

Physicochemical approaches to gold and silver work

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1. Introduction

Expressions of social (political and economic) and religious power, prestigious objects are manufactured in specific materials. Among them metals, in particular gold and silver, because they have properties that result in perceived specific visual aspects (Todd & Norman 2018) that can be enriched by illumination (Matsumoto et al 2016). Transmission, refraction, absorption, scattering and reflection of light in gold and silver surfaces modify the appearance of the shapes. Perceived as both materials and colours (Okazawa et al. 2011), precious metals have a lustrous appearance (Fleming 2014) and are thus among the most appropriate for the production of significant objects.

More than their mechanical properties (ductility, malleability, strength, etc.) that make precious metals and particularly gold to be easily shaped by plastic deformation, their major asset is based on their optical properties, because metals have high reflectivity. In the past, silver was commonly alloyed with copper, which results in a whitish shining material (for example in Sumerian the same word is employed to designate silver, white and bright, Warburton 2014), as silver is whitish over almost all the light spectrum (Roberts & Clarke 1979). Gold, silver and copper were alloyed to produce gold alloys with colours that go from yellow to red, green and white, depending on the amounts of alloying elements (Rapson 1990), and a reflectivity that increases with growing silver amounts (Shiraishi & Tilley 2014). It is also possible to employ thin gold foils to obtain polychrome effects, because the reflectivity of gold at the high extreme of the light spectrum makes it look yellow, whilst a gold leaf of 100 nm thick transmits a bluish-green light (Choudhury 2014, Saeger & Rodies 1977).

It is consequently possible to obtain with gold and silver alloys multiple colour effects in jewellery and ware even when these metals are employed alone (with no other materials, but with possible addition of metallic elements such as wires and granules), or when they are applied as thin layers on a substrate (plating, gilding, silvering, etc.). Precious metals can also be combined with more or less precious and colourful materials, such as gems and enamels, providing to the final object colour, lightness, volume, transparency, etc. Therefore, the use by the goldsmith and the silversmith of a wide-range of materials and techniques finely enhances the object by changing its visual perception. The artisan can also entrust it with a “role” or a “value” when certain colours are used (“colour-code”), when certain elements are added, or when certain motifs are applied by chasing, engraving, punching, etc. at the surface of a precise shape. Coins and liturgical cups are common examples of the roles assumed by objects with precise shapes, made from precious metals.

The technologies and materials employed in an object construction depend on the artisan’s skill, on the workshop traditions, and on chronological and territorial knowledge diffusion at a specific time, as well as on access to materials (Guerra 2008). There is indeed great reliance on access to sources of raw materials, and thus to opened trade routes and to the savoir-faire and workshop practices that voyaged along those routes and that had over time influenced creation. Nonetheless, the technologies and materials employed in a certain period are also related to fashion (indirectly connected to exchange). By the end of the 19th century, archaeological jewellery was produced employing the finest techniques of the art of working gold (Guerra 2006, 2007). In the early 20th century, Art Nouveau creators, who reinvented antique jewellery, produced colourful items constructed with many materials that were combined with gold and silver (Tissot et al. 2018), sometimes enhanced by patination (Tissot et al. 2016a).

Goldwork and silverwork enclose major information on a society, because their structure and composition contain information on their manufacture, use, disclaim and degradation. This information can be acquired by the detailed study of the many aspects of the objects, which includes their description (dimension, morphology, iconography, typology, etc.) and the data collected by employing physicochemical methods. With an appropriate analytical protocol, it is possible to finely describe the construction details of an object (including identification of the technologies and tools used by the goldsmith and the silversmith). It is also possible to identify the materials employed, and occasionally to situate the origin of the raw materials and of the items production, and follow their trade routes (Guerra & Calligaro 2003, Guerra 2004a, 2014a,b, Guerra & Tissot 2016, Tissot et al. 2015). In the sections below are outlined major achievements in the study of goldwork and silverwork, based on the many physicochemical methods that are offered today. Because it has recently been observed an increase of the atmospheric corrosion of precious metals, a short section on this question was also included above.

2. Considerations on analytical protocols

A large number of physicochemical techniques, often developed in other areas of science and for other research goals, have been applied to the study of cultural heritage. Based on these techniques, efficient analytical protocols can be established after a good definition of the query and after considering the specificities of the objects under study. In our case, among the specificities of gold and silver objects are those that exclude sampling: their small size, their scarcity, their value, and their mounting by joining multiple parts. Consequently, and contrary to many other cases, the study of items made from precious metals is widely based on exam and non-destructive analysis.

The observation of the morphology and structure of an item, at several depths and scales, by using different lights and radiations, makes available information on quite a few technological steps related to mounting, decorating and finishing (Guerra 2008, 2012, Tissot et al 2018, Ashkenazi 2017, Mongiatti et al. 2011). It is important to register detailed macrophotography images of those technological steps. Despite the difficulties caused by the high reflectivity of precious metals (MacDonald et al. 2014), attempts have been made to replace 2D by 3D imaging (Regert & Guerra 2015, Esquès et al. 2008).

The accurate description of an object's construction is one of the main phases of study, because understanding an object is essential to establish an analytical protocol. In fact, in a general way, the analytical techniques can be divided into three types – elemental, isotopic and structural – each of them providing specific information on the object. For example, if elemental analysis can be applied in evidencing wide-ranging questions, isotopic analysis typically gives information on the origin of the metals and on the circulation of metals and items. Because requiring a sample, isotopic analysis is occasionally applied to the analysis of silver alloys (Gale and Z. A. Stos-Gale 1981, Ponting et al 2003, Stos-Gale & Gale 2009), but barely to the analysis of gold alloys (Standish et al. 2013).

Therefore, the development of an analytical protocol has to consider the choice of the most appropriate physicochemical techniques to solve one question, taking into account the object manufacture, and after considering the analytical limitations. After selection of the type of information that has to be searched – elemental, isotopic or structural – it is necessary to choose the most appropriate techniques that can provide this information, considering the nature of the query, the type of object under study, and the technical characteristics essential to achieve the objective. The technical performance parameters that play an important role when studying gold and silver work are typically: spatial resolution, depth of analysis, limits of detection, and portability.

Spatial resolution is a quite important parameter when analysing small objects consisting on several joined small parts. To give an example, Figure 1 shows a detail of an earring decorated with several elements in gold under the stereomicroscope and under the scanning electron microscope (SEM) combined with energy dispersive spectroscopy (EDS). The EDS analysis of the earring provides the elemental composition of the base-sheets and of the added parts (in this case granules), as well as the composition of the filler used to obtain the joints (Table 1). The filler metal, of lower melting point than the parts to be soldered (Maryon 1949, Humpston & Jacobson 2010), contains, in the case of the earring, higher Ag and Cu contents than the base-sheets and the granules. The use of particle induced X-Ray emission (PIXE) with an incident micro beam of protons (Guerra 2007, Ager et al 2013, Šimić 2017) or of X-ray fluorescence spectrometry (XRF) with polycapillary focusing optics (Scrivano et al. 2017) would have also been a possible analytical solution in this case. EDS, PIXE and μ XRF can be used to construct elemental maps, which are very useful in several situations, for example when estimating the composition of solders employed to join the object's parts (Lemasson et al 2015, Troalen et al. 2014). However, SEM-EDS has the unique advantage of providing together with elemental analysis high-resolution imaging of the surfaces, which is essential when studying objects made from gold and silver. By using an equipment with a field emission gun (FEG), the images obtained can be improved for particular studies (Tissot et al. 2015).

Depth of analysis has to be considered when either the surface or the bulk offer incomplete information on the object, for example when the surface was naturally or artificially modified. In this case, it is necessary to obtain information from both the first layers and the bulk by using specific techniques, or by combining techniques of surface and bulk analysis based on their effective penetration depths (Demortier & Ruvalcaba-Sil 2005, Demortier 2009, Martínón-Torres et al. 2012, Fourdrin 2016). For example, in the case of gold alloys, the effective penetration depth of EDS is inferior to 1 μ m, and that of XRF is between 8 and 60 μ m (Troalen et al. 2014). In addition to elemental analysis, structural analysis (for example XRD, X-ray diffraction) can be employed in this case to identify the compounds present at the object surface and SEM to provide their morphology. These compounds give information either on the chemical surface treatments artificially applied, for example by patination (La Niece & Craddock 1993), or on the natural corrosion products that grow on the surfaces (Gusmano et al. 2004, Reiff et al 2001, Caridia et al 2013, Tissot et al 2015).

When searching for the origin and trade routes of silver and gold, the analytical techniques selected have to be either isotopic or elemental. In general, structural analysis provides no information on this point. Elemental analysis has to be carried out with good detection limits, because trace elements that may link the object to a source of metal have to be determined. In this case, PIXE can be used for the study of silverwork (Guerra & Abollivier 2016, Rodrigues et al. 2012), but more hardly of goldwork (Nixon et al. 2011, Guerra 2004b). A powerful technique in the area of provenancing, with high spatial resolution and providing elemental maps, is XRF with synchrotron radiation (SR), either with energy-dispersive (Radtke et al. 2013) or with wavelength-dispersive (Tissot et al. 2015, Radtke et al 2016) spectroscopy. Another technique frequently used for provenancing that combines low detection limits with high spatial resolution, is LA-ICP-MS (Watling et al. 1994, Gondonneau & Guerra 1999, Guerra et al. 1999, Guerra 2005a). With the disadvantage of collecting small samples by laser ablation (Wagner et al 2017) and thus not appropriate when elemental maps are necessary or when the objects are made by joining multiple small parts, it has the advantage of when combined with a Multi-Collector (LA-MC-ICP-MS) to also provide the isotopic ratios (Standish et al 2013, Ponting et al 2003). The small sampling might be a gain when sampling and analysis are carried out in separated phases (Glaus et al 2012).

At last, portability is widely searched when analysing silver and gold items. On one hand, the institutions where the objects are conserved or exhibited increasingly impose not to move them for analysis, and on another hand, as above-mentioned, the objects can barely be sampled. Therefore, the use of portable equipment has been growing for the study of precious metals, even if only a few techniques are available in portable configuration. Equipment that can easily be moved for in-situ analysis are mobile and handheld XRF, whose application in the study of gold and silver objects has been widely increasing (Guerra & Rehren 2009, Adrimi-Sismani et al. 2009, Melcher et al. 2009, Hauptmann & Klein 2016, Guerra et al. 2017). Portable equipment has, however, lower levels of performance than large facilities hosted in laboratories. It would have been impossible to carry out the study of the earring shown in Figure 1 using handheld XRF. A spot beam of several millimetres (typically 3 mm) would have only provided an average composition of all the alloys employed in the earring construction, instead of the elemental composition of each of the joined parts and the solders.

3. Searching for technologies

Thermomechanical processes transform gold and silver into objects. The creative process of making silverwork and goldwork includes the use of sophisticated making techniques of shaping, decorating, assembling and finishing. These techniques that require strong skill, follow alloying and melting, used to obtain the base alloys to be worked.

The initial question regards whether the object is made by shaping one piece and how that piece was shaped. Otherwise, it has to be defined how the several pieces that constitute the object were shaped (casting, hammering, rolling, etc.) and how they were assembled (mechanical or thermal joining). Composite objects that are more complex require more consideration, because their shaping and mounting may employ several techniques. Much of the information on the creative process of silverwork and goldwork can be searched by using techniques of exam. Figure 2 shows the mechanical mounting of a comb in gold, horn and enamel, made by René Lalique in 1901-1902, under a stereomicroscope (white light) and using a portable digital X-ray radiography system. The head of the two gold screws are visible on the reverse of the comb, but the entire screws are only visible under X-rays. In spite of the high attenuation of X-rays in gold and silver alloys, X-radiography provides information on the invisible parts of the objects (Guerra et al. 2009, Perea et al 2013, Mongiatti et al. 2010) and on their structure, which, in addition to manufacturing details, may reveal previous restorations and corrosion processes (Lang & Middleton 2005, Morigi & Casali 2018, Barham 2007).

When the mounting technology is identified, observation under the stereomicroscope is frequently sufficient to verify whether the suggested techniques are employed. In spite of their many types and heights (3 to 25 cm), the traditional anthropomorphic and zoomorphic metallic figurines (Guerra et al. 2017) produced for ritual offerings by the Incas are frequently made using standardised technologies, and are thus a good example of this situation. These figurines, made of gold, silver or spondylus shell, were used in the Capacocha ceremony (Benson 2001), because several of them, often with their miniature garments in textile, feather, etc., were found with the sacrificed children in mountaintop shrines (Cerutti 2010). Traditional figurines are hollow, made by joining several hammered parts (Shuler-Schömig 1981, Rowe 1996, La Niece & Meeks 2000). A female hollow figurine is regularly made by soldering five gold or silver sheets, as shown in Figure 3. Under the stereomicroscope, the seams corresponding to the expected assemblage by hard soldering can be searched. It is also possible to define under the stereomicroscope how the anatomical motifs were obtained (Figure 4), usually by using in repoussé and chasing.

The resolution limitations and the highly reflective gold and silver surfaces under white light make, however, difficult to observe very small details under a stereomicroscope. It is in certain

cases more convenient to use SEM, because with an incident electron beam it is possible to obtain high-resolution images and, for metals, to overcome the problem of surface reflectivity. As already mentioned, another advantage of SEM is that it can be combined with EDS to provide elemental information with high spatial resolution. To understand the soldering technology employed in the construction of the ritual Incan figurines, it is necessary to observe and analyse the joints, as shown in Figure 5 for a male gold figurine studied using SEM-EDS. In addition to the surface morphology, the composition of the parts to be soldered and the solders could be determined, showing that the solder alloys contain high Cu contents to lower the melting point.

4. Silver and gold as colours

Silver whitish and gold yellowish, reddish, greenish and whitish alloys can be combined to produce polychrome objects. From the analytical point of view, the search for the use of metallic polychrome effects is one of the easiest questions to be solved, when are excluded objects with surface treatments. In fact, it is sufficient to determine the elemental composition of the alloys employed in the production of the metallic parts, or the nature of the applied compounds in the case of, for example, niello inlays (Oddy et al 1983).

The combination of silver whitish and gold yellowish alloys produce bicolour objects, a very widespread practice for example in the Andean area, such as in the Vicús' workshops. Many bicolour metallic objects are attributed to that pre-Columbian culture that developed around 400 B.C. in the Piura area, north of Peru, in particular remarkable nose rings of several types (Vetter & Guerra 2018). The bicolour part of one of those nose rings is shown in Figure 6, with a detail of the mounting by hard-soldering the whitish and the yellowish parts. The gold alloys employed are quite common, containing about 10 wt% Ag. The only analytical difficulty in this case is the analysis of the smallest parts, which means the wires and joints. They are, however, in this case large enough to be analysed in-situ, using a mobile XRF equipment with a spot beam of 1mm.

The Andean area also gives one of the major examples of the skilful work of combining the alloying metals to obtain gold alloys of particular colours and reflectivity. The symbolic Incan figurines above mentioned (Figure 3) are made using standardised technologies and by employing artificial alloys that accomplish precise requirements (Guerra et al. 2017). Their analytical study was carried out in-situ, in Peruvian and European institutions (Guerra & Núñez-Regueiro 2017), because their size allows employing handheld XRF with a 3 mm spot beam. It was shown that the alloys employed in the manufacture of the silver figurines are of very high quality (the copper content in the alloy is often below 1 wt%) and those employed in the production of the gold ones contain low copper contents and high silver amounts. Silver frequently reaches 30-50 wt% in the gold alloys, which keeps the yellow colour of gold, but significantly increases the reflectivity of the surface. The searched effect could be an interpretation based on visual perception, connecting the object and the shining sun, as there is a relation between the sun and gold (Berthelot 1986) and between the sun and shiny objects (Sauders 1998).

The skilful combination of gold with the alloying metals to obtain sophisticated polychrome effects can be found in Ancient Egypt, where the art of the goldsmith includes the combination of alloys of different colours and shades to produce composite objects. One example comes from tomb 72 excavated in Cemetery A at Harageh (Engelbach and Gunn 1923), an intact burial of a young girl, dating to the mid-late 12th Dynasty (c. 1875-1795 B.C.), where were found five fish pendant amulets (Grajetzki 2014) today in the collection of the National Museums Scotland. The analysis using XRF, with a spot beam of about 1 mm, of the body and tail of one of the fishes (Acc. n. A1914.1081) has shown that it was produced with gold alloys of different

colours. A yellowish alloy (containing 17 wt% Ag) was used for the body, and a whitish one (containing 56 wt% Ag) was used for the tail (Troalen et al. 2015).

The use of gold alloys only to produce jewellery with different colours is a traditional practice in the Egyptian workshops, well represented by the more or less elaborate beads in the shape of cowrie shells, which in the Middle Kingdom (*c.* 2050-1710 B.C.) were regularly strung in girdles found in female burials (Grajetzki 2014). Beads of this type were also found in burials from other periods (Troalen et al. 2014). The simplest ones are those dated to the First Intermediate Period (*c.* 2181-2055 B.C.). Pierced at each end, they were made by embossing gold sheets, where the shell's aperture was represented by a groove. In the collection of the Petrie Museum of Egyptian Archaeology (University College London) are one string of twelve gold cowrie shell beads (UC18092) enhanced with small whitish ring beads (Figure 7), found in the undisturbed tomb 7923 at Qau (Brunton 1927, p. 45, pl. 46), and a group of four specimens (UC42397). Using a portable XRF spectrometer with a spot beam of 1 mm (the same used in Adrimi-Sismani et al. 2009), the cowrie shell beads could be analysed in-situ. The small ring beads over and on each side of the cowrie shell beads, were also analysed, but data obtained represent average compositions.

Data plotted in the diagram of Figure 8 for the two groups of cowrie shell beads show that despite the use of gold alloys only, two different polychrome effects were searched. String UC18092 is a metallic bicolour item, as it contains elements in two colours of gold: the yellow-green cowrie shell beads are strung with whitish ring beads. The four cowrie shell beads UC42397 were made to produce another colour effect, a kind of colour gradient. In fact, their alloys have similar Ag/Au ratios, but increasing Cu contents, which produces gold alloys in shades of yellow, yellowish and reddish.

5. Tracing trade routes and marking the dates

The movements of people have contributed to the spread and transmission of ideas, beliefs, savoir-faire, technologies, and of goods and materials. Extended distance pathways resulted in trade routes and exchange networks that much influenced past economy, but which are challenging to reconstruct, in particular when documentary sources and historical evidence are missing. Attempts to trace trade routes are consequently carried out based on finds of objects.

Among the goods that travelled along the pathways, were rare materials and items that needed specific skill for their manufacture. Consequently, prestigious objects made from gold and silver contain information that should contribute to the definition of networks, when the exploited sources of metals or the workshops that produced the objects can be localised, or when a change of supply can be identified. Nonetheless, it is difficult to relate an object to a metal or to a workshop. Gold and silver processing is thermomechanical, resulting in loss of information between the first and the last steps of production. Indeed, gold and silver objects are usually made from alloys produced by mixing different metals, in general previously refined. These processes cause a loss of information on the original metals. Besides the alloy production, other actions contribute to the loss of information on the initial metals. After use, the object is disclaimed and usually reused (gold and silver are too expensive to be thrown away), which means melted (possibly refined) to produce other objects. During periods of weak economy, precious metals are constantly mixed and recycled.

It is, however, possible for certain items – in particular coinages, because their issue is controlled by an authority and information is often cited in documentary sources – and for specific periods, situations, and areas of influence, to obtain through the analysis of goldwork and silverwork evidence on exchange networks. The information obtained very much depends on the analytical technique(s) that is(are) used. It is of course very difficult to search for hints

on the metal provenance when the object cannot be moved for analysis, or when it cannot be sampled. As referred above, provenancing involves the use of either isotopic analysis or elemental analysis with good detection limits.

Even though, in the particular case of gold, it is possible using exam to determine whether its origin is alluvial. In fact, the presence of PGE inclusions (naturally occurring platinum group elements) at the object's surface is an indicator of this type of gold deposits. However, their absence simply indicates the use of a different gold, which can also be alluvial, but from a geological region deprived of PGE deposits. It is interesting to refer that the few published work on the analysis of Egyptian gold jewellery often refers the presence of variable quantities of PGE inclusions in the items, indicating the exploitation of alluvial sources (Troalen et al. 2014, Troalen & Guerra 2016, Guerra & Pagès 2018). Figure 9 shows one PGE inclusion at the surface of a hollow Egyptian penannular earring made from an alloy containing high Ag contents. Almost invisible under the stereomicroscope using grazing white light, the inclusion clearly appears under the SEM. The EDS analysis has shown that it is, as expected, a rutheniridosmine.

The use of techniques that determine a few minor and trace elements might not provide information on the localisation of the sources of metals, but might allow identifying a change of supplies that occurs at a certain period, and provide a *terminus post quem* for certain productions. It is representative of this situation the Mapuche female ritual and daily use silver jewellery. Because of migration and of local political problems, the use codes and the technologies employed in the jewellery manufacture were regrettably nearly lost.

Said to be connected to the women's social status, the earrings, brooches, finger rings, etc. in silver significantly flourished in the 19th century in Chile and Argentina, in particular in Araucania and Patagonia. The ritual items, among them earring and the brooches (tupos), may reach very large dimensions (Bennewitz 1992, 1997). Like the tupos, the earrings have served as support for codified messages, and the ritual ones could have been transmitted through several generations. The daily use earrings were presumably constructed in different phases, related to the several life stages of women. Symbolic motifs and elements in silver were added to the earrings to represent life events like puberty, pregnancy, etc.

The exam using optical microscopy, SEM, and X-radiography of ritual and daily use earrings of different types revealed that the first ones were made by skilled silversmiths contrary to many of the second ones (Guerra & Nunez-Regueiro 2012, Nunez-Regueiro & Guerra 2016). μ PIXE analysis of the different parts of the earrings (Guerra & Nunez-Regueiro 2012) has shown that the silver alloys are of very variable quality, with silver contents within the range of 60-90 wt%. Nevertheless, the most interesting result is related to the alloying elements. In addition to Cu, the alloys of several pieces also contained Zn and Ni. The amounts of those three elements in the silver alloys used in the production of the earrings are shown in Figure 10, together with those found for a few ceremonial tupos and daily use finger rings analysed using the same protocol.

The intensification during the 18th century of the commercial relations in Araucania and Patagonia, resulted in the use of silver coins to produce silver jewellery either (as shown in Figure 11) by directly joining them (mechanically or thermally) to base plates and other supports (Bennewitz 1992, 1997), or by reuse, which includes reshape and melting as described and photographed by Claude Joseph (Joseph 1928, 1930). From 1871 onwards in the Chilean mints and from 1896 onwards in the Argentinean mints, a new whitish alloy, the cupronickel, replaced silver (Auer 2001). The recycling of coins and jewellery certainly integrated the new alloy, justifying the presence of these elements in the composition of the jewellery produced after introduction of the cupronickel in the area. The presence of Zn and Ni in the alloys is thus a chronological indicator, because these elements point out a *terminus post quem* for the

jewellery production. Interestingly, the objects dedicated to ceremonies are those that, in general, do not contain Zn and Ni, which could indicate a former production and thus reinforcing the suggestion of transmission through several generations.

Several silver supplies could have been used for the manufacture of the (suggested) oldest objects, but constant recycling of items to produce new jewellery makes more difficult to search for the origin of the silver. Despite the determination by PIXE of several trace elements in the silver alloys, such as Au, As, Sn and Sb, which can be used for silver fingerprinting, it is difficult to relate the Mapuche silver to South American sources. Silver from one of the main Andean sources, the mines at Potosi, in Bolivia, is characterised by high Au and low In contents (Guerra 2000, 2004a). If high Au contents are, in the case of silver alloys, easy to determine using PIXE, this technique has inadequate detection limits for the determination of low In contents. It should be emphasized, however, that gold and silver from several sources situated in the American continent could be characterized using precise trace elements, determined using nuclear reactions, such as Pt in Colombian gold, Pd in Brazilian gold, In in Bolivian silver, and Sn and Sb in Mexican silver (Guerra 2000, 2004a).

Fingerprinting gold and silver could be successfully achieved in other areas of influence, even in the case of complex societies, during difficult periods, and when long-distance trade networks were used. By using ICP-MS, SR based techniques, and nuclear reactions, it was possible to address questions related to, for example, the Islamic expansion (Gondonneau & Guerra 1999, 2002), the Byzantine Empire (Meyers 1992, 2003), the Roman Empire (Ponting et al 2003), the Asiatic nomadic confederations (Radtke et al. 2013), etc. Based on the analysis of appropriate items it is sometimes even possible to search for the evolution of the gold and silver supplies used in the manufacture of coins and jewellery during long periods (Guerra 2005a,b, Guerra et al. 2007)

6. Attempting to preserve

Because atmospheric corrosion threatens several collections, the aim of this section is to offer a brief introduction to the challenging analytical questions associated to the study of the corrosion mechanisms of objects made from alloys of precious metals. In indoor conditions, gold alloys and silver alloys corrode mainly in the presence of sulphur (sulphidation), through the formation of sulphide salts (Faraldi et al 2014, Ingo et al. 2015, Guerra & Tissot 2016). The grown corrosion products result in multihued spots and stains at the surface of the tarnished objects, modifying their aspect, as shown in Figure 12, and thus their perception, leading to their restoration.

When not properly carried out, restoration interventions are operations that might have serious consequences in the objects preservation as well as on the information related to their production, like tool marks, that might also be removed. Not to cause damage, neither to the object nor to the information contained in it, only the corrosion layer should be removed. Its efficient removal depends on the understanding of the corrosion processes, which requires the previous full description of the involved corrosion mechanisms. To achieve this goal, both the corrosion layer and the substrate have to be characterised and the environmental conditions described.

As stated, jewellery, ware, coins and other objects are made not from pure metals but from alloys. The role of the alloying elements in the corrosion processes has to be searched, at different stages of corrosion, because the corrosion mechanisms of an alloy and of the pure alloying elements are not the same. Using XRD, ultraviolet visible (UV-vis) spectrophotometry, contact angle goniometry, ellipsometry and SEM-EDS, recent studies on the corrosion mechanisms of pure Cu, pure Ag, and sterling silver (an alloy of 7.5 wt% Cu and

92.5 wt% Ag, widely used in the production of silverwork), submitted to artificial sulphidation at the same environmental conditions, demonstrated that the corroded layers grow in different structures. Contrary to those of pure Ag and Cu (Tissot et al. 2017), the corroded layers of sterling silver grow in layer-by-layer structures (Tissot et al. 2016b).

The colours attained at different stages of corrosion by the corroded surfaces of sterling silver are related not only to the thickness of the corrosion layer, but also to the formed layer-by-layer corrosion structure where are contained corrosion products which composition is variable over time. In fact, at the early stages of corrosion of sterling silver, Cu compounds prevail over the Ag compounds, but the latter become dominant for longer periods (Tissot et al. 2016b, 2017). There are no publications focusing on the use of the same type of described protocol to determine the corrosion mechanisms of gold alloys submitted to sulphidation, but as these alloys consist of a mixture of silver, copper and gold, comparable corrosion processes are expected.

The layer-by-layer corrosion mechanism observed for sulphidated silver-copper alloys makes the removal of the corrosion layer grown at the surface of objects made from precious metals difficult to carry out without the analytical identification of the corrosion products whose composition, as referred, depend on the stage of corrosion. Another difficulty comes from the corrosion layer thicknesses that for sterling silver and alloying elements only reach a few hundreds of nm (Tissot et al. 2017). Despite the availability of successful removal techniques based on mechanical, chemical, electrochemical, and laser ablation cleaning methods (Siano & Salimbeni 2010, Palomar et al. 2016a, 2016b, Novakovic et al 2013, Hacke et al 2003), the thinness of the corrosion layers, grown at the surface of precious metals submitted to sulphidation, limits their effectiveness. Difficulties encountered by several researchers when using cleaning techniques (Palomar et al. 2016a, 2016b, Lee et al 2003) may be explained by the thinness of the corrosion layers.

Therefore, cleaning operations are risky when both the composition of the corrosion products and the thickness of the corroded layer are unknown. The removal of the corrosion layer is far more difficult to achieve when the alloys are patinated, a decoration technique often employed to create polychrome effects in jewellery and ware (Rudoe 1993, Tissot et al 2018) that consist of a controlled corrosion process in specific areas to form the motif. Corroded patinated silver surfaces become dull and present spots and stains in shades of grey, caused by a two-phase corrosion mechanism that consists on the dissolution of the artificial patina followed by the natural formation of Ag and Cu sulphur compounds (Tissot et al 2016a). The compounds that constitute the original patina, artificially grown, and the corroded layer, naturally grown, are chemically similar and can hardly be distinguished before cleaning.

7. Conclusion

Used in the production of prestigious objects, precious metals are perceived as both materials and colours. Their skilful combination can either entrust the object with a role or a value, or enhance it with polychrome effects. From the elaboration of the alloy until the finished object, the production of jewellery and ware in gold and in silver includes several steps that require specific expertise. Information on those different steps can be acquired using physicochemical methods, which are of exam or analysis. According to the query, the latter are elemental, isotopic, or structural. In some cases, the objects – as well as the raw materials – circulated in exchange networks, sometimes to be used far from the workshops where they were produced. Information on their circulation, use, disclaim and degradation can also be searched using specific analytical protocols.

If, in general, the techniques employed in shaping, decorating, assembling and finishing an object can be detected with rather common physicochemical methods, provenancing gold and silver were only successfully achieved for some particular cases. In fact, it remains difficult to carry out provenancing, because particular physicochemical techniques are necessary, and because gold and silver are reused by melting. Re-melting operations involve the mixing of metals and alloys from different origins with consequent loss of information.

In spite of the large number of physicochemical methods nowadays available for the construction of analytical protocols, the analysis of objects in gold and in silver have certain constraints. In addition to non-destructivity, which makes exam a major part of those protocols, when studying gold and silver work, spatial resolution, depth of analysis and limits of detection are performance parameters that play an important role. In addition, in-situ analysis using portable equipment has been widely increasing, because the objects do not have to be moved for analysis. Many questions on gold and silver work were solved using in-situ analysis; however, the information obtained on the objects is, in general, more limited and not related to queries on provenancing.

Even if provenancing remains a difficult analytical question, the atmospheric corrosion mechanisms of gold and silver alloys provides presently the most challenging analytical queries. Made from alloys, the objects are submitted to corrosion processes where the alloying elements play important roles. The corrosion mechanisms of silver alloys (Ag-Cu) were recently studied showing that the corrosion layer, of only some hundreds of nm thickness, contains compounds that change with time. The corrosion mechanisms of ternary gold alloys, certainly of the same type, are today not yet fully identified.

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Figures and Table captions

Figure 1 – Detail of an earring decorated with granulation under the stereomicroscope and under the SEM (FEI Philips XL 30 CP operated at 20 kV). The image obtained with the SE detector shows three soldered granules to the base-sheet.

Figure 2 – Comb “Bumblebees and umbels” in gold, horn and enamel, created by René Lalique in 1901-1902 (Calouste Gulbenkian Museum, Acc. n. 1160, Gomes Ferreira 1997). (a) The head of the gold screws used in the mounting; and (b) the X-radiography showing the mounting system with screws (Smart 225 Andrex with Fuji and Dürr storage image plates and a Dürr digitizer; operating conditions: voltage tension 130 kV with 3 mA current, 90 s acquisition time, and 93 cm focus to detector distance).

Figure 3 – Details under the stereomicroscope of the mounting of an hollow female figurine produced in Incan times for ritual offerings by joining one element that reproduces the body, legs and head to the other elements that represent the hair, the crotch and the feet.

Figure 4 – Under the stereomicroscope it can be seen for the female figurine produced in Incan times for ritual offerings the solder in the joints and the tool marks that show the use of chasing to represent the hair.

Figure 5 – Detail under the stereomicroscope and the SEM of one Incan male figurine in gold. The rectangular in section wire bent to form the ear was hard soldered to the head. EDS data show that the solder contains high Cu contents: (1) head sheet 1 wt% Cu, 28 wt% Ag, 71 wt% Au; (2) solder 6 wt% Cu, 14 wt% Ag, 80 wt% Au; (3) solder 5 wt% Cu, 20 wt% Ag, 75 wt% Au; (4) ear wire 2 wt% Cu, 23 wt% Ag, 75 wt% Au.

Figure 6 – Bicolour area of an unprovenanced nose ring attributed to the Vicús culture with a detail of the region where the whitish and yellowish wires are assembled using hard-soldering.

Figure 7 – One of the cowrie shell shaped beads threaded with small gold ring beads from string UC18092 found in undisturbed tomb 7923 at Qau.

Figure 8 – Ternary diagram representing the Au, Ag and Cu contents (in wt%) obtained by XRF for the gold cowrie shell shaped beads and ring beads UC18092 and UC42397.

Figure 9 – PGE inclusion at the surface of an hollow Egyptian penannular earring (Acc. n. AF2044, the Louvre Museum) under the stereomicroscope and under the SEM. EDS analysis shows that the base sheet contains high silver contents (55 wt% Au, 42 wt% Ag and 3 wt% Cu) and that the PGE inclusion is a rutheniridosmine (24 wt% Ru, 32 wt% Os and 44 wt% Rh).

Figure 10 – Diagram representing the Cu, Zn and Ni contents (in wt%) in the silver alloys obtained by μ PIXE for the ritual and daily use silver Mapuche feminine jewellery.

Figure 11 – Mapuche finger ring consisting of a silver strip to which was soldered one 10 cents Argentinean silver coin, struck by the Buenos Aires mint in 1881-1883.

Figure 12 – Evolution of the corroded surface of a gold Iron Age torc (Acc. n. Au1139, National Museum of Archaeology, Lisbon, Portugal) between 2009 (on the left) and 2012 (on the right).

Table 1 – EDS data obtained for each region of interest in the earring decorated with granulation of Figure 1 (FEI Philips XL 30 CP with an integrated Link Isis 300 EDS system operated at 20 kV; analysis in spot mode with 300 s acquisition time; calculation with ZAF matrix correction model).