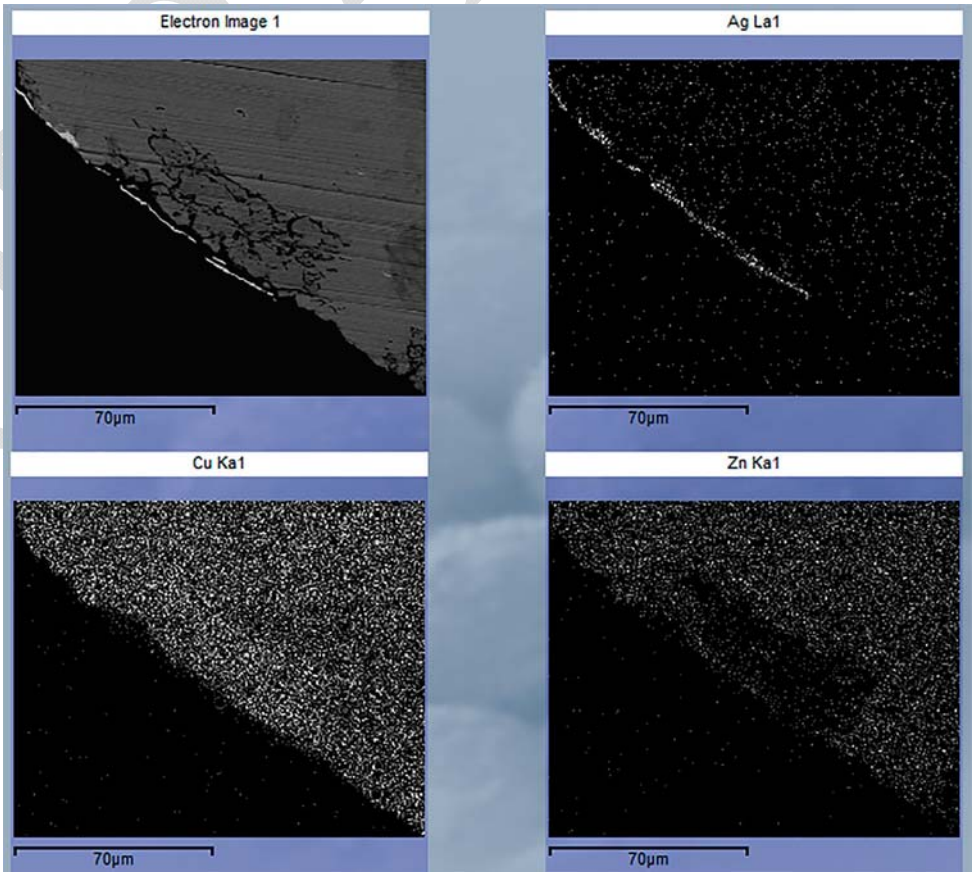


Fig. 6 SEM micrograph and mapping analysis of Cu/Zn/Ag of silvered brass cross section with dezincification corresponding to a fragment extracted from sample 1

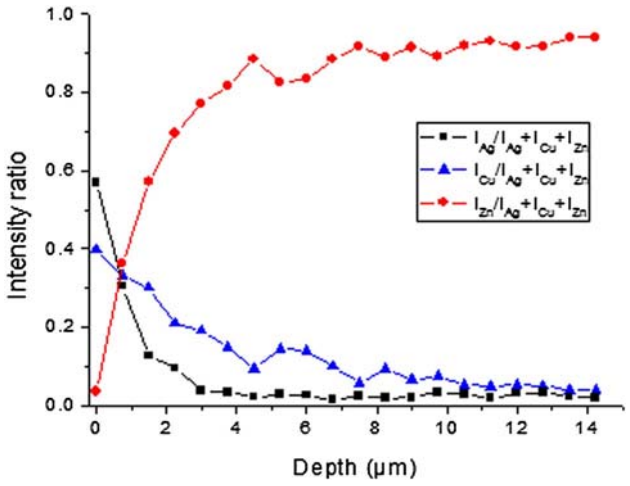


Fig. 7 LIBS profile performed on the same original silversmith piece of Fig. 3 (sample 1) but in a different area, showing a Cu enrichment on surface (dezincification process)

methodology, but it is probably that was made during a restoration in twentieth century. A higher number of pulses (about 10), which correspond to a thickness of 6–7 1m, were required to ablate silver as can be seen in Fig. 9a. According to SEM-EDX profiles, silver coating can reach also a thickness of 5–10 1m in some areas (Fig. 9b).

Replacement pieces that are composed only by Ag has not been detected in this group, what means that all the samples has suffered an electrochemical deposition.

The visual impact produced by LIBS measurements was measured by optical microscopy. In the different samples studied, prints or craters of 200–300 1m in diameter were obtained with our irradiation conditions but can be reduced in size if it is required by the curator. These areas tend to blacken by oxidation and deposition of particles, resulting in blackish appearance that alcohol can remove, leaving a footprint of only 150 1m in diameter that is undetectable to the naked eye, but can be observed by binocular microscope.

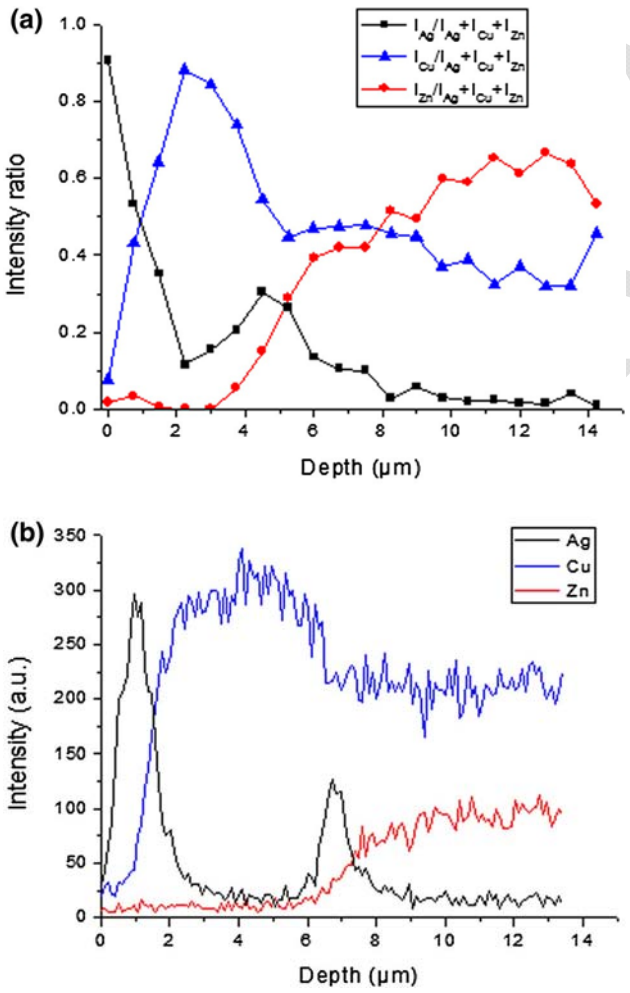


Fig. 8 LIBS and EDS profiles performed on original silversmith piece with restoration (sample 3)

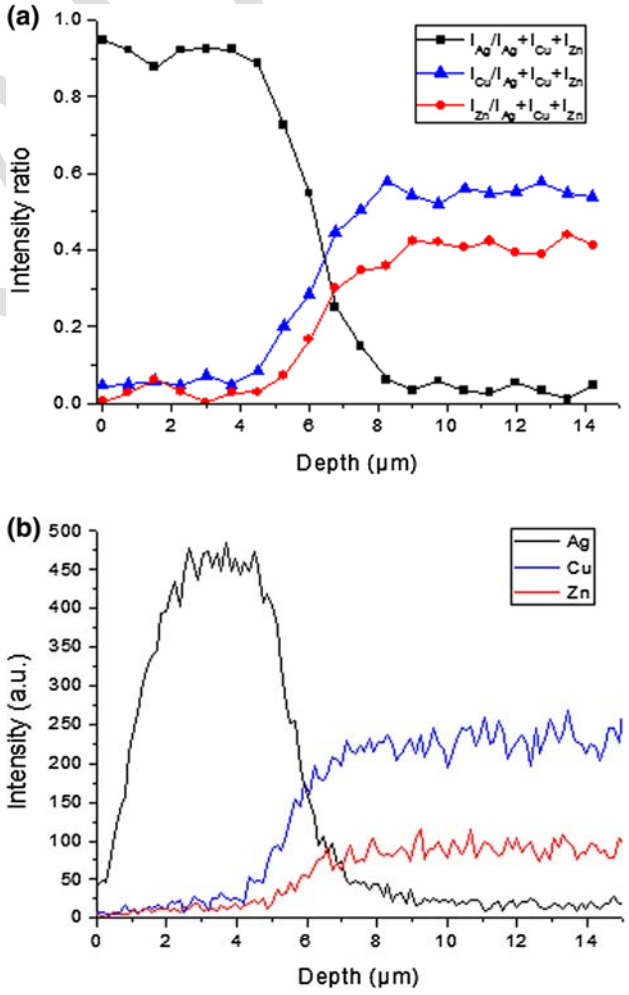


Fig. 9 LIBS and EDS profiles performed on replaced silversmith piece (sample 5)

This minimum invasive technique can be assumed to silversmith studies as the impact is not easily appreciated by eye and give us information from various areas of the pieces, in a fast way and in situ, a process that is not possible with SEM-EDX.

In summary, LIBS depth profiles show the presence of a silver outer layer in most of the surfaces and evidence corrosion processes with alloy missing in addition to the restoration of some zones with copper. These results were corroborated with optical and electronic microscopy.

4 Conclusions

LIBS analysis through the depth profiling mode allowed discriminating and classify five silversmith pieces of a canopy employed in Spanish Catholic ceremonies into three groups:

- The first group comprises three original pieces of brass covered by a thin layer of silver with a thickness of 2 1m deposited by the Ruolz process.
- The second corresponds to an original piece with a restoration process where a double layer of silver sandwiched with a copper layer between them covered the brass. These additional layers of silver and copper were due to the restoration of the piece which suffered an erosion/corrosion problem. The thicknesses were about 2–4–3 1m from the top surface to the brass matrix.
- The third was a replaced piece which exhibited a thicker layer of silver (about 5–10 1m) deposited also by the Ruolz methodology but probably in a later restoration.

Through this study, we have demonstrated that LIBS method is an efficient way to characterize silversmith pieces with a minimal damage. The ability to perform depth profiling has evidenced the different regions or layers covering the brass matrix of specimens and has provided information to discriminate original pieces from those with a restoration process or simply with replaced ones. Furthermore, LIBS offered a key issue to explain the restoration process by detecting a dealloying phenomenon without the need of sampling or significant damage of the piece, in contrast to vacuum techniques.

Acknowledgments This study has been partially supported by the agreements IAPH&UPO and the Excellence Project of Junta de Andalucia HUM-6775 (RIVUPH).

References

1. F. Colao, R. Fantoni, P. Ortiz, M.A. Vazquez, J.M. Martin, R. Ortiz, N. Idris, Quarry identification of historical building materials by means of laser induced breakdown spectroscopy, X-ray fluorescence and chemometric analysis. Spectrochim. Acta B 65(8), 688 (2010)
2. P. Ortiz, M.A. Vazquez, R. Ortiz, J.M. Martin, T. Ctvrtnickova, M.P. Mateo, G. Nicolas, Investigation of environmental pollution effects on stone monuments in the case of Santa Maria la Blanca, Seville (Spain). Appl. Phys. A Mater. Sci. Process. 100(3), 965 (2010)
3. T. Ctvrtnickova, L. Cabalin, J. Laserna, V. Kanicky, G. Nicolas, Laser ablation of powdered samples and analysis by means of laser-induced breakdown spectroscopy. Appl. Surf. Sci. 255(10), 5329 (2009)
4. M.P. Mateo, T. Ctvrtnickova, G. Nicolas, Characterization of pigments used in painting by means of laser-induced plasma and attenuated total reflectance FTIR spectroscopy. Appl. Surf. Sci. 255(10), 5172 (2009)
5. P. Ortiz, R. Ortiz, J.M. Mart´ın, M.A. Va´zquez, T. Ctvrtnickova, M.P. Mateo, G. Nicola´s, A. Go´mez, Characterization Of Crust And Deposits Found In Churches of Seville, in *Proceedings of the 8th International Symposium on the Conservation of Monuments in the Mediterranean Basin,* vol. II, pp. 116–130 (2010)
6. C. Fotakis, D. Anglos, V. Zafiropulos, S. Georgiou, V. Tornari, *Lasers in the Preservation of Cultural Heritage: Principles and Applications* (Taylor & Francis, New York, 2007)
7. V. Lazic, R. Fantoni, F. Colao, A. Santagata, A. Morona, V. Spizzichino, Quantitative laser-induced breakdown spectroscopy analysis of ancient marbles and corrections on the variability of plasma parameters and of ablation rate ‘‘Q’’. J. Anal. At. Spectrom. 19, 429 (2004)
8. Y. Yoon, T. Kim, M. Yang, K. Lee, G. Lee, Quantitative analysis of pottery glaze by laser induced breakdown spectroscopy. Microchem. J. 68, 251 (2001)
9. D. Anglos, Laser-induced breakdown spectroscopy in art and archaeology. Appl. Spectrosc. 55, 186A (2001)
10. F.J. Fortes, J. Cun˜at, L.M. Cabalin, J.J. Laserna, In situ analytical assessment and chemical imaging of historical buildings using a man-portable laser system. Appl. Spectrosc. 61, 558 (2007)
11. M. Castillejo, M. Mart´ın, D. Silva, T. Stratoudaki, D. Anglos, L. Burgio, R.J.H. Clark, Laser-induced breakdown spectroscopy and Raman microscopy for analysis of pigments in polychromes. J. Cult. Herit. 1, S297 (2000)
12. F.J. Fortes Roma´n, L.M. Cabal´ın Robles, J.J. Laserna Va´zquez, Aplicaciones de las te´cnicas la´ser en ana´lisis y conservacio´n del patrimonio, in PH, ed. IAPH, vol. 74, pp 74–93 (2010)
13. A. Nevin, G. Spoto, D. Anglos, Laser spectroscopies for elemental and molecular analysis in art and archaeology. Appl. Phys. A 106(2), 339–361 (2012)
14. V. Spizzichino, R. Fantoni, Laser induced breakdown spectroscopy in archeometry: a review of its application and future perspectives. Spectrochim. Acta B 99, 201–209 (2014)
15. K. Melessanaki, M. Mateo, S.C. Ferrence, P.P. Betancourt, D. Anglos, The application of LIBS for the ana´lisis of archeological ceramic and metal artifacts. Appl. Surf. Sci. 197, 156 (2002)
16. L.E. Garcia-Ayuso, J. Amador-Hernandez, J.M. Fernandez-Romero, M.D. Luque de Castro, Characterization of jewellery products by laser-induced breakdown spectroscopy. Anal. Chim. Acta 457(2), 247 (2002)
17. A. Arafat, M. Na’es, V. Kantarelou, N. Haddad, A. Giakoumaki, V. Argyropoulos, D. Anglos, A.G. Karydas, Combined in situ micro-XRF, LIBS and SEM-EDS analysis of base metal and corrosion products for Islamic copper alloyed artefacts from Umm Qais museum, Jordan. J. Cult. Herit. 14(3), 261 (2013)
18. M. Ouja, M. Castillejo, W. Maracineanu, M. Simileanu, R. Radvan, V. Zafiropulos, D. Ferro, LIBS analysis of metal artefacts from Sucevita Monastery, Romania. Lasers in the Conservation of Artworks, p. 133 (2008)

19. Y. Lou, Q. Zhou, R. Li, Detection of Silver Jewelry with Orthogonal Double-pulse LIBS, Mechatronics and Intelligent Materials Iii, Pts 1–3 706–708, 752 (2013)
20. J.J. Laserna, L.M. Cabalın, F.J. Fortes, LIBS as an advanced tool in the chronocultural study of archaeometallurgical objects. International conference on conservation strategies for saving indoor metallic collections with a special section on legal issues in the conservation of cultural heritage, Cairo, Egypt (February, 2007)
21. S. Guirado, F.J. Fortes, V. Lazic b, J.J. Laserna, Chemical analysis of archeological materials in submarine environments using laser-induced breakdown spectroscopy. On-site trials in the Mediterranean Sea. Spectrochim. Acta B 74–75, 137–143 (2012)
22. A. De Giacomo, M. Dell'Aglio, F. Colao, R. Fantoni, V. Lazic, Double-pulse LIBS in bulk water and sumerged bronze samples. Appl. Surf. Sci. 247(1–4), 157 (2005)
23. M. Simileanu, R. Radvan, N. Puscas, Underwater LIBS investigations setup for metals identification. Univ. Politeh. Buchar. Sci. Bull. Ser. A Appl. Math. Phys. 72(4), 209 (2010)
24. J. Asmus, J. Elford, D. Magde, V. Parfenov, Underwater inverse LIBS (iLIBS) for marine archaeology, in *Proceedings of SPIE 8790, Optics for Arts, Architecture, and Archaeology IV*, vol. 8790 (2013)
25. M.P. Mateo, T. Ctvrtnickova, E. Fernandez, J.A. Ramos, A. Yanez, G. Nicolas, Laser cleaning of varnishes and contaminants on brass. Appl. Surf. Sci. 255(10), 5579 (2009)
26. V.V. Golovlev, M.J. Gresalfi, J.C. Miller, D. Anglos, K. Melesanaki, V. Zafiropulos, G. Romer, P. Messier, Laser characterization and cleaning of 19th century daguerreotypes II. JCH 4, 134s–139s (2003)
27. P.V. Maravelaki, V. Zafiropulos, V. Kilikoglou, M. Kalaitzaki, C. Fotakis, Laser-induced breakdown spectroscopy as a diagnostic technique for the laser cleaning of marble. Spectrochim. Acta B 52, 41 (1996)
28. M. Abdelhamid, S. Grassini, E. Angelini, G.M. Ingo, M.A. Harith, Depth profiling of coated metallic artifacts adopting laser-induced breakdown spectrometry. Spectrochim. Acta B 65, 695–701 (2010)
29. K.A. Tereszchuk, J.M. Vadillo, J.J. Laserna, Depth profile analysis of layered samples using glow discharge assisted laser-induced breakdown spectrometry (GD-LIBS). Spectrochim. Acta B 64, 378–383 (2009)
30. L.P. del Campo, F. Marmolejo, A. Gomez, A. Bocalandro, M. Bethencourt, Tradicio´n e innovacio´n en las artes industriales: el palio de plata de 1871 de F. Isaura, in PH, ed. IAPH, vol. 69, pp. 20–33 (2009
31. D. Scott, D. Stevens, Electrotypes in science and art. Stud. Conserv. 58(3), 189–198 (2013)
32. A. Lins, Gilding techniques of the renaissance and after, in *Gilded metals: history, technology and conservation*, ed. by T. Drayman-Weisser (Archetype Publications Ltd, London, 2000), pp. 241–265
33. S. La-Niece, in *Silvering in Metal Plating and Patination*, ed. S. La-Niece, P. Craddock (Butterworth-Heinemann Publishers, 1993), pp. 201–210
34. E. Turner, in *Silver Plating in the 18th Century in Metal Plating and Patination*, ed. S. La-Niece, P. Craddock (Butterworth-Heinemann Publishers, 1993), pp. 211–222
35. M. Bethencourt, A. Go´mez, Aplicacio´n de te´cnicas anal´ıticas SEM/EDX y metalogra´ficas para la datacio´n y restauracio´n de una pieza de orfebrer´ıa religiosa del Siglo XIX, in *Libro de Proceedings del XI Congreso Nacional de Materiales,* pp. 221–224 (2010)
36. CNR-ICR, Materiali lapidei: Campionamento. Normal 3/80, 1–6 (1980)