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Non-destructive analysis of cultural heritage artefacts from Andalusia, Spain, by X-ray diffraction with Göbel mirrors

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ABSTRACT

The characterization of the phases present in artefacts has been normally carried out using XRD (Bragg–Brentano geometry) that requires sampling from artworks, being a destructive technique. However, X-ray diffraction with Göbel mirrors permits directly to study rough artefacts without sampling. Grazing incidence attachments can be used to characterize as much the superficial layer as the underlying ones in flat samples to obtain information about the depth profile of some samples. The combination of Göbel mirrors and measure at low fixed incidence angles allow to obtain information about the depth profile of bent samples.

This work reports the alteration processes on the surface of the following cultural heritage artefacts: a rivet and a nail extracted from Pardon Gateway, located in the North façade of Mosque-Cathedral of Cordoba; a Roman arrow and a button from a Roman jacket obtained from an excavation in Baena (Cordoba); organ pipe from Cathedral of Zaragoza; lead seals from Seville City Hall collection.

The main objective of this paper is the study through a totally non-destructive analytical method, X-ray diffraction with Göbel mirrors, of the superficial alteration of some metallic artefacts from cultural heritage. This knowledge allows us the election of appropriate methods to carry out the restoration of these artefacts.

1. Introduction

Several techniques have been used to characterize the materials and its products of alteration, but many of them only give chemical composition and frequently require the sampling and the destruction of the material (grinding, solution, heating, etc.). Also, the material is altered during the analysis, being important to use techniques that give information of the phases present without any destruction (non-destructive techniques) or sampling.

Conventional techniques of X-ray diffraction requires necessary sampling from artworks and grinding of the extracted samples, being, in this form, destructive analytical methods.

Parafocusing Bragg–Brentano geometry leads to a 2θ-shift of the X-ray reflection, if the sample is not precisely positioned on the focusing circle. A sample displacement can occur if the sample has an uneven surface, as frequently happens in samples coming from archaeology or cultural heritage [1].

Graded Multilayer Optics ("Göbel-Mirrors") have proved as very useful beam conditions for parallel-beam diffraction without sampling [2–4]. Grazing incidence reflectometry can be also used in flat samples without sampling. High-resolution XRD and XRD using capillary are used more frequently to study samples from cultural heritage but in these cases, sampling is necessary.

The Göbel Mirrors are a device, based on a layered crystal, which, mounted on a D-5000 Siemens diffractometer, transforms the primary divergent X-ray beam into a highly brilliant, parallel beam. If dimensions of an object are adequate (up to 60 cm in bulk), it can be directly analyzed by XRD, without sampling. Even a rough, irregular surface, both on flat and bent objects, is suitable for the analysis. The XRD analysis using Göbel mirrors is therefore, totally non-destructive and very useful to study artefacts from Cultural Heritage [5–7]. It can be obviously very adaptable to study the surfaces of these artefacts, giving information of degradation and corrosion processes and information about pigments, ceramics, metals, patinas, crusts, etc., used to manufactured artworks.

All the samples studied in this work belong to historic metals of Spanish Cultural Heritage.

Simply stated, metal corrosion is a process of chemical dissolution. Cations migrate from the metal substrate and react with available anions to form the metal salts that constitute tarnish layers and corrosion crusts. The character and chemical makeup of the corrosion products depend on the nature of the substrate and the

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environment to which it is exposed. Analyses are necessary to study the alterations imposed on an artifact in order to contribute to the development of adequate conservation and restoration treatments. The study of the alteration products formed in the surface can be realized using conventional XRD technique (powder diffraction measurements) that requires sampling of external products from metal artefact or XRD with Göbel mirrors, which permits directly the study of metal surfaces without sampling.

Most frequently used copper alloys are brasses (Cu–Zn), copper–nickel (Cu–Ni 70:30 or 90:10) and bronzes (Cu with Sn, Al or Si). Bronzes are used for the construction of different types of artworks, statues and monuments of cultural relevance, due to its high stability to environmental corrosion [8]. The corrosion of bronze monuments has been studied by several workers [9–13]. This interest is mainly due to the increasing awareness of air pollution damages to the cultural heritage. Some works have contributed to a better understanding on the reaction mechanisms of environmental deterioration [10].

Frequently, the first reaction that takes place is the oxidation of the metallic base exposed to the atmosphere to produce cuprous ions. In a chloride polluted atmosphere, cuprous chloride is formed. This is an unstable compound that in the presence of oxygen and environmental humidity turns into basic copper chloride with simultaneous production of hydrochloric acid. The presence of this acid will induce a new cyclic reaction of copper until the total consumption of the metal. Only if the cuprous chloride is eliminated, these damaging cyclic processes ("bronze disease") would be stopped [8,14,15].

Environmental conditions produce iron oxides and other compounds derived, such as oxyhydroxides or hydroxides in iron implements. The most common compound formed is goethite, which gives the brown and dark reddish brown colours to monuments. In poorly drained zones, lepidocrocite, an isomer of goethite, has been frequently reported [16]; it gives a bright orange colour. Vesuvianite, calcium magnesium iron aluminium silicate hydroxide ($Ca_{10}(Mg,Fe)_2Al_4(SiO_4)_5(Si_2O_7)_2(OH,F)_4$), named after its discovery locality, Mount Vesuvius (Campania, Italy) is rarely found in iron artefacts that have been buried during long time. This mineral is produced by the reaction between iron from artefacts and silicates present in the soil.

Other metals, such as lead employed in alloys were also widely used in antiquity, especially in organ pipes and lead seals manufacturing. Depending on the characteristic of the environment to which it is exposed, lead is quite reactive, forming anglesite ($PbSO_4$), cerussite ($PbCO_3$), hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) or plumbonacrite $Pb_5O(CO_3)_3(OH)_2$. The presence of lead carbonate compounds is responsible for the unsightly, white and powdery "white rust" of lead and can be localised on the surface in the form of pits [17]. The carboxylic acids formic, propanoic, tannic and acetic acids formed by cellulose hydrolysis from woods or parchment paper used for storing lead artefacts in museums or that support organ pipes can convert the lead surface of artefacts in voluminous corrosion compounds, and in some cases, the artefacts may be corroded in bulk through a progressive peeling of the corrosion layer [18–20].

The main objective of this work is the use of a totally non-destructive analytical method, X-ray diffraction with Göbel mirrors, for the study of the superficial alteration of some metallic artefacts, so much bent as flat ones, proceeding from important artworks, since in most of the cases cannot be taken samples for the study by conventional method of powder diffraction. Grazing incidence X-ray diffraction is offering the possibility of depth profiling studies; it is possible to record normal X-ray diffraction patterns as a function of X-ray penetration depth. The penetration depth of X-ray is affected by the diffraction geometry, sample absorption and reflectance of X-rays. In this case, measures using Göbel mirrors and low fixed incidence angles were done to study superficial and underlying layers of metallic samples.

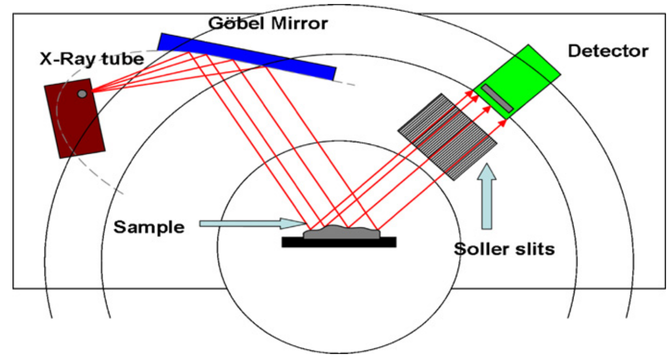

Fig. 1. Experimental procedure for non-destructive analysis by X-ray diffraction with Göbel mirrors of artefacts belonging to cultural heritage.

2. Materials and methods

The phases formed during the alteration processes on the surface of the following cultural heritage artefacts have been studied:

(a) A Rivet extracted from the Pardon Portico, located in the North façade of the Mosque-Cathedral of Cordoba (Spain). The gateway leaves (dated on March 1377) were made with pine wood covered with bronze plates. From the same Portico, studies were carried out in two other places.
(b) A piece of bronze with a high degree of alteration in its surface.
(c) An altered piece containing nails used for knocking the bronzes to the wood. All these pieces were extracted by experts and restorators using physical methods. Artefacts were not scraped to obtain powders, analysis were realized directly over the pieces. After adequate study and restoration, artefacts will be returned to its original places.

Other samples for the research were:

(d) A Roman arrow and a button from a Roman jacket obtained from an archaeological excavation in Baena (Cordoba, Spain).
(e) Organ pipes from the Cathedral of Zaragoza (Spain).
(f) Lead seals from Seville City Hall collection.

The crystalline phases on the surfaces of samples were characterized by X-ray diffraction (XRD) using a Siemens diffractometer model Kristalloflex D-5000 with Göbel mirrors. Graded multilayer optics creates a highly parallel incident beam while suppressing Kβ-radiation. By capturing a large solid angle, the mirror turns otherwise unusable radiation into a useful parallel beam. The Göbel mirror enables the investigation of irregularly shaped samples surfaces and reduces the requirement for the exact sample position (Fig. 1). Also, low fixed incidence angles X-ray were used in complement with Göbel mirrors.

To calculate the depth of the layer that is analyzed by X-ray diffraction is used ABSORBDX which is a program belonging to the software suite DIFFRACplus evaluation package [21,22].

The scanning electron microscopy (SEM) study was carried out with a JEOL JSM5400 microscope equipped with energy dispersive X-ray analyzer.

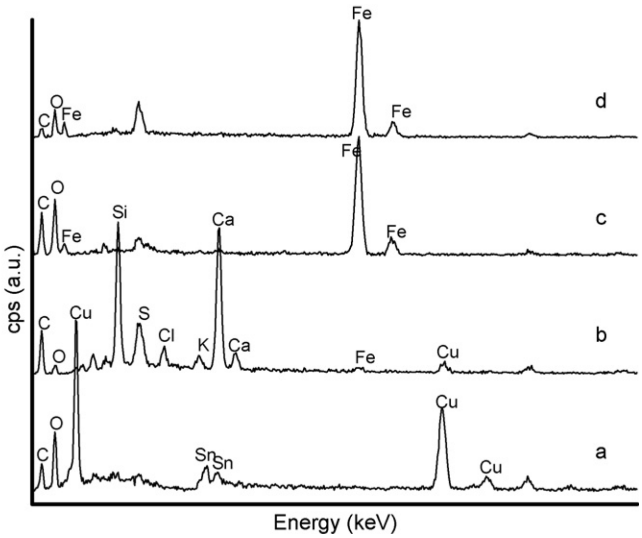

Fig. 2. EDX analysis of: (a) a rivet from the Pardon Portico of the Mosque-Cathedral of Cordoba and of a zone corresponding to a Roman jacket button from Baena's archaeological excavation, where surface crust was removed, showing the presence of Cu and Sn. (b) Superficial products formed on the piece of bronze from Pardon Portico, showing the presence of Cu, Cl, Si, S, Ca, Fe, K and O. (c) Powder taken from the nail, that shows the presence of Fe and O. (d) A Roman arrow from Baena's archaeological excavation, after removing the surface crust, showing the presence of Fe.

3. Results and discussion

3.1. Pardon-Portico of the Mosque-Cathedral of Cordoba

The elemental analysis of the rivet (sample a) from the Pardon Portico shows that the original material is constituted by copper and tin (Fig. 2a). The X-ray diffraction pattern (obtained using Göbel mirrors) of this sample shows the presence of the diffractions at values 42.8° and 49.7° of angle 2θ (Fig. 3a), corresponding to alpha bronze (B), according with the file 44-1477 of JCPDS. This piece was cleaned by restorators before studying and no degradation products are detected.

The elemental analysis of the superficial products formed on the bronze (sample b) shows the presence of copper, chlorine, silicon, sulphur, calcium, iron, potassium and oxygen (Fig. 2b). The XRD pattern measured with Göbel mirrors shows that the surface of the sample is constituted by atacamite [$Cu_2Cl(OH)_3$] (At), gypsum [$Ca(SO_4)2H_2O$] (Gy), quartz (SiO_2) (Q) and weddellite [$Ca(C_2O_4)2H_2O$] (We) (Fig. 3b). Atacamite has been detected previously in copper and copper alloys exposed outdoors due to environmental contamination [8,14]. This environmental contamination is also responsible of the presence of gypsum and other compounds. The weddellite, also present, may be formed by reaction between environmental gypsum and rests of calcite with oxalate ions from the dissolved acid. In urban areas oxalic acid is abundant in rain and mists [23] or it may be secreted by microorganisms, such as fungi and liquens [24].

The punctual chemical analysis of the nail (sample c) shows the presence of iron and oxygen (Fig. 2c). X-ray diffraction on the surface of the nail using Göbel mirrors confirms the presence of goethite [α-$Fe^{3+}O(OH)$] (Goe), lepidocrocite [γ-$Fe^{3+}O(OH)$] (Lep) and [$FeO(OH)$] (Fig. 4). These iron oxyhydroxides or hydroxides are frequently formed in the surface of iron artefacts due to environmental contamination. Also, gypsum (Gy) and quartz (Q) are present in the sample due to this factor.

3.2. Roman samples

Elemental analysis of a zone corresponding to a Roman arrow, where surface crust was removed, shows the presence of iron. Punctual chemical analysis carried out by EDX in the arrow is shown in Fig. 2d. X-ray diffraction analysis carried out with Göbel mirrors on the superficial covered area of crust shows the presence of calcite (Calc) and quartz (Q), deposited during the burial in the soil. Also

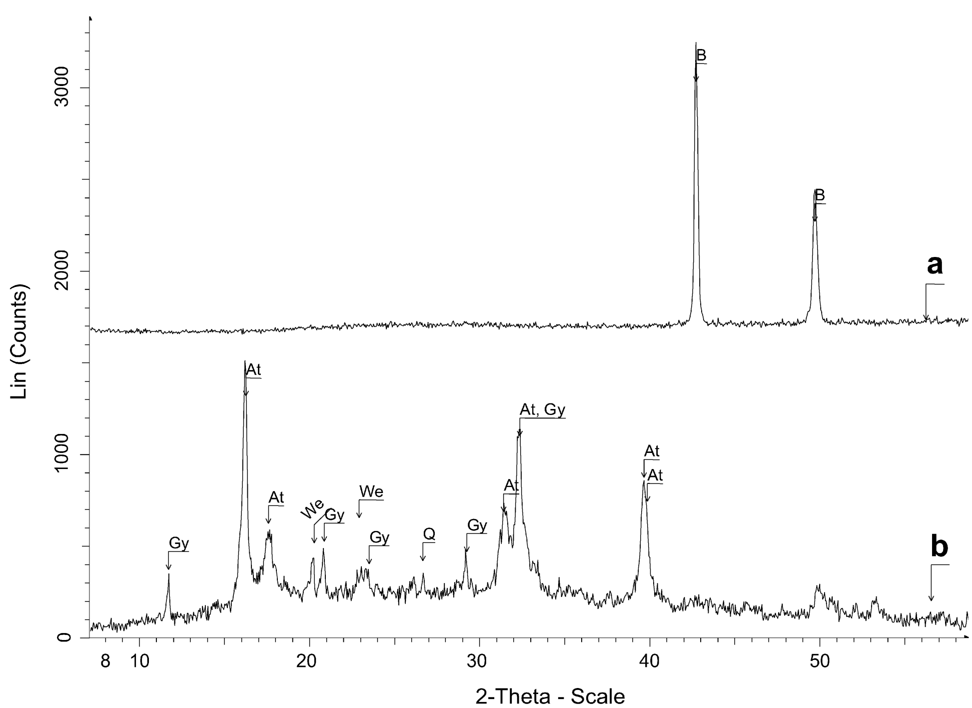

Fig. 3. X-ray diffraction pattern with Göbel mirrors of: (a) a rivet extracted from the Pardon Portico of the Mosque-Cathedral, corresponding to alpha bronze. (b) Superficial product on the altered bronze of the Portico, corresponding to atacamite (At), gypsum (Gy), quartz (Q) and weddellite (We).

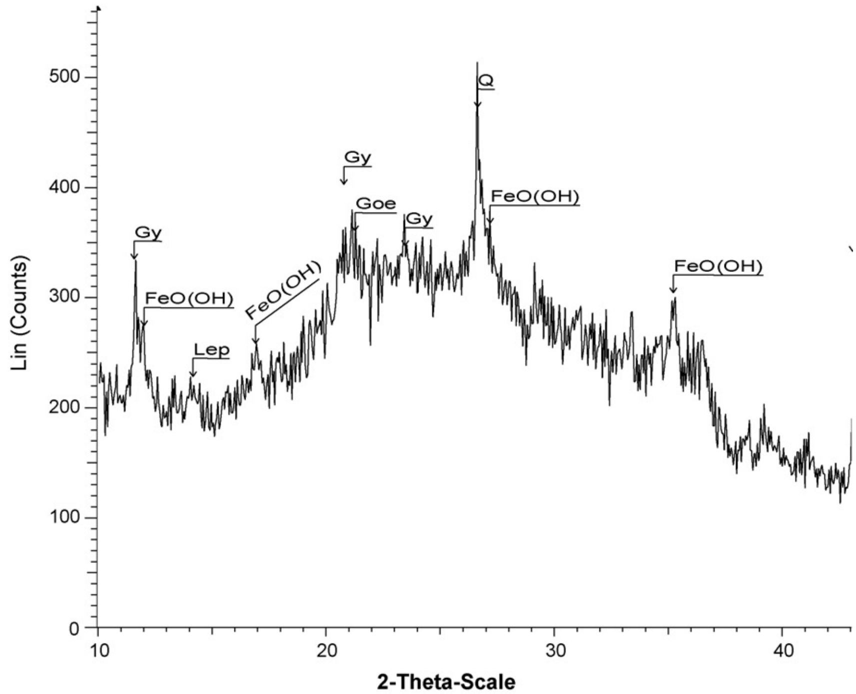

Fig. 4. X-ray diffraction pattern with Göbel mirrors of the altered iron nail of the Mosque-Cathedral of Cordoba, showing the presence of goethite (Goe), lepidocrocite (Lep), [FeO(OH)], gypsum (Gy) and Quartz (Q).

vesuvianite (Ves) was found (Fig. 5). Vesuvianite (calcium, magnesium, iron, aluminium, silicate hydroxide) is rarely found in iron artefacts that have been buried during long time. This mineral is produced by the reaction between iron from artefacts and silicates present in the soil.

Elemental analysis of a punctual zone corresponding to a Roman jacket button, where surface crust was removed similarly to the arrow sample cited before, shows the presence of copper and tin (similar to Fig. 2a). Studies realized on the surface of the sample by X-ray diffraction with Göbel mirrors only shows the

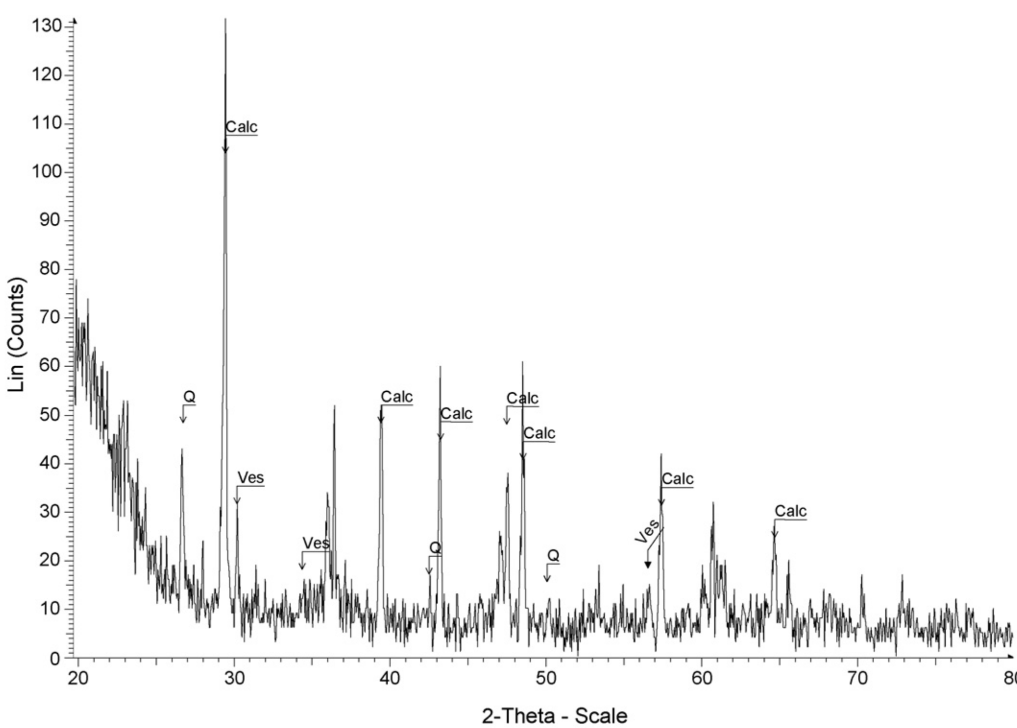

Fig. 5. X-ray diffraction patterns of the superficial covered area of crusts of a Roman arrow, using Göbel mirrors, showing the presence of calcite (Calc), quartz (Q) and vesuvianite (Ves).

presence of calcite, quartz (figure not shown) that were deposited from the soil. The crusts deposited on the surfaces of arrow and button are very thick and, except in punctual areas cited before, do not permit the study of the underlying material (bronze) and its alteration products.

3.3. Organ pipes and lead seals

3.3.1. Organ pipes

The atmospheric corrosion of lead-rich organ pipes in Spanish church has recently attracted the attention of organ builders. Organ pipe corrosion leads to the gradual development of cracks and holes which destroy the function of the pipes. When this occurs, the historic lead organ pipes have to be replaced by new ones, and a part of the sounding cultural heritage is lost forever. It is not clear why these organs are corroding. However, the church environment to which these organs are exposed is characterized by relatively low temperature and high relative humidity.

Another characteristic is the presence of large amounts of wood structures around organs. The studied pipe organ is enclosed in wood furniture. The humidity in combination with alteration products of wood (organic vapors acid, such as acetic or formic, and aldehydes produced by the hydrolysis of the hemicellulose during aging) can react with lead forming corrosion products, mainly lead carbonates. In extreme cases, they can cause a complete destruction of the artefact.

Crystalline corrosion products were analyzed; the diffractometer was equipped with Göbel mirrors and the measures were realized at low fixed incidence angles, which can be used to characterize as much the superficial layer as the underlying ones without any effect of the roughness and obtain information in the depth profile of the sample.

The organ pipes are not flat, it is necessary to use a parallel X-ray beam; the beams diffracted by the sample are collimated using a parallel slit analyzer and not a divergent beam that obtained with Bragg–Brentano geometry. The alteration layer of the organ pipes is very thin. When the study is realized using coupled θ–2θ angles diffraction, the peaks of bulk components (lead-rich organ pipe) are very intense compared to the alteration products (figures not shown). The employment of a fixed low incidence angle (θ) increases path length through the sample and decreases X-ray penetration into the bulk. This method provides better sample peak detection for the attempt of analyzing more superficial layers and of trying to observe products of alteration, such as lead carbonates (hydrocerussite and cerussite), phases that were observed in analysis of other organ pipes [25,26].

This procedure is new in this work and can be employed for study of artefacts belonging to cultural heritage. In organ pipes samples, the application of low incidence angle offers many information without scrapping into the corrosion thin layer.

The diffraction profiles of the sample was acquired under fixed incidence angles, at 1° (θ) and 5° (θ), all the other parameters were kept constant. Fig. 6 shows the diffraction patterns of the same sample belongs to organ pipe at two incidence angles, 1° (θ) and 5° (θ). The XRD patterns of the 1° incident angle (θ) gives information about the more external layer. The crystalline phases detected can be attributed to tin (Sn), lead (Pb) and hydrocerussite (HC) (Fig. 6a).

However, it is also evident that there is a certain evolution of the diffractogram from the surface to the depth of the sample. In particular, the pattern taken at 5° (θ) (Fig. 6b) shows higher intensity of the peaks corresponding to tin (Sn). In the organ pipe's surface is possible to detect the alteration process because the pattern at 1° (θ) shows some conversion of lead to hydrocerussite;

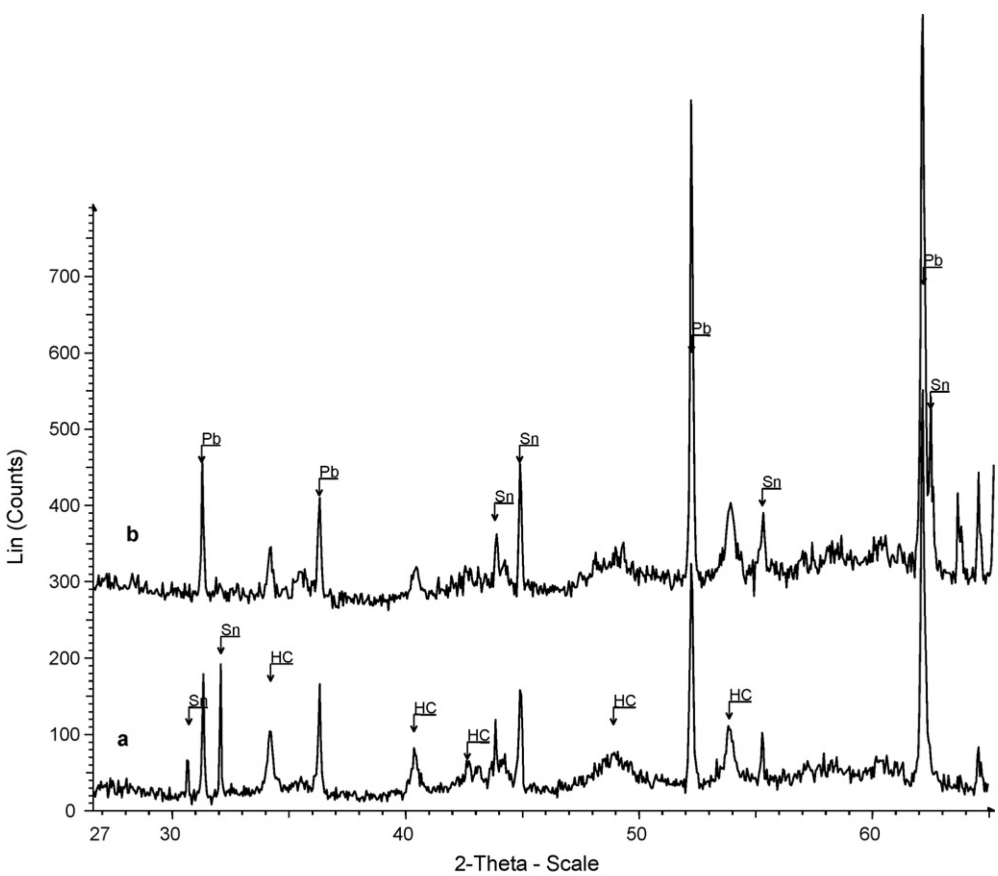

Fig. 6. (a) XRD pattern at 1° incident angle of an organ pipe, tin (Sn), lead (Pb) and hydrocerussite (HC). (b) XRD pattern at 5° incident angle of the same pipe.

Table 1
The depth for 90% contribution of the measured intensity for 1° and 5° in the study of organ pipes

	Pb (μm)	Sn (μm)	$Pb_3(CO_3)_2(OH)_2$ (μm)
$\theta = 1°$	0.149	0.211	0.306
$\theta = 5°$	0.645	0.912	1.350
θ–2θ couple	1.195	1.657	2.655

peaks of lead decrease and peaks corresponding to hydrocerussite increases.

In order to get the depth of the analyzed layer of the organ pipe, it is considered the global chemical composition (lead, tin and hydrocerussite), the density of these phases, the wavelength of X-ray radiation ($\lambda = 1.54$ Å), the diffraction angle for each compound (strongest peak, Pb $2\theta = 31.28°$, Sn $2\theta = 30.73°$, $Pb_3(CO_3)_2(OH)_2$ $2\theta = 34.15°$), and finally the incidence angle. The depth for 90% contribution of the measured intensity for these angles is described in Table 1.

Due to the studied organ pipe has a curved and rough surface, obtained information cannot be comparable with that it would obtain in case of thin layers. With employment of fixed low incidence angles (1° and 5°), although it obtains major information about superficial layers, we cannot obviate that X-ray beam gets also in the bulk of the sample.

In another sonorous organ pieces, alloy composition is about 50% of lead and 50% of tin [27]. However, in the case of the samples studied in this work, the composition is about 90% of lead and 10% of tin, determined by X-ray diffraction semiquantitative analysis, what is corroborated by the presence of alteration products of lead (hydrocerussite) and no presence of alteration products of tin, such as cassiterite or romarchite [25,26]. In this form, the depth for 90% contribution of the measure intensity of the alloy layer would be, according with Table 1, approximately of $x = 0.155$ μm at $\theta = 1°$ and $x = 0.671$ μm at $\theta = 5°$.

3.3.2. *Lead seals*

Lead seals from the Seville City Hall collection had suffered significant alterations, losing not only the external figurative prominence, but also some of them were corroded in bulk through a progressive peeling of the corrosion layer. This represents an alteration in the entire sample, showing superficial powdery "white rust", composed of lead, hydrocerussite and cerussite, whose study was carried out by X-ray diffraction with Göbel mirrors.

Lead seals were stored in a hole made in cardboard and we suggested that the superficial alteration might be due to the storage in enclosures in the museum for a long period [28]. To check this suggestion, the following experiment was performed. In a beaker containing water and CO_2 was introduced a rectangular piece of lead whose length was longer than the water. On this piece of exposed lead, a piece of cardboard was put and the beaker was covered. After 3 months, the stored lead layer was covered with a white powder that the X-ray diffraction shows as hydrocerussite and cerussite. The same experiment was repeated without using cardboard and in this case, white powders did not appear after 3 months of treatment.

The cellulose hydrolysis has provided carboxylic acid (mainly acetic acid) that dissolves the PbO of the surface forming lead carbonate after reaction with CO_2 and humidity of the atmosphere.

4. Conclusions

The data obtained in this work show that X-ray diffraction with Göbel mirrors is a good method for the characterization of the irregular surfaces from artefacts belonging to cultural heritage because allow non-destructive study (without sampling) of them. The combination of Göbel mirrors attachment and measure at fixed low incidence angles allow to obtain information about the depth profile of sample, being a very important application in the artworks.

Bronze in the rivet from Pardon Portico of Mosque-Cathedral of Cordoba was detected using X-rays diffraction with Göbel mirrors, and on the surface of the bronze, wedellite, atacamite and gypsum were detected as alteration products. Goethite, lepidocrocite and FeO(OH) appeared on an iron nail proceeding of this Portico too.

The study demonstrated that metallic point of a Roman arrow was composed of iron. On the surface, it was found calcite, quartz and vesuvianite. The Roman button was covered with a thick crust, formed by calcite and quartz. The surface of these materials is affected by environmental and soil in which they were buried.

Lead from seals and organ pipes were altered to hydrocerussite by the method used for storing these materials in the museums and in the churches where they were.

Acknowledgment

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