
INVESTIGATION OF THE WALL PAINTING MATERIALS IN THE SAN BARTOLOME CHURCH FAÇADE (SEVILLE)

Maria Dolores Robador^{1*} and José Luis Perez-Rodríguez²

¹ *University of Seville, Technical Architecture Faculty, Avda Reina Mercedes s/n, 41012 Seville, Spain*

² *Materials Science Institute of Seville (CSIC-Seville University), Americo Vesputio 49, 41092 Seville, Spain*

(Received 21 July 2016, revised 6 October 2016)

Abstract

Wall paintings have been found in the façade of San Bartolome Church in Seville. The red colour was composed of calcite and iron oxides pigment. Another layer constituted by calcite was deposited over this red layer. Gypsum produced by environmental contamination or previous restoration was present in both layers. In other zones of the façade, the red layer was found without the presence of gypsum; however, cement was detected. In this last case, red colour was probably applied more recently. All studied colour layers were covered by an acrylic resin. The mortars were composed of calcite and quartz.

Keywords: X-ray diffraction, Scanning Electron Microscopy, infrared spectroscopy, differential thermal analysis, thermogravimetry

1. Introduction

The San Bartolome church is located on a site where there was previously a mosque transformed into a synagogue. Later, a Catholic church was built there. The actual building was finished in 1791. The church was built according to a Latin cross divided into three areas, and a choir in height was located at the foot of the church. The style of the building is neoclassical. The building has three façades attached to the neighbouring houses by the head of the church. The façade shows geometric decoration on the walls, simulating blocks and other elements. Today, the decoration of the external walls of the building shows a high degree of alteration. The decoration of the façades was fundamental to the city of Seville but was lost in the 19th century. The restoration, which will take place in the Church of San Bartolome, intends to recover part of this ornamentation. Images of the building façade are shown in Figure 1.

*E-mail: lolarobador@us.es

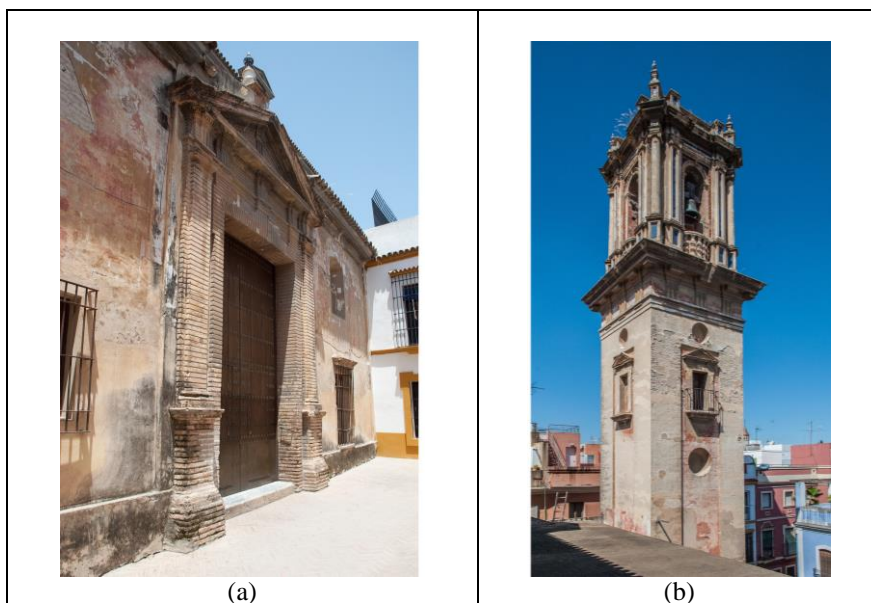


Figure 1. Images of the San Bartolome church façade: (a) entrance, (b) tower.

A multi-technique analytical approach for the identification of the pigments employed to create wall paintings is crucial to gain a deeper knowledge of the raw materials and manufacturing techniques and to inform preservation methodology. Several works have recently been published concerning the characterisation of pigments from cultural heritage artefacts [1-3].

Study of masonry and coating materials from historic buildings typically involves different analytical techniques. The application of observation and analysis methods to the field of cultural heritage objects allows a detailed and accurate knowledge on their physicochemical structure. The analysis provides useful information for defining the gamut of pigments available on local and regional scales, and understanding the techniques of colour preparation and applications through centuries [4-8]. Different complementary techniques can be used for the determination of elemental composition, crystalline phases, etc. and in general, to get a sufficiently complete characterization of the materials and pigments employed. Nowadays, non-destructive techniques such as micro-Raman [9-10], X-ray diffraction [11-14], X-ray fluorescence [15] are applied to artworks study [16-20]. Even when they are portable, these equipments give precise information about the composition of the cultural heritage artefacts. However, it is difficult to get information beyond the surface layer, on all layers of the polychrome from the support to the most external one. Sometimes, the portable devices have difficulties to analyse all parts of the artefacts, due to the object geometry, heterogeneity of the surface, etc. Whenever possible, the preparation and study of cross-section samples taken from the artworks are very helpful in the identification of all the painting components, from the support to the top layers, using other experimental techniques, such as micro-FTIR (Fourier

Transform Infrared spectroscopy), micro-Raman, SEM-EDX (Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectroscopy), etc.

The differential thermal analysis (DTA) and thermogravimetry (TG) have been used to characterize these materials as well as to quantify them. Thermal analysis techniques provide an aid in the analysis to the extent that calcium carbonate is exactly determined [21]. These techniques have been used to characterize hydrated calcium oxalates of monument patinas [22-24], mortars and cement of historical façades [25], black crusts on ancient mortars, patching material seriously discoloured and carbonaceous materials in damaged layers on monuments [26-28]. Atmospheric depositions on historic buildings were evaluated by combined thermal analysis and combustion techniques [29]. The protection made by acrylic resin has been studied by thermomechanical properties [30]. Thermal characterization and kinetics of three different origins class-G cement have been also studied [31].

The objective of this work is to study pigments, techniques of preparation and causes of deterioration of the wall paintings, in order to provide information for the restoration.

2. Methods

The sample cross sections were observed and photographed using a Nikon OPTIPHOT (x25, x50 and x100) optical microscope. X-ray diffraction patterns (XRDs) were recorded on a PANalytical diffractometer X'Pert Pro MPD using Ni-filtered Cu K α radiation and an X'Cellerator detector with an angular aperture of 2.18° (2 θ) and step size of 0.016°.

Elemental chemical analyses of the cross sections were performed using a HITACHI S-4800 SEM instrument equipped with a Bruker X-Flash Detector 4010 energy dispersive X-ray (EDX) analyser at an accelerating voltage of 20 kV. Samples were coated with a carbon film prior to SEM analysis.

Fourier transform infrared spectroscopy (FTIR) measurements were performed using a Jasco FTIR 6200. Simultaneous TG-DTA measurements (STDQ600, TA Instruments) were carried out at a linear heating rate of 10 °C min⁻¹ over the temperature range from ambient temperature to 1000 °C under flowing air, N₂ or CO₂.

3. Materials

Seventeen samples were taken at different heights in different zones of the façade of the Saint Bartolome Church. The samples were taken from the northwest (samples 1 to 9), southwest (samples 10 and 11) and the north-east (samples 12 and 13), respectively of the tower of the church (see Figure 1b). In addition, 4 samples (14-17) were taken from the façade of the main entry of the church (see Figure 1a). These samples provided an opportunity to acquire more in-depth knowledge about the wall painting of this monument. Photographs of some of the samples are shown in Figure 2. Sample 2 shows two thick layers,

one layer featuring a white colour located over the other layer with a red colour (Figure 2a). Sample 10 shows a thin red layer followed by a white layer; finally appears the mortar (Figure 2b). Sample 11 shows a white layer followed by a red layer deposited over the mortar (Figure 2c). Sample 12 shows a red layer deposited over the mortar (Figure 2d).

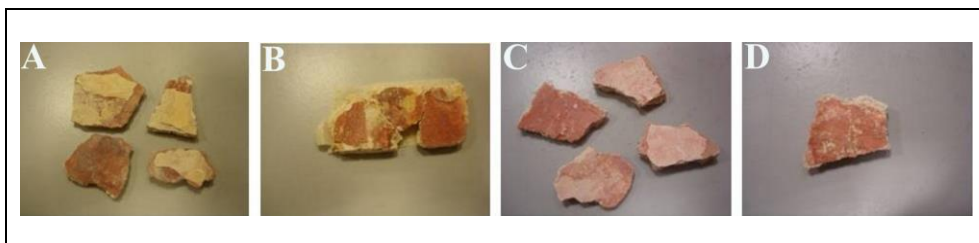


Figure 2. Photographs of the samples from San Bartolome church façade: (A) sample 2, (B) sample 10, (C) sample 11, (D) sample 12.

4. Results

Sample cross-sections, examined with optical microscope and scanning electron microscope coupled with energy dispersive X-ray spectroscopy, are shown in Figure 3.

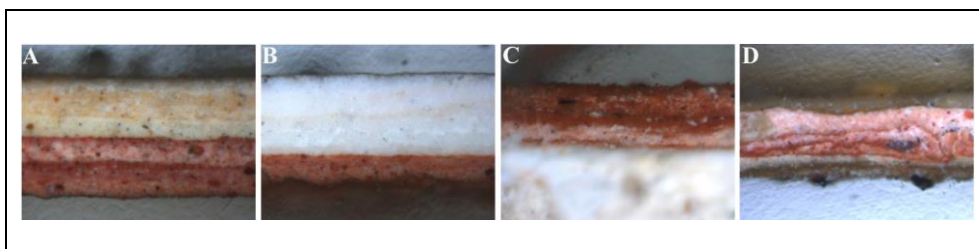


Figure 3. Microphotography (x100) of cross-sections: (A) sample 2, (B) sample 11, (C) sample 12, (D) sample 15.

The cross-section of sample 2 showed the presence of two layers of red colour followed by other layer of white colour showing heterogeneous colour with some brownish zones (Figure 3a). The chemical analysis of the cross-section was carried out by EDX coupled to the SEM. The chemical analysis of the white colour layer showed the presence of Ca and small proportions of Si, Al and Mg (Figure 4a). The red layers are also composed of Ca accompanied of Si, Al and Fe (Figure 4b). A punctual chemical analysis carried out on red particles present in this layer of red colour showed the presence of iron (Figure 4c) attributed to pigments constituted by iron oxides. The chemical analysis carried out by EDX on mortars taken in all studied samples showed high contents of Ca and Si and small percentages of Al, Mg, K and Ti. Punctual analysis of some particles present in the mortar showed a high proportion of Si, typical of quartz

(Figure 4d). Other particles were constituted by Si, Al and K (Figure 4e), typical of feldspars and mica.

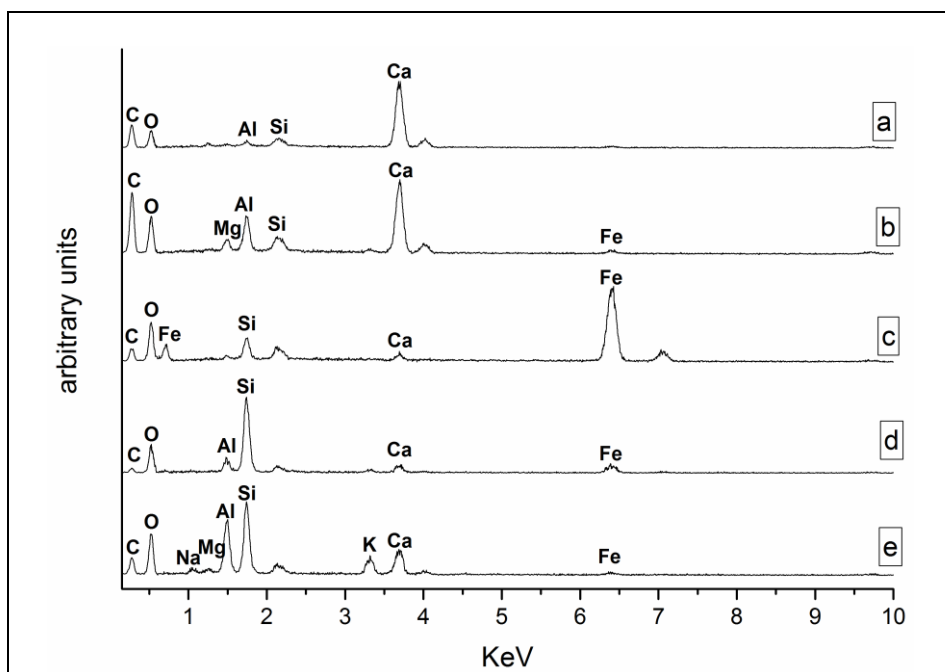


Figure 4. Chemical analysis performed by EDX: (a) white layer of sample 2, (b) red layer of sample 2, (c) punctual analysis of red particles present in sample 2, (d) mortar present in all studied samples and (e) particles present in the mortars.

The X-ray powder diffraction was applied to characterize the minerals present in the different layers of the wall paintings. The X-ray diagram of the white layer of sample 2 showed the presence of calcite (97%) and a small percentage of quartz (3%) (Figure 5a). These data suggest the application of a layer constituted by lime. The red layer is constituted by calcite (89%) quartz (6%) iron oxide (5%). These data suggested the presence of iron oxides as pigment, as was confirmed by EDX. The mortar separated from different samples is constituted by calcite (49%), quartz (36%) gypsum (14%) and mica (< 5%). The mortar was formed with lime and inert material (quartz and mica). Gypsum appears in the mortar but not in the colour layers.

The chemical analysis carried out by EDX of the red layer of sample 12 showed the presence of O, Si, Al, Fe. In addition appeared S and Ca attributed to gypsum. Punctual analysis of white particles present in this red layer is shown in Figure 6a. The X-ray powder diffraction showed that the superficial layer of white colour located over the red colour is constituted by calcite, gypsum and a small proportion of quartz (Figure 5b). The red layer was constituted by calcite, gypsum, quartz, iron oxides and dolomite (data not shown) The chemical analysis showed that iron oxide was also used as a pigment in this sample (Figure 6b). The XRD confirmed that the mortar of this sample was constituted

by calcite, quartz and a small percentage of gypsum, feldspars and mica (data not shown).

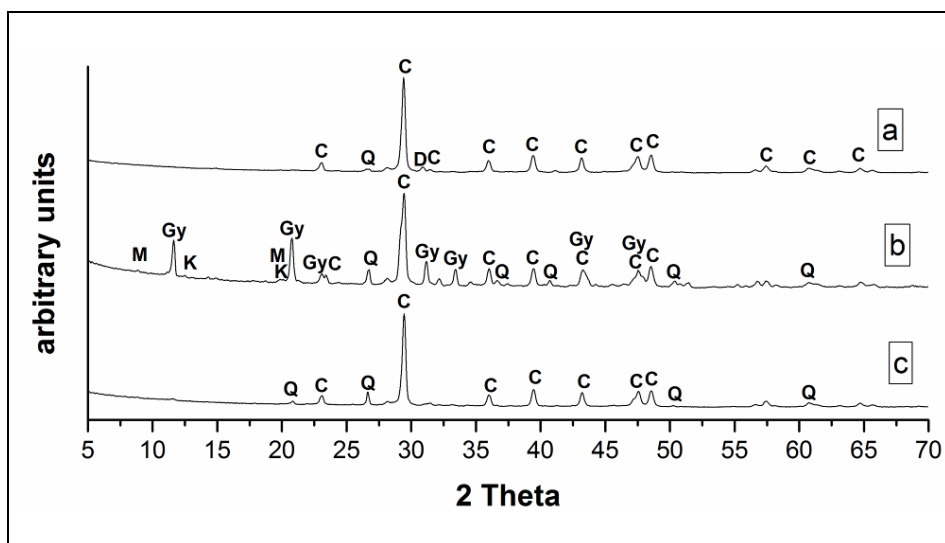


Figure 5. XRD of layers separated of samples from San Bartolome church façade: (a) white layer of sample 2, (b) white layer of sample 12 and (c) white layer of sample 10. C = calcite, D = dolomite, M = mica, Gy = gypsum, K = kaolinite and Q = quartz.

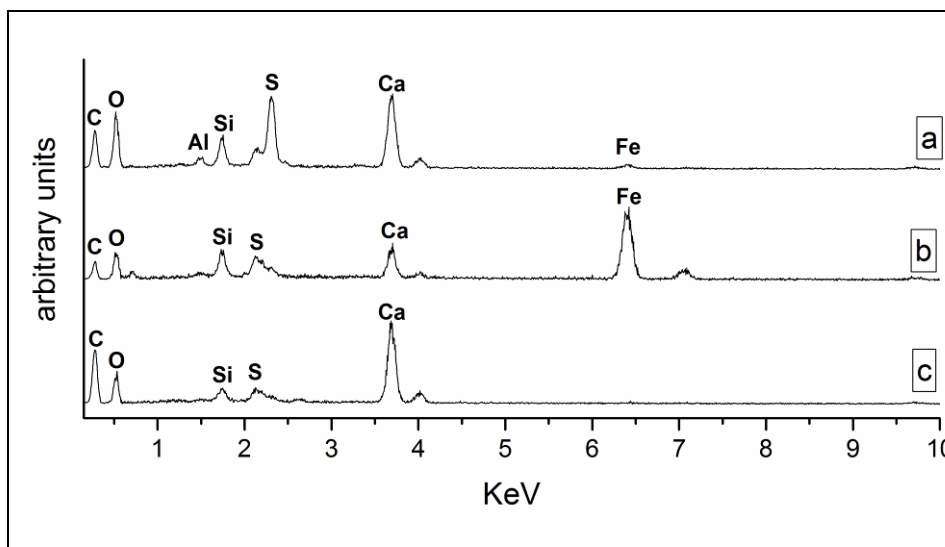


Figure 6. Chemical analysis performed by EDX: (a) punctual analysis of white particles present in the red layer of sample 12, (b) punctual analysis of red particles of sample 12, and (c) white layer of sample 11.

The cross section of Sample 10 showed a white layer also composed mainly of calcite as it is shown in the XRD diagram of Figure 5c. The white and red layers of Sample 11 showed similar compositions to Sample 2. The EDX of

white layer of sample 11 is shown in Figure 6c. Sample 15 and the other samples studied in this work showed compositions similar to the samples previously described.

FT-IR microspectroscopy in reflectance mode was used on the surface of the San Bartolome Church façade to identify the possible presence of consolidant, binding media, varnishes or adhesives applied in previous restoration efforts. In the 20th century, the use of polymers was widely extended, and they are now frequently found on the façades of monuments.

Sample 2 showed a white layer deposited over two layers of red colour (Figure 3a). The FT-IR microscopy study performed on the surface of these layers (Figure 7) showed bands at 2980, 2885 and 2840 cm^{-1} , which are associated with the stretching vibrational modes of the hydrocarbon skeleton. Two bands appearing at 3696 and 3621 cm^{-1} associated with OH together with the band at approximately 1000 cm^{-1} was attributed to silicates. The broad band between 3500 and 3200 cm^{-1} may be attributed to the presence of water and also to N-H groups present of compounds that it is usually added to increase the efficiency of the thickener. The absorption bands at 2500 and 1600 cm^{-1} were attributed to CO_2 in the air and to the water present in the sample, respectively. The peak at 1756 cm^{-1} was ascribed to the stretching vibration produced by the carbonyl in ester groups. The bands at 1448 and 1384 cm^{-1} were assigned to the asymmetric and symmetric stretching vibrations ($\nu_{\text{C-O}}$), respectively of the ester group. Bands associated with carbonates and gypsum were also detected. These data confirm the presence of an acrylic synthetic resin, probably Polaroid B72, applied for consolidation of the wall painting.

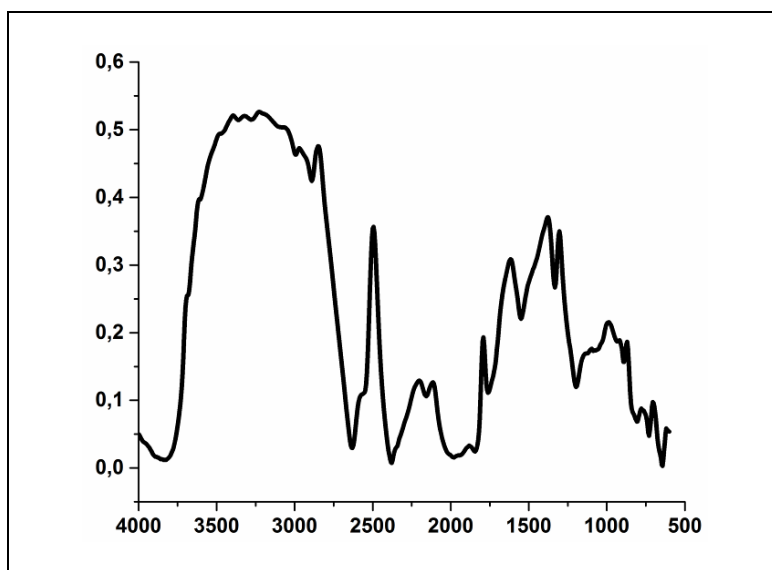


Figure 7. FTIR spectra of sample 2.

Sample 12 showed a red layer that was also treated with the same resin. The thermal study of this sample (Figure 8a) shows mass loss and an endothermic effect at 150 °C, attributed to gypsum. A high mass loss (18%) and an endothermic effect appearing between 600°C and 740°C are attributed to calcite. The high mass loss and exothermic peaks between 225°C and 500°C were produced by the decomposition of the acrylic resin. The X-ray diffraction study confirmed the presence of calcite and gypsum in this sample (Figure 5b). Figure 8b shows DTA-TG curves of mortar from sample 12. Peaks attributed to gypsum and calcite can be observed. The endothermic at 573°C is attributed to the transformation of α -quartz to β -quartz.

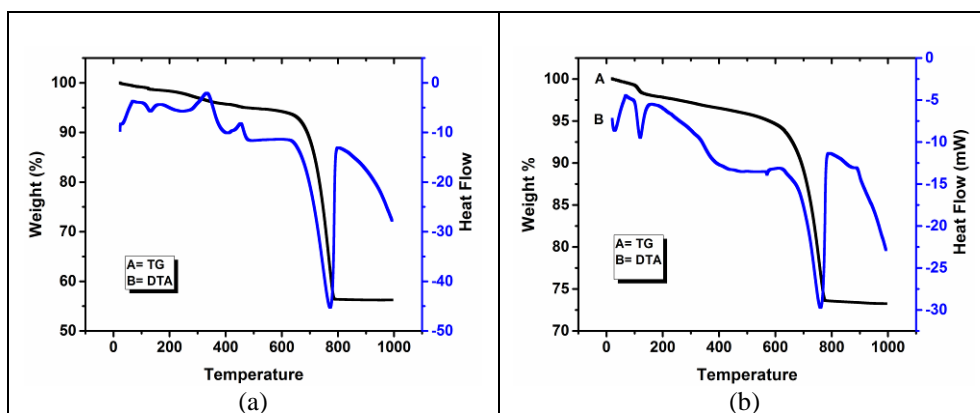


Figure 8. DTA-TG curves of: (a) red layer of sample 12, (b) mortar of sample 12.

5. Conclusions

In this work, the characterization of pigments, techniques of the preparation and cause of the deterioration of the San Bartolome church wall paintings have been critically discussed. Complete identification was only achieved by the combined use of the different techniques.

The studies showed the presence of two layers, white and red in colour; calcite was the main component in both layers. Iron oxides were found in the red pigment. The white layer, which covers the red layer, could be attributed to a plastering that was recently carried out.

Gypsum was found in the mortars. Gypsum was detected in the white and red colour layers of a zone of the wall painting (i.e. sample 12 located at the top of the tower wall); however, it was not found in other zone of the wall painting (i.e. sample 2 located at the bottom of the tower wall). The presence of gypsum may be attributed to a constitution of the material, restoration material containing in cements and reintegration mortars or environmental contamination. However, gypsum did not appear in the wall painting of other zone, which probably was applied in other restoration.

The studied mortar samples were constituted by calcite (49%), quartz (36%) gypsum 14% and mica (<5%). The mortar was formed with lime and inert material (quartz and mica).

The FT-IR microscopy and DTA/TG study performed on the surface of these two layers confirmed the presence of an acrylic synthetic resin, probably Polaroid B72, applied for the consolidation of the wall painting.

Acknowledgment

The financial support of the Ministerio de Economía y Competitividad, Secretaria de Estado de Investigación, Desarrollo e Innovación (BIA2014-55318-R) is gratefully acknowledged.

References

- [1] J.L. Perez-Rodriguez, M.C. Jimenez de Haro, B. Siguenza and J. Martinez-Blanes, *App. Clay Sci.*, **116** (2015) 211.
- [2] A. Duran, J.L. Perez-Rodriguez, M.C. Jimenez de Haro, M.L. Franquelo and M.D. Robador, *J. Archeol. Sci.*, **38** (2011) 2366.
- [3] M.D. Robador, L. De Viguerie, J.L. Perez-Rodriguez, H Rousseliere, P. Walter and J. Castaing, *Archaeometry*, **58** (2016) 255.
- [4] A. Almagro, *Artigrama*, **22** (2007) 155.
- [5] F. Delamare, *Revue d'Archéometrie*, **7** (1983) 85.
- [6] M.C. Edreira, M.J. Feliú, C. Fernandez-Lorenzo and J. Martin, *Anal. Chim. Acta*, **434** (2001) 331.
- [7] G.A. Mazzocchin, F. Agnoli and M. Salvadori, *Talanta*, **64** (2004) 732.
- [8] I. Garofano, A. Duran, J.L. Perez Rodriguez and M.L. Robador, *Spectrosc. Letters*, **44** (2011) 560.
- [9] J.L. Perez Rodriguez and A. Duran, *Spectrosc. Lett*, **47** (2014) 223.
- [10] R.J.H. Clark, J. Van der Weerd, *J. Raman Spectrosc.*, **35** (2004) 279.
- [11] A. Jurado-López, O. Demko, R.J.H. Clark and D. Jacobs, *J. Raman Spectrosc.*, **35** (2004) 119.
- [12] S. Svarcova, C. Koci, P. Bezdiccka, D. Hradil and J. Hradilova, *Anal. Bioanal. Chem.*, **398** (2010) 1061.
- [13] A. Duran, J.L. Perez-Rodriguez, T. Espejo, M.L. Franquelo, J. Castaing and P. Walter, *Anal. Bioanal. Chem.*, **395** (2009) 1997.
- [14] A. Duran, J. Castaing and P. Walter, *Appl. Physics A*, **99** (2010) 333.
- [15] A. Gianoncelli, J. Castaing, L. Ortega, E. Doorhyées, J. Salomon, P. Walter, J.L. Hodeau and P. Bordet, *X-Ray Spectrom.*, **37** (2008) 418.
- [16] A. de Viguerie, A. Duran, A. Bouquillon, V.A. Sole, J. Castaing and P. Walter, *Anal. Bioanal. Chem.*, **395** (2009) 2225.
- [17] W. Faubel, S. Staub, R. Simon, S. Heissler, A. Pataki and G. Banik, *Spectrochim. Acta B*, **62** (2007) 669.
- [18] S. Bruni, S. Caglio, V. Guglielmi and G. Poldi, *Appl. Phys. A*, **92** (2008) 103.
- [19] G. Van der Snickt, W. De Nolf, B. Vekemans and K. Janssens, *Appl. Phys. A*, **92** (2008) 59.
- [20] M.L. Franquelo, A. Duran, L.K. Herrera, M.C. Jimenez de Haro and J.L. Perez-Rodriguez, *J. Mol. Struct.*, **404** (2009) 924.

- [21] J.L. Perez-Rodriguez, A. Duran, M.A Centeno, J.M Martinez-Blanes and M.D Robador, *Thermochim. Acta*, **512** (2011) 5.
- [22] J.L. Perez-Rodriguez, A. Duran and L.A Perez-Maqueda. *J. Therm. Anal. Calorim.*, **104** (2011) 467.
- [23] A. Duran, M.D. Robador and J.L Perez-Rodriguez, *Int. J. Archit. Herit.*, **6** (2012) 342.
- [24] A. Moropoulou, A. Bakolas and K. Bisbikou, *Thermochim. Acta*, **269** (1995) 779.
- [25] D.A Brosman, J.P Sanders and S.A Mart, *J. Therm. Anal. Calorim.*, **106** (2011) 109.
- [26] C. Sabbioni, G. Zappia, N. Ghedini, G. Gobbi and O. Favoni, *Atmos. Environ.*, **32** (1998) 215.
- [27] C. Gembinski, A.E. Charda, B. Price and A.R McGhie. *J. Therm. Anal. Calorim.*, **59** (2000) 601.
- [28] N. Ghedini, C. Sabbioni and M. Pantani, *Thermochim. Acta*, **406** (2003) 105.
- [29] C. Riontino, C. Sabbioni, N. Ghedini, G. Zappiaa, G. Gobbi and O. Favoni, *Thermochim. Acta*, **321** (1998) 215.
- [30] A. Cataldi, A. Dorigato, F. Deflorian and A. Pegoretti, *J. Mater. Sci.*, **49** (2014) 2035.
- [31] M.V. K ok, *J. Therm. Anal. Calorim.*, **115** (2014) 1533.