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Study of a 9th century Silver Earrings Set from Mikulčice: Corrosion,
Conservation and Maintenance

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Summary

The presented study deal with the degradation processes of the silver objects, buried for a long time in human graves and with their appropriate methods of conservation and restoration after excavation during archaeological research. It was used for this study a set of earrings from the 9th century A.D. found in Mikulčice, in the southeast of Czech Republic. To understand the mechanisms and process of corrosion and the manufacture and decoration techniques of the earrings was performed: structural study by photo-documentation in the optic stereo-microscope and by radiography, and microstructure and elemental analysis with scanning electron microscopy with energy dispersive X-ray (SEM-EDS). It was also made detailed metallographic analysis of one pure silver earring fragment to study manufacture technique and the buried silver corrosion process.

Related to silver earrings set maintenance conditions was study the atmospheric corrosion of silver in museum environments. For that, it was measure the corrosion rate and film thickness by galvanostatic reduction technique, of 15 silver samples placed in exhibition and storage rooms from the National Museum and Museum of Decorative Arts of Prague.

O presente estudo relaciona os processos de degradação dos objectos de prata, enterrados por períodos longos dentro de sepulturas e os seus métodos apropriados de conservação e restauro após a escavação durante uma investigação arqueológica. Para este estudo foi utilizado um conjunto de brincos do século IX d.C encontrados em Mikulčice, no sudeste da Republica Checa. Para entender os mecanismos e processos de corrosão assim como de manufactura e técnicas de decoração foi realizado: estudos estruturais por documentação fotográfica no microscópio óptico e por radiografia, e análises de microestrutura e elementares no microscópio electrónico de varrimento equipado com detector de energia dispersiva de raio-X (SEM-EDS). Foi também realizado uma análise metalográfica detalhada de um fragmento de brinco de prata puro para estudar as técnicas de manufactura e os processos de corrosão da prata arqueológica.

Relacionado com as condições de manutenção dos brincos de prata foi estudado a corrosão atmosférica em contexto museológico. Para tal, foi medido a taxa de corrosão e espessura de filme pela técnica de redução galvanostática, de 15 amostras de prata pura colocadas em salas de exibições e de reserva do Museu Nacional e do Museu de Artes Decorativas de Praga.

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Introduction

The presented study deal with the degradation processes of the silver objects, buried for a long time in human graves and with their appropriate methods of conservation and restoration after excavation during archaeological research. For elaboration of this study was used a set of silver earrings from the 9th century A.D., from the period known as Great Moravia Empire, found in Mikulčice, in the southeast of Czech Republic.

The structure of the project is divided in three parts related to the archaeological silver earring set: the first part is the study of the mechanisms and process of corrosion of silver and the second part is the study of conservation methods for archaeological silver.

The study of the corrosion process mechanism was made mainly in the Institute of Chemical Technology – Faculty of Chemical Technology, Department of Metals and Corrosion Engineering. This part consisted from solving two independent problems: the first is related to the corrosion damage of archaeological silver objects and the second to the atmospheric corrosion of silver.

For solution of the first problem, mainly scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDS) was used to study the extent of silver earrings corrosion damage. The SEM-EDS analysis covered photo documentation, corrosion products identification, and semi-quantitative analysis of the metallic core. On the bases of these results was attempt to discovering of manufacture and decoration techniques. It was also made a metallographic analysis on one pure silver earring fragment for a more detailed study of the silver corrosion damage and manufacture technique.

The second problem is related to the maintenance conditions for the archaeological silver objects exposed in exhibition or in depositary conditions. It was study the atmospheric corrosion of silver in museum environments. For that, it was measure the corrosion rate by electrochemical reduction technique, of silver samples placed in exhibition and storage rooms at the National Museum and Museum of Decorative Arts of Prague.

The second part of the thesis is the study of the conservation and restoration methods of archaeological silver findings. It was made the conservation intervention of silver earrings set in the Institute of Archaeology of the Academy of Sciences of the Czech Republic, Prague.

1. Conservation Research

1.1 Collection of Silver Artefacts from Mikulčice

The study of archaeological silver corrosion and conservation procedures was done on a silver earrings set from 9th century A.D., from the period known as Great Moravia Empire, found in Mikulčice, in the southeast of Czech Republic [Annexes I, fig. 4.1].

The set of archaeological silver findings belongs to the Archaeological Museum of Mikulčice, in the south Moravia. This museum has a collection since the excavations made in the 60's, by the archaeologist Lumír Polaček, from the archaeological Mikulčice site, among others. The set of silver earrings suffer in recent times (25th of September 2007) a fire from their museum [Annexes I, fig. 4.2 and 4.3], so it was send to conservation intervention and study in the Institute of Archaeology of the Academy of Sciences of the Czech Republic, Prague [2].

The collection has a total of 47 objects, namely, 1 ring, 25 earrings, 2 temple earrings and 19 earrings fragments. For the purposes of this study was selected 28 objects made of silver was from above mentioned collection, since the others were found to be from copper or tinned copper. From the 28 was chosen 14 earrings, 11 earring fragments, 2 temple earrings and 1 ring from the set [figure 1 and 2].

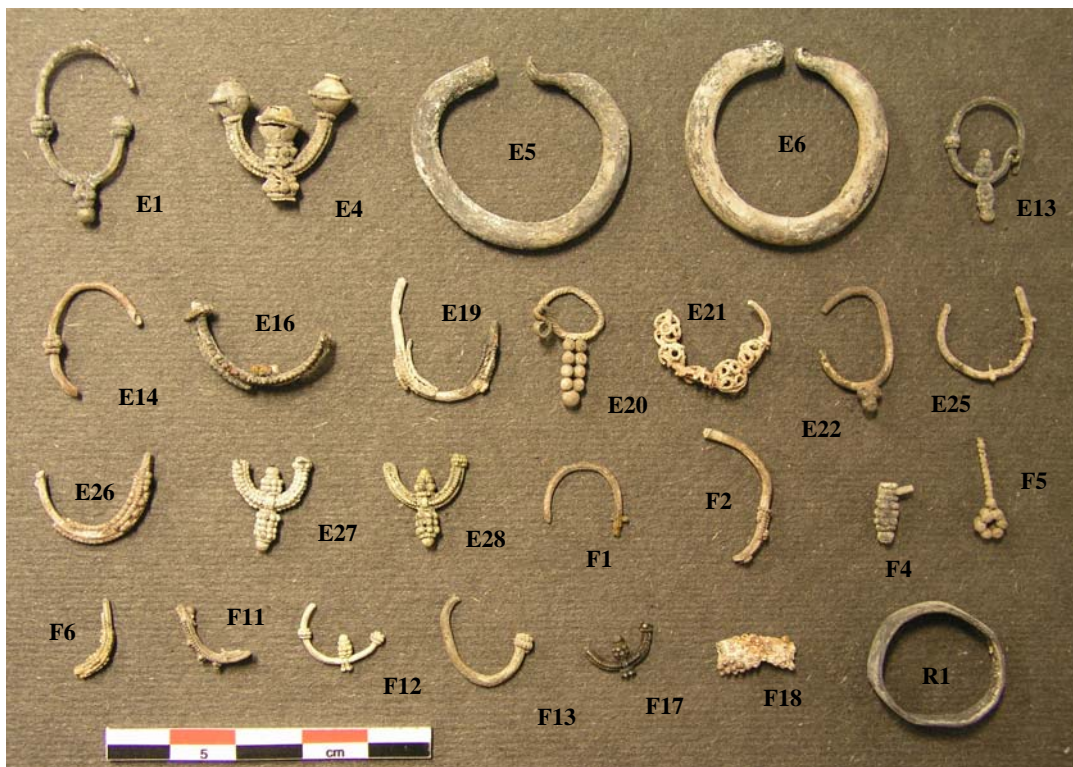


Figure 1.1 – Set of the silver artefacts from Mikulčice.



Figure 1.2 – Silver earrings from Mikulčice.

1.1.1 Historical and Cultural Context

Great Moravia Empire was an important period from the history of the Central Europe since was the rise period of the Czech and Slovaks from the 9th century to the early 10th century [3]. Great Moravia was named by the Byzantine emperor Constantne VII Porphyrogenitus (AD 913-959), to the ninth-century Slav state on the Middle Danube [1]. This period has been studied in the last 15 years and there are many sites from the Great Moravia Empire in Czech Republic and Slovakian countries [Annexes I, fig. 4.1] [3].

Mikulčice is the centre near the river Morava, between Hodonín and Břeclav (currently in southeast Czech Republic near the Slovakian border). In this site was found a pre-Great Moravia settlement from the 7th and 8th century. In this settlement was discovered a workshop for glass, jewellery and iron. In the 9th century the settlement become a fortified city with stone walls, several churches, a basilica and a palace. Around the churches were located many stone vaults and graves. Those belonged to the members of the powered families, in which was found swords and spurs in men graves, and silver and gold jewels on women and children graves. This jewellery was made in home workshops that had active contact with the Byzantine and Carolingian Empire and Adriatic cultural regions [1, 3].

The jewellery from the Great Moravian period developed naturally from the jewellery used in the Danube region from about 500AD [1]. It was quite inspired and influenced by the Carolingian, Byzantine, Eastern Mediterranean and Adriatic art styles. This was due to the spread of Germanic population in Rome, in Byzantium and in Mediterranean lands which brought influences of the technical and typology to the Germanic kingdoms and other civilizations, such as the Avars and Slavs [4]. Nevertheless, during the peak of the Great Moravian Empire in the second half of the 9th century the jewellery was unique in its execution and had a distinctive style [4, 5].

1.1.2 Manufacture and Decoration Techniques

The jewellery from this period was very extravagant and exuberant. It was made from gold, silver and copper in several decoration elements, as by cast in high relief, or sheets decorated with repoussé or cloisonné enamel, stamping or punching techniques, or with filigree and granulation elements, gilding, or the addition niello inlays or coloured glass and precious stones [4]. These kinds of jewellery become very popular among the aristocratic women and could be found several earring pairs in their graves [1]. There are several reports about the use of these earrings typology not in the ears but looped in the hair and/or sewn on to headdresses [1, 5, 6][Annexes I, fig. 4.4 and 4.5].

There are two temple earrings or temple ring in the jewellery set, called in czech “záušnice” - S-shaped earrings [6]. These types of temple earrings or temple rings are typical from the Slavic area (Danube origin) from the 7th to 13th century, and were often found in rural cemeteries in graves of lower social women. They are characteristic of being with simply round forms and one end finishing in spiral, and usually made of bronze but can be silver plated [5].

The Great Moravian jewellery has been much studied stylistically and typology, but not much the technology [7]. The silver earrings set have the typical decorative techniques from this period, as the granulation and filigree work and were done mainly with gold and silver alloys.

This jewellery is characterized to have basic oval shapes forming a “lock” or upper arch and a “basket” or lower arch, with the addition of a central point as a stem or pendant. The lock is usually a simple wire, but in more luxurious earrings is all decorated. The basket is the decorative part, usually with filigree and granulation. Normally, the connection of the lock and the basket of the earrings is placed a “cluster” or “grape bunch”. This is formed with bosses and/or granules. Some earrings have fine filigree, as twisted wire and beaded wire shape. The earrings started with this simple forms and decorative elements as two or three bosses, clusters and granules’ pendants. In the mid of the 9th century the Great Moravia jewellery reached its peak and the earrings typology was more diverse, with the addition of decorative elements such as “globules”, “cups” and “drums”. Some earrings were hybrid with the diffusion of these decorative elements [5]. There are several typologies as: earrings decorated on the upper arch or lock; moon or lunar shaped earrings; pointed grapes’ earrings; column earrings; nine to six cups earrings (cups made of fine filigree work); four, six and seven drum earrings or with hollow spheres (globules) [Annexes I, fig 4.6] [5, 8]. The silver set contains some of these hybrid and complex typologies.

Filigree is an ancient decoration technique which can be found, for example, in Egypt, Greece, Roman, Portugal, Byzantine, Western Europe, Russia, and in Islamic jewellery works. It consists in a wirework that can be in openwork (e.g. Annexes I, fig 4.6 e) and f) or used in a base (e.g. Annexes I, fig 4.6 a), g) and h), in this case the central wire [9, 10]. Initially the wire is drawing in a drawplate, which can vary the thickness and is in round cross sections [9]. Then the wire passes through four steps before is final form: annealing, straightening, twisting and flattening. The annealing is made to soften the wire to facilitate the bent; the straightening is made by fixing the wire end in a vise and the other in pliers; the wire is pulled sharply in way to stretches it. The twisting is done with two wires around each other with help of pliers and the flattening is made with a hammer. The final shape can be present in several forms as round, flat, square, textured, twisted, spiral, beaded, wrapped and braided wire [10]. For this decorative patterns is used several tools as tweezers, chisels and also hands help.

Granulation is the name of the decoration by tiny metallic balls, also in openwork or in a base. The granules production is made by using small bits or cut wire pieces and placed in charcoal' holes base. Then the charcoal is heated till the metal melting temperature and the granules are rapidly formed by total fusion to spheres [9].

The granules and filigree welding is made in a tiny point between the base metal (granule, wire or sheet) and the granule or filigree wire. The weld/solder is diffused homogeneously into the base metal, so there is no line of demarcation between them [10]. Nowadays there are diverse filigree and granulation welding methods, but, researchers still have doubts to explain the ancient welding techniques and the process steps, which craftsmen achieved to produce the excellent jewellery details [11]. It has been studied several methods from ancient art manuscripts, as from Theofilus and Pliny, and investigators, as Oppi Untracht [10], Diane Carrol [11] and Irina Ravich [12], among others, have testing and made several re-creations of granulation welding methods comparing the results with ancient jewellery. Some of the more common granulation methods and names are the amalgam method (with mercury), chemical, sintering, and classical. However, in the Mikulčice silver set it can be found the use of a conventional silver-copper-lead solder, which will be explained in the Experimental Procedures.

The classical method it described with the use of copper salts in the welding process, called also as *fusion welding bond* [10]. Firstly the granules and wires are placed in the structure base (metal sheet, central wire, etc.) forming the decorative pattern with a solution of an organic binder and a flux with a fine powdered copper compound, called by Pliny as

santerna. The organic binder must be a resin or glue, as gelatine or albumen (a colloidal substance), from animal or fish glues or vegetable gums (ex. Arabic gum) [10, 11]. The flux, normally borax – sodium borate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) - flux, or *nitrum* (Niter) – sodium nitrate, sodium bicarbonate and sodium chloride – served to cleaning the metal surface and protect the metal from oxidation during the heating [11]. The copper compound should be a copper salt, as copper chloride (CuCl_2 , or Cu_2Cl_2), copper sulphate (CuSO_4) and copper acetate ($\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$) [13], or alternatively as a copper hydroxide ($\text{Cu}(\text{OH})_2$) or a copper oxide, such as black copper oxide (CuO - tenorite) and red copper oxide (Cu_2O - cuprite) [10]. In ancient manuscripts, as for example Pliny, referred the use of a mineral named *chrysocola*, which translated means “gold-solder”, “gold-glue” or “gold-join” [11]. Currently this mineral is known a hydrated copper silicate, but in ancient times *chrysocola* corresponds to copper carbonate used in the production of gold and silver jewellery, e.g. Malachite, which can lead to misunderstandings [11]. Much quantity of copper could be harmful for the jewellery object since after the annealing it forms black copper oxide on the surface. So, it was added some quantity of gold and/or silver (e.g. seventh part) to this *santerna*. The glue holds the granules and wires in position, and also the present carbon acts as a reduction agent in which reduces the metallic copper from its compounds during the annealing. Consequently, the reduced copper dissolves and diffuses in adjacent to silver surfaces, thus decreasing the melting point of the metal in soldered areas during the annealing [9, 10, 11]. After the welding, the object is brushed with a brass wire brush and pickled to remove any remains of oxides from the surface [10].

From the Mikulčice silver set the two *záušnice* were copper plated with silver and three earrings were found to be gilded. The silver plating and gilding is the process of application a gold or silver thin coating layer, respectively, on the object surface (usually less noble metals), in way to obtain gold finish. There is many ancient gilding or plating methods, as leaf, foil plating, and amalgam or fire gilding [15].

The silver plating of the *záušnice* was made by the application of a thin silver foil on the copper base and wrapped on it by hammer. For secure it could be used a glue, hammered in grooves or soldered [14]. There were no signs of soldering, so the most possible option was glued or secure by cold work.

The other three earrings were gilded, but it was not entirely determined their gilding technique. In these centuries the gilded methods were mainly fire gilding. But, by elemental analysis (see 3.1 Silver Earrings Set Analysis section) it was not detected traces of mercury. The fire gilding technique is made by the preparation of a gold amalgam, which is prepared

by dissolving of fine leafs of silver-gold alloys or ternary silver-gold-copper alloy (with high content of gold and silver) in mercury. The metallic surface is firstly cleaned and then the amalgam is applied with a hard brush. After that the surface is heated until the mercury from the surface evaporates. Then the object surface is burnished to obtain a glaze, bright yellowish colour [14].

Another technique that should possibly be used for the earrings gilding, is the electrochemical gilding, also known as immersion or replacement gilding. This method consists in the immersion of the object in a solution containing gold salts, in which an electrochemical reaction takes place and the gold deposits in the metallic surface. During this reaction less noble metal e.g. copper is dissolved and the reduced gold is deposited in a very thin and homogeneous layer. This method was not very common. Nevertheless, there are some ancient references about this method applied [15].

1.2 Mechanisms and Processes of Silver Corrosion

Silver is present in earth's crust in limited extent in native form or in the alloy with gold (electrum), or as a mineral, such as argentite/acanthite (Ag_2S) and chlorargyrite (AgCl), among others. Silver sulphides accompany sulphide lead or copper ores [16]. One example of ore is the galena (PbS) which has traces of silver that can be extracted from reduced lead by cupellation [17].

The archaeological silver objects were usually manufactured from nearly pure silver or from silver-copper alloys, in which copper content rarely exceeds 10%. Silver could be used also for plating of copper objects or for soldering. Silver artefacts can survive for several hundred years buried in soil with limit extent of corrosion damage. However, depending on the environmental conditions could be observed different forms of corrosion attack (uniform or selective corrosion) and various types of corrosion products of silver (sulphides - tarnishing, chlorides – mineralization) [16, 18].

Corrosion is an unpleasant or undesired form or deterioration of a determinate material, in this case silver metal. This deterioration is due to the interaction of the metal with the environment which, over time, changes the chemical and physical properties or mass of the metal to more thermodynamically stable compounds [18, 19]. The metals are not stable in most natural environments, so they react with other components to form these stable compounds, mainly with oxygen and sulphur. These compounds are identical to the minerals or ores of the metal found in nature, where they are extracted by the process of smelting, the reverse of oxidation [19, 20].

Table 1.1 – Silver chemical and physical properties [14, 21].

Principal oxidation number	Ag ¹⁺
Atomic weight (g.mol ⁻¹)	107.87
Density at 20°C (g.cm ⁻³)	10.5
Melting point (°C)	960.8
Boiling point (°C)	2162
Linear expansivity (°C ⁻¹)	18.9 x 10 ⁻⁶

1.2.1 Atmospheric Corrosion of Silver – Silver Tarnishing

The study of atmospheric corrosion of silver is essential for the preventive conservation of silver artefacts. The atmospheric corrosion of silver is a formation of a thin black layer of silver sulphide on the metallic surface. This type of corrosion doesn't affect the metallic core of the object, since it becomes stable with time, but can change severely the original appearance of the object, in aesthetic and legibility point of view [18]. But, for long time exposure in air, this *tarnishing* layer can grow to the inside forward the metallic core. One problem of the corrosion of the pos-excavated artefact is the exposal to the atmosphere (oxygen and pollutants), that can increase significantly the corrosion of the metal surface that was intact under soil [16].

Atmospheric corrosion of silver consists in an electrochemical process in the metallic surface of the silver objects that forms a uniform black corrosion film named *tarnishing*. This type of corrosion attacks chemically the metallic surface into metallic ions and consequently reduces the metal to corrosion products. This corrosion process is performing in the metallic surface of the object, named corrosion cells. These are in contact with the atmosphere and the metal by an electrolyte, usually water from moisture or relative humidity [19, 22].. The others variables that influences the corrosion rate: the contaminants or pollutants (ex. sulphur dioxide, hydrogen sulphide, and chloride) and impurities in the air (ex. as dust is hygroscopic); the copper percentage in the metal alloy; the initial exposure conditions; sample mass; nature of the formed corrosion products [19].

The relative humidity influences the atmospheric corrosion by the formation of water adsorption layers in the metallic surface of the artefact. Nevertheless, silver corrosion in dry environments is also possible, since the main responsible of silver tarnishing is hydrogen

sulphide (H₂S), but more slowly. The chemical and physical properties of the corrosion products and the presence of impurities salts (hygroscopic compounds) can also increase the water adsorption content [19?]. The water will bond in the molecular form to the metallic surface by Lewis base bonding (donation an electron pair) from the oxygen atom (net charge transfer from the water molecule to the surface) on the electron-deficient adsorption sites of the metal. The “critical relative humidity” is when the aqueous films are greater than approximately three monolayers, which corresponds to relative humidity higher than 50%-60% [table 1.2] [18].

Table 1.2 – Relationship between the relative humidity and the number of water monolayers, at 25°C and stable conditions (determined experimentally by quartz crystal microbalance method on a different number of metals¹) [19].

Relative humidity (%)	Number of monolayers
20	1
40	1.5-2
60	2-5
80	5-10

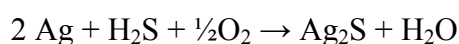
The water content will dissolve the gaseous constituents (the really responsible for silver corrosion as oxidant agents) on the metallic corrosion, and serve as an electrolyte for the electrochemical reactions. In this way, water acts as an intermediary for the corrosion reactions occur. If there is no humidity in the atmosphere it only forms a thin dull oxide film, which is stable, and protects the metal as a passive film that can prevent the access of gases and further corrosion. In these cases, the corrosion is only superficial. However, this passive film can stop its passivity by chemical attack of pollutants [19]. On other cases, the corrosion products are non preventive due to be not adherent to the metallic surface or are too soluble (ex. nitrates) and so are easily dissolve out exposing new metallic surface to the atmosphere and continue corrosion [20].

The redox reactions consist in two or more electrode reactions: oxidation of the metal (anodic partial reaction) and the reduction of an oxidizing agent (cathodic partial reaction). This system results in an electron flow and thus a current, that can be expressed by the Ohm’s law: $I=E/R$. It can occur several reactions depending on the reaction potential, pH and

¹ P.A. Schweitzer. 1999. *Atmospheric Degradation and Corrosion Control*, New York: Marcel Dekker [19].

presence of oxygen (or other pollutants) – aerobic and anaerobic conditions [Annexes II, table 4.1] [16, 19, 20]. The consumption of the electrons in the cathode will determine the rate of corrosion of the metal in the anode (more electrons consumption, more corrosion of the metal). By the silver Pourbaix diagram is possible to see the relationship between the potential variation and the variation of pH of the electrolyte [Annexes II, figure 4.7]. However, this diagram has standard values in a water electrolyte at 25°C, and doesn't refer to the presence of other specimens or variations that can influence silver corrosion [20].

In normal conditions or relative humidity and temperature the corrosion of silver is only the formation of a transparent and protective silver oxide film, Ag₂O [24]. In the presence of atmospheric pollutants, silver start to tarnishing changing the patina colour, from iridescent to completely darkening. Values around 100nm thickness of the tarnish layer becomes completely dark. The most dangerous silver and copper *tarnishing* agent is the hydrogen sulphide (H₂S). This compound can *tarnish* silver in low concentrations as part per trillion (ppt), and in indoor atmospheres the lever for H₂S can reach 50-100ppt, enough to *tarnish* silver [14, 24]:



There are many other that can influence and/or participate in the corrosion process as catalyser or form other silver corrosion products [14, 19]. These pollutants are O₃, H₂O₂, SO₂, COS, Me₂S₂, NO₂, HNO₃, NH₃, HCL, Cl₂, HCHO, and HCOOH. These pollutants can be the also the result of either natural or anthropogenic processes, and may undergo a variety of chemical changes during transport in the atmosphere [18, 19]. Ultraviolet radiation and ozone can also accelerate the silver corrosion or participate in the corrosion products darkening [18, 25].

The corrosion products forming during *tarnishing* of silver-copper alloys are normally a mixture of silver and copper sulphides, among others [Annexes II, table 4.2]. The copper is more susceptible to corrode than silver, so, silver-copper alloys with high copper content will *tarnish* faster than pure silver, and the corrosion rate levels will increased with the increasing of copper content [14].

1.2.2 Corrosion of Buried Silver – Silver Mineralization and Embrittlement

Archaeological silver is the silver that had been buried under soil or under sea for a long time [18]. During this long time exposition the metallic object interacts with the surrounding environment, and corrodes in a different form from the atmospheric corrosion,

named intergranular corrosion. This corrosion type is characterized to act in the metallic core, and with time, silver objects become seriously fragile and brittle. Corrosion of buried silver results in the change of the original properties and cause undesired alterations of the object: embrittlement and loss of ductility of the metallic core; formation of various corrosion products; loss of gloss and darkening of the surface; loss of the original material and the original surface details; loss of legibility and understanding of the information of the object [26].

The initial corrosion of buried silver is the same as in the atmospheric corrosion: *tarnishing* formation. Usually silver reacts mainly with sulphur and chloride compounds to form thermodynamically more stable compounds, similar with the silver ores found in nature, as Argentite (Ag_2S) and Chlorargyrite or horn silver (AgCl) [16, 20]. Chlorides are the compounds that participates more in the intergranular corrosion of silver. Initially, it is the responsible for the break of the passive silver oxide film, and starts to corrode from metallic surface to the metallic core [20]. However, in the soil there are other substances present which will interact with silver and originate other corrosion products: carbonates, oxides, hydroxides, sulphates, nitrates, phosphates, bromides, etc. Phosphates (PO_4^{3-}) and bicarbonate are usually connected to the decomposition of organic matter, as deceased animals/human, bones or dung. Nitrates are connected to the decomposition of animal/human waste [20]. The decay of organic matter is also responsible for the silver corrosion due to their production of complex organic compounds, as ammonia, nitrates and acetic acid, which forms very soluble silver salt [24]. In anaerobic soils it can have microorganisms that can contribute to the metallic corrosion. An example is the anaerobic sulphate-reducing bacteria that produce sulphide ions that can facilitate the corrosion [20].

Not all the corrosion products can be detected in analysis on archaeological silver objects, due to have high solubility, so are continuously washed by water during the burial. The most common corrosion products found in ancient silver artefacts are silver sulphides, silver chlorides and silver bromide [Annexes II, table 4.2] [20]. The corrosion products identified on a silver artefact can be amorphous or in crystal form, depending on the surrounding environment, and can also incorporate impurities from the surrounding elements, as calcium, silicon, aluminium and iron.

A silver artefact after thousand years burial, and depending on the soil environment, it can be found completely mineralized and brittle [26]. The metal mineralization is due to the substitution/replacement of the metal to its mineral, usually in horn silver (Chlorargyrite), preserving the original shape of the object, [18]. This usually happens in very acid or very

basic environments and the corrosion products are very soluble and non-protective [18, 16, 20]. The partial replacement or not completely mineralization of an artefact is named as pseudomorph [18, 20].

Silver embrittlement is the typical corrosion found in burial silver, and is a consequence of long term corrosion and microstructural changes, that initiates with external forces during burial and internal residual stress [26]. It also depends on the chemical composition of the alloy, in which the alloy elements can implicate one or more embrittlement types, and the object manufacturing process (e.g. casting, cold working, chasing, engraving, stamping, annealed, etc.) responsible for residual stress [26, 27]. The residual stress and is associated to microstructural changes in the grain size growth, in which the larger grains are more susceptible to crack leaving micro-cracking that become over time into macrocracks [26]. Silver embrittlement can be corrosion-induced or microstructurally-induced, or both act synergistically, which can be very harmful for an artefact [26].

Corrosion-induced embrittlement is due to intergranular corrosion, and it results in intergranular fractures surfaces in fine granular appearance, from the surface silver chlorides layer to the metallic core [26, 27]. It is related to segregation of copper to the grain boundaries – also named discontinuous or cellular precipitation – that occur very slowly in solid state [27]. The copper segregated in the grain boundary areas is localized, in which the soil electrolyte with substantial chloride content increases the susceptibility to corrosion attack. The external areas of the grains or grains boundaries have higher energy – where crystal lattice meets another – so becomes more anodic, and corrode more intensively in comparison with the inner volume of crystal grains [20]. So, in microscopic level, the grains will corrode from the borders to the inside, and in macroscopic level, the metallic surface will corrode towards the metallic core [28].

In binary silver artefacts with high concentration of copper, or ternary silver alloys with several percents of gold and copper, and also in gilded silver or silver plated objects, also occurs selective corrosion in the grain boundaries. The less noble metal – copper or silver - will corrode in contrast with the noble metal – silver or gold. As referred above, the corrosion products formed can be too soluble and washed away producing fissures and cracks in the gilded or plated layer to the metallic core [18, 20].

Microstructurally-induced embrittlement is the consequence of low temperature ageing due to segregation of an impurity element(s) (e.g. copper, lead) in the grain boundaries [27]. Results are sharper, narrow and displaced intergranular cracking than the intergranular localized corrosion [26]. Synergistic embrittlement is the action of both

corrosion-induced and microstructurally-induced embrittlement - corrosion along slip lines; deformation twin boundaries, segregation bands. The large grains sizes and cracks from fractures along grain boundaries facilitate penetration of intergranular corrosion into the metallic core, increasing corrosion and decrease the metal resistance [26, 27].

2. Experimental Procedures

2.1 Silver Earrings Set Analysis

For the presented study of the silver earrings set from the 9th century A.D, found in Mikulčice, Czech Republic, was made for a better understand of the earrings manufacture and decoration techniques used. It was performed structural study by photo-documentation in the optic stereo-microscope and by radiography, and microstructure and elemental analysis with scanning electron microscopy with energy dispersive X-ray (SEM-EDS). It was also made detailed metallographic analysis of one pure silver fragment to study manufacture technique and the buried silver corrosion process.

2.1.2 Material and Methods

The radiography of the silver set was performed in the Institute of Archaeology of the Academy of Sciences of the Czech Republic, Prague.

The optic stereo-microscope documentation was performed in the Institute of Archaeology of the Academy of Sciences of the Czech Republic, and in the Institute of Chemical Technology – Faculty of Chemical Technology, Department of Metals and Corrosion Engineering, Prague. It was used the optic microscope Olympus SZ60 and digital camera Olympus C-5050, and made documentation on the silver earrings before, during and after the conservation, and also during the metallographic analysis.

The microprobe and metallographic analysis were performed at the Institute of Chemical Technology, Faculty of Chemical Technology on the Department of Metals and Corrosion Engineering. There was used the scanning electron microscope (SEM) Hitachi S 450 equipped with the energy dispersive X-ray analyser (EDS) Kevex Delta V. It was also performed SEM-EDS analysis on the metallographic sample after etching, in the Institute of Physics of the Academy of Sciences of the Czech Republic, with Jeol Superprobe 833 equipment. The metallographic analysis was performed with the light metallographic

microscope Olympus PME 3 connected with digital camera Olympus C 3040 and Olympus C7070 Zoom for image documentation.

2.1.3 General Results

With radiography it was possible to evaluate the metallic core preservation state and to observe some details, such as the manufacture and decoration techniques. In general the earrings are in bad preservation state, since most of them are incomplete or with loss of material, have brittle metallic core, and deformations. The metallic core condition state is not completely identified by the radiography observation, but is possible to compare between the earrings of the same thickness and observe which are more mineralized and brittle. The more density ones (more white) are in better condition state of the metallic core, and the others are more mineralized, which corresponds to most of the earrings from the set [Annexes III, fig. 4.8]. Therefore, the earrings more mineralized are E1, E4 (central sphere) E11, E13, E14, E25, F1, F2, F5, F6, F11, F12, F13 and F18.

In some earrings is possible to observe some details of the manufacture or decoration techniques, such as the decorative elements (granules and filigree) and structural supports [Annexes III, fig. 4.9]. The earrings E27 and E28 seem to be with dense metallic core, but by observation under the stereo-microscope it was discovered that both were gilded. The same state was revealed at the temple earrings. In these cases it was possible to observe with radiography the second metallic layer which consists of a foil [Annexes III, fig. 4.10]. The gilding and foil layers can protect the inner base metal from corrosion [23].

By observation under the stereo-microscope it was possible to distinguish dirt and dust residues on the earrings surface, probably from the museum fire debris, and the formation of corrosion products with different composition thickness and colour. It was observed grey, black, dark red, yellowish, bluish green and orange surfaces colours on different earrings from the set [Annexes III, fig. 4.11 to 4.18]. These are due to contamination by impurities, such as iron corrosion products, and/or formation of silver and copper corrosion products, identified later by microprobe analysis. It was also observed signs of fragility and brittleness in all the earrings. Some are incomplete, with material loss, with many fractures and very brittle [Annexes III, fig. 4.19 and 4.20].

It was also possible to distinguish the silver foil from the two temple earrings [Annexes III, fig. 4.21] and gilding layer from two earrings [Annexes III, fig. 4.22].

By the microprobe analysis it was made metallic core alloys and corrosion products identification, and in some cases, semi-quantitative analysis. Also it was studied the

decoration techniques of the earrings, welding, soldering and plating/gilding methods. The microprobe analyses were made before the earrings intervention or any cleaning process, so, it was only possible to analyze the surfaces of broken or scratched areas of a few earrings.

It was revealed that the earrings were manufactured from pure silver, alloying with several percents of copper, from 1% to 5% [Annexes III, fig. 4.23]. Some earrings had small content of gold in the alloys, from 1% to 3% [Annexes III, graphics 4.1 and 4.2, and table 4.3]. This amount of copper and gold is too few to state that the earrings are from a ternary silver alloy Au-Ag-Cu. In the more decorative earrings (with more granules and filigree) were detected traces and/or several percents of lead, and few cases with traces of zinc. These metals are related to soldering, which were often add in solder in way to increase the molten metal fluidity during annealing [Annexes III, fig. 4.24 and 4.25, graphics 4.3 and 4.4]. It was confirm three gilded earrings and three silver-plated [Annexes III, fig. 4.26, graphics 4.5 and 4.6].

The identified corrosion products were quite the same for all the earrings. It was detected sulphur, chlorine and oxygen [Annexes III, graphics 4.7 to 4.12], which are related in several literatures as common component of silver and copper corrosion products, as silver and copper sulphides, chlorides, and sulphates. The presence of oxygen is mainly related to soil constituents, namely to silica (SiO_2), alumina (Al_2O_3), calcium carbonate (CaCO_3) and iron oxides and hydroxides. This is possible to deduce from the detected traces of iron, calcium, aluminium, titanium, silicon and barium, which are elements related to impurities from soil, and phosphorus, an element related to human body decomposing.

Characteristic silver corrosion damage was photo-documented by microprobe: microfissures in the metallic surface, fresh fractures (probably made during or after the museum fire) with the distinctive intergranular corrosion found on archaeological silver and copper precipitation above a gilded layer, due to copper segregation above the metallic surface [Annexes III, fig. 4.27 to 4.30, graphic 4.13 to 4.16].

2.1.4 Metallographic Results

From the silver set it was chosen the F6 earring fragment sample for metallographic investigation [Annexes III, fig. 4.31 to 4.34]. This was chosen since is a small fragment of a earring that shows interesting features for the field study, such as the characteristic intergranular corrosion of archaeological silver which was present in all the earrings [Annexes III, fig. 4.35 to 4.37]. This fragment is a good selection to characterize the microstructure and study the mechanism of corrosion process, the formation of observed

corrosion products and the manufacture technique. It was also raised other questions in this fragment, as if was gilded or not, since it has a yellow patina similar to gold metallic lustre and it was detected gold in the metallic surface. A sample from this earring fragment was taken by simple breaking a very small piece (approx. 1,5x 1,5mm) in an area where nearly all granules surrounded the earring central wire.

The metallic core was made from pure silver with copper and small amount of gold, approximately ~93% weight Ag, ~5% weight Cu, ~2% weight Au, and with no or very low signs of impurities or corrosion products. These measurements were made on the fresh fracture surface of the fragment, and it was observed a concentration gradient in the values of silver content from the metallic core to the metallic surface [Annexes III, graphic 4.17 and 4.18]. Silver concentration is higher in the centre and lower in the border/surface of the earring (~84%).

Some measurements were very high in gold content (~10%), but not detected any gradient as silver. The fragment surface and fracture surface has a gold lustre shine, and the microprobe analysis determine gold in this areas. This could be due to the fact that the earring was gilded on an Ag-Cu-Au alloy central wire. However, there are no signs of a gilding layer seen on other earrings, which should be probably removed by previous interventions of chemical cleaning, such as a hot concentrated sulphuric acid bath. Nevertheless, there are no records of previous interventions on the silver set collection.

The earring fragment sample was prepared to metallographic analysis in an epoxy resin, grinding on silicon carbide sandpapers and polish in diamond paste [Annexes III]. Then, it was photo-documented in stereo-microscope, where is possible to observe the severe brittle metallic core, with intergranular corrosion – cracks, failures, and material loss - mainly in the fragment surface and granules. It is also possible to distinguish the solder area – area between the wire and granules – which is very porous, and in some areas with large air bubble voids [Annexes III, fig. 4.40]. It is noticeable a slightly “watermark” around the wire and granules borders, which could be due to none completely drying of the sample surface after polishing which leaves re-precipitated salt in the fragment surface; or small pores in the metallic core related to more corroded areas forming several corrosion layers into the metallic core [28], which could be seen in figure 4.37, Annexes III; or Cu α phase that was formed during the soldering into the metallic core.

The intergranular corrosion is observed mainly in the granules surface rather than in the central wire. The open grain boundaries are more visible near the metallic surface, with open voids between the grains, in direction to the metallic core. In these areas is possible to

observe small black spots responsible for the “watermark” [Annexes III, fig. 4.39]. In the soldered area is possible to observe a more porous and spongy texture, with several heterogeneous grey particles [Annexes III, fig. 4.40 to 4.42]. By microprobe analysis it was determinate that these grey particles are high in copper content, and probably were pure copper from the granulation welding process and the voids are related to the gases release from the copper salts during annealing or from the carbonisation of organic glue [Annexes III, fig. 4.43 and 4.44, graphics 4.19 to 4.21].

It was done a map distribution analysis in the smallest granule from the earring fragment sample since it presented severe embrittlement and distinctive and clear solder areas for analysis. The map analysis identified silver, gold, copper, chloride and sulphur concentration distribution [Annexes III, fig. 4.45 to 4.50]. The distribution of the elements in the map analysis is quite heterogeneous. Silver, gold and sulphur are very homogeneous either in the solder either in the wire and granule metallic core, so the earring was not gilded. However, silver is slighted less in the solder. Copper and chlorides are in localized areas, especially in the solder and at grain boundaries, and they seem to be not related to each other. This can be seen by the blue and red circles: the blue circle is pointing to a localized chloride area and the red circle is pointing a localized copper area. Comparing these circles with the other elemental maps, it is possible to see that chlorides are bonded with silver in the metallic core and solder; and copper is not associated to silver since the copper concentration areas correspond to voids in the silver elemental map. So, the chlorides must be related to silver corrosion products such as silver chlorides. The copper concentration areas may be related to copper segregation in the grain boundaries and to residues of copper powder/filings used in granulation solder that didn't dissolved completely during annealing.

It was apply an ammonium persulfate/potassium cyanide etchant for few seconds, but the sample was too corroded so the etchant effect was too strong and “burned” much the granules and the wire surface [Annexes III, fig. 4.51]. Nevertheless, it is possible to observe the wire centre with fine lines defining the grain boundaries [Annexes III, fig. 4.52]. These lines are the most corroded areas of the metallic core (more energetic lines), in this case the intercrystalline corrosion of the metallic core together with silver embrittlement.

It was done another elements distribution map on SEM-EDS of the earring solder area, for the elements silver, copper, chlorides and gold [Annexes III, fig. 4.53 to 4.58]. In the second electron image and backscattering images is possible to observe: black areas, which correspond to voids; light grey areas, corresponds to silver-copper alloy with increased Ag content; slightly grey small heterogeneous areas, correspond to silver chlorides and in

dark grey heterogeneous areas, correspond to nearly pure copper. Gold is slightly homogeneous.

2.1.4 Discussion and Conclusion

The silver set preservation state in general is bad. Most of them are incomplete or with significant material loss (e.g. granules and filigree decoration, and abrasion of the surface). It was observed many fissures, fractures and cracks which confirm the extremely embrittlement state. All present tarnishing from varied corrosion products and impurities from soil. The presence and quantity of these impurities and corrosion products confirm the non-stabilized previous condition of the earrings set. The earrings suffered from the museum fire, although they weren't exposed to high temperatures during the museum' fire, due to have any signs of melting or any fire damage, especially the tinned earrings, since their melting point of tin is around 232°C. Nevertheless, the earrings which had copper corrosion products on the metallic surface (e.g. copper carbonates and chlorides) during the oxidizing atmosphere of the fire, converted into Tenorite, a hard black cupric oxide (CuO) [30]. Even so, it wasn't detected any oxygen peak during microanalysis [Annexes III, graphic 16]. Since the measurement was made in a rough and porous surface, it could interfere with the lower energy electrons which, then, aren't detected. In this case, I propose the application of X-Ray diffraction analysis for the compounds identification.

The presence of silver and copper corrosion products above the metallic surface of the gilded earrings is due to porosity of the gilded layer. Silver and copper corrosion products can penetrate and creep out from the pores or other imperfections of the gold layer, form a black tarnishing above the gilding layer [23]. Fire gilding technique is characterized to this type of corrosion effect, since it has pores formed by mercury volatilization during annealing [Annexes III, fig. 4.59 and 4.60, d)] [23]. This gilding technique was very common in ancient times, but, it wasn't detected any mercury traces on microprobe analysis – because mercury X-ray peaks coincide with the gold peaks and only at relative high mercury content is possible to distinguish presence of this element. Nevertheless, it can't be excluded the electrochemical gilding referred in the introduction. In the same figure 60 b) of the Annexes III, shows a foil flanking off similar to what was observed in the temple earrings [23].

It was concluded the use of two types of soldering techniques on the granules and filigree: binary silver-copper alloy with traces or several percents of lead and zinc for the more ornamented earrings or in the bigger granules - e.g. Earring 16 was used a binary silver-copper alloy (~35% Ag; ~65% Cu) with lead and copper filings for soldering the central

granules circle [Annexes III, figure 24 and 25, graphic 3 and 4]; and the use of classical granulation welding with copper salts - *fusion welding bond* – in the small granules and fine filigree – e.g. Fragment 6 [Annexes III, figure 4.40 to 4.44, graphic 4.19 to 4.21].

The silver concentration gradient observed in the fragment 6 central wire is due to selective corrosion of copper, from the core to the metallic surface. Copper is washed away to the soil or re-precipitated in the earring surface and silver forms silver corrosion products forward the metallic surface, such as silver chlorides and sulphides, since the concentration of chlorides was higher on the metallic surface. By the microprobe analysis, it was confirm that chlorides are associated with silver chlorides. There are rare reports about the identification of cuprous chlorides on archaeological silver objects [23].

It was also observed severe intergranular corrosion in great extension on the earring fragment wire and granules. This is due to localized corrosion attack on the less noble metal, copper. Since copper is not soluble in silver, silver-copper alloys present two-phase alloys with inhomogeneous microstructure. During long time burial copper from supersaturated solid solution segregate in the grain boundaries regions, which consequently become copper-enriched. Notice also that in the solder areas which were welded with copper salts, will also present pure copper-enriched areas. Between the copper concentrated areas and silver will form a different potential and result in galvanic corrosion on a microscopic scale, starting at the metallic surface [23]. Subsequently, by galvanic corrosion it will form corrosion products in the metallic surface – silver sulphides and chlorides, and copper sulphides, oxides and carbonates, among other silver and copper compounds. These corrosion products will favour the formation of micro-fissures and cracks, together with stress-corrosion cracking, facilitating the entry of more contaminants and corrosion attack into the metallic core.

2.2 Museums Evaluation

Archaeological silver objects are one of the most precious artefacts that a museum can have. The conservation and restoration methods for archaeological silver artefacts as cleaning and stabilization are limited, since ancient silver is often in very fragile and embrittlement state. The intervention of these objects must be as less as possible to avoid damage and material loss. After conservation intervention silver objects must be kept in stable environment conditions and free of pollution, to avoid more contamination and further corrosion. For this purpose, it was studied the atmospheric corrosion of silver in order to relate it with good maintenance practice of silver objects that are going to be stored or to display. 15 samples from pure silver sheet were exposed in different museums environments

(storage and exhibition rooms), in order to determine the corrosion rate of silver in these environments conditions, and compare the results of the different conditions under which the samples were subjected. The evaluation of corrosion rate was specified by electrochemical galvanostatic reduction of corrosion products at samples after exposition.

2.2.1 Materials and Methods

It was prepared 15 pure silver samples to place in a museum storage and exhibition room in way to calculate, by electrochemical reduction, the corrosion rate. Is was placed five samples in an exhibition room of the Museum of Decorative Arts (MDA), five in the storage room and five more in an exhibition room of the National Museum (NM), in Prague. The samples placed in the MDA were placed in an exhibition room of a permanent display - *Stories of Materials Treasury* – were most of the objects on display are from metals, as jewellery, liturgical objects and decorative arts objects. Three were placed inside some showcases and the other two were hanged in the corners of the room [Annex IV, fig. 4.61 to 4.64]. In the storage room of the National Museum, the samples were placed in the same conditions as the others objects of the museum, as for example, inside acid free paper, inside wood or metal cupboard and one in the middle of the room [Annex IV, fig. 4.65 to 4.68]. In the NM exhibition room - *Decorations and Medals of European Countries in the 19th and 20th Centuries* - it was placed one sample in the middle of the room and four more inside the showcases.

The samples of pure silver (10 mm x 15 mm) were prepared according to the Draft International Standard ISO/DIS 11844-2, with no corrosion inhibitor, stabilization or protection compounds [31]. All the samples had to be more than six months in air exposure [Annex IV, table 4.4] and after it were measure the corrosion rate by electrochemical reduction with the galvanostatic measurement technique [Annex IV, fig. 4.69 and 4.70]. This technique consists in the reduction of the silver corrosion products by application of a constant current density and monitoring of time when the reduction of silver corrosion product occurred – potential around -0,7mV. Evaluation is performed from recorded graphic of potential versus time [Annex IV, graphic 4.22 and 4.23]. By the Faraday's law was calculated the corrosion rate, in mg/m².year, and film thickness, in nanometres.

2.2.2 Results

The results were diverse and satisfying. It was not expected completely tarnishing in the samples in six months of exposure. However, it was expected higher levels of corrosion on the samples which were exposed in external environments, as the ones placed inside showcases, cupboards and acid free papers. This was confirmed, and possible to see in naked eye, the samples n° 71, 72 and 29 were very tarnished compared with the samples placed in save environments [Annexes IV, fig. 4.71]. The most tarnished ones were the samples n° 71 and 72, placed in the exhibition room of the MDA. These samples' patina changed extensively to dark iridescent colour.

From the samples which were in save environments were slightly or no tarnished at all [Annexes IV, fig. 4.72]. The samples that have slight tarnishing are possible to observe that started tarnishing from the borders and corners. The more tarnished from these sample selection is the sample n° 25. It was quite tarnished as sample n° 18. Both were placed in the same environment, NM storage room, but the sample n° 25 stayed inside a metallic cupboard.

Next table is expressed the results of the corrosion rate and thickness evaluation for all the samples, made by galvanostatic measurement technique. In general the samples have low values of corrosion rate per year and film thickness. The samples with more critic values are from the Museum of Decorative Arts, the n° 71 and n° 72, which have an accelerated corrosion rate per year, and formed more corrosion film. From the samples of the National Museum storage room, the ones kept in the wooden cupboard were with lower values from the ones kept in the metallic cupboard. Nevertheless, the acid free paper seems more efficient as protection on the metallic cupboard than in the wooden. The values from the National Museum exhibition room are relatively identical. Taking in account that the sample n° 29 was placed in the middle of the room, more exposed to humidity and air pollutants of the museum' visitors, the other samples which were placed in the showcases have identical values, as the sample n° 8.

Table 2.1 – Values of the corrosion rate and thickness of the corrosion film from the samples placed in the Museum of Decorative Arts and National Museum.

	Corrosion Rate (mg/m².year)	Thickness of the corrosion film (nm)
Samples MDA, Exhibition room		
Sample n°20	0,0005	15,52
Sample n°33	0,0013	4,24
Sample n°69	0,0032	9,79
Sample n°71	0,025	76,17
Sample n°72	0,026	79,44
Samples NM, Exhibition Room		
Sample n°8	0,0052	13,05
Sample n°10	0,0030	7,61
Sample n°16	0,0034	8,70
Sample n°29	0,0051	14,80
Sample n°32	0,0046	11,53
Samples NM, Storage Room		
Sample n°18	0,008	26,00
Sample n°25	0,0067	20,24
Sample n°27	0,00021	0,65
Sample n°30	0,0013	4,13
Sample n°68	0,00079	2,39

2.2.3 Discussion and Conclusion

The corrosion rate and film thickness study by the galvanostatic measurement technique is very simple and efficient. The results obtained were quite satisfactory, due to the tarnishing was visible from the samples in the exhibition and storage rooms, and graphics and values obtained. Even if the values were low and the samples didn't present much corrosion, from seven to nine months in museum conditions the results were very distinct and comparable.

The more tarnished samples were from the Museum of Decorative Arts, Prague. These samples (n° 71 and n° 72) corroded to about 80nm thickness, which corresponds to almost a total of metallic surface blackening (~100nm) [14]. However, there are significant differences in tarnishing in the samples that were within the showcases. This proves that the

respective museum provides a high-quality preventive conservation system and good protection for the exhibit inside the showcases.

The samples placed in the National Museum of Prague exhibition hall and storage room didn't had such high corrosion levels as the Museum of Decorative Arts. From the exhibition hall samples, only the samples n° 8, n° 29 and n° 32 had higher corrosion values and present similar corrosion values. However, the sample n° 29 was in the middle of the room and the other inside showcases. In these cases these samples should had been prove lower values, taking in account that the showcases should protect from the corrosion agents and moisture coming from the room. Therefore, the preventive conservation system and protection of this museum is not the most effective.

Relative to the samples placed in the storage room of the same museum, they show slightly higher corrosion rate values and film thickness. The samples n° 18 and n° 25 reached corrosion values in which began to notice the visible tarnishing, for values around 26nm [Annexes IV, fig. 4.71 a)]. The samples placed inside acid-free paper were less corroded, and the samples placed inside the metal cabinet were more corroded than those remained in the wooden cabinet. Taking in account that a museum storage room is where is placed most of museum arts and collections, and are expected to be stored for more decades or even centuries, it is essential to provide good packing, protection and maintenance solutions so that the objects don't present serious corrosion problems. Therefore, the preventive conservation system and protection of the storage room is reasonable. Is suggested to continue to use acid free paper in silver objects, or Minigrip ® bags, and change the metal cupboards to plastic cupboards.

3. Conservation Intervention of the Archaeological Silver Set

This chapter describes the conservation and restoration methods for the Mikulčice earring silver set, made in the Institute of Archaeology of the Academy of Sciences of the Czech Republic, Prague.

3.1 Objectives and Conservation Project

By the silver earrings set analysis it was concluded that they present bad conservation state, with intercrystalline corrosion, tarnishing and several corrosion products, as silver chlorides and sulphides, and basic copper chlorides and oxides. According to these

observations the goals of the earrings intervention were superficial cleaning of the dirt, tarnishing and corrosion products above the limit of the original surface for a better profile observation, stabilization, consolidation, protection and maintenance proposal.

The conservation projects follow the objectives: 1° mechanical cleaning of the dirt and corrosion products with wooden stick, scalpel, and in some cases with ultrasonic needle or a soft abrasive [18, 32]; 2° chemical cleaning of the iron contamination and corrosion products (silver sulphide, silver chloride, copper sulphide, basic copper chlorides and copper oxides), with low concentration solutions of formic acid, ethylenediamine tetraacetic acid disodium (EDTA disodium), and at few earrings thiourea [18, 24, 33, 34, 35, 36, 37, 38]; 3° stabilization with application of a tarnishing inhibitor or a chlorophyll solution only in the case of pure silver objects [24, 39]; 4° consolidation and protection apply an acrylic resin as Paraloid B72[®], and in the cases of assembly fragments, granules and filigree wire also use the same resin [18, 24, 34]. The storage was done in a Minigrip[®] bag with silver inhibitor paper, Silver Saver[®], and the assembled earring are placed in a polypropylene box with a polyethylene foam base and wrapped in a Japanese' paper parcel [18, 33].

3.2 Intervention Procedures

Firstly all the silver artefacts were degreased with ethanol with a cotton swab. Then under binocular, it was removed the residues and traces of dirt, dust and corrosion products above the original surface. This step was made with scalpel, wooden stick, brush and in some cases with ultrasonic needle. The ultrasonic needle was handled carefully and used mostly in more dense or thick corrosion products layers, as the layers of silver chlorides and copper oxides. However, the ultrasonic needle vibrations were too dangerous to the brittle earrings and could lead to undesired fractures, as well as scalpel. The surface was again degreased and cleaned with ethanol.

The tarnishing removal was proceed by chemical cleaning with different solutions, as a solution of as a solution of 5% of formic acid in water, a solution of 5% EDTA disodium in water, and 5% of thiourea in water. All the solutions were prepared with some quantity of methyl hydroxymethyl cellulose gel, Tylose MH 1000[®], in way to increasing viscosity forming a gel to avoid deep penetration of the reactive into the metallic core of the object. The solutions were applied with cotton swab locally on the earrings, and removed with distilled water. In most of the cases it was needed to apply a higher concentration of formic acid and/or EDTA disodium both to solution of 10% in water, since the results weren't satisfactory. With this higher concentration it was possible to remove more corrosion

products. However, in some earrings, mainly the gilding ones, wasn't possible to remove completely the corrosion products. Some areas were also difficult to remove tarnishing as in the decorative elements of granulation and filigree.

A particular case of the silver set was the ring intervention. It was used the three solutions in 10% in water, but still difficult to remove completely the tarnishing. Since the metallic core wasn't too fragile it was proceeded to a mechanical cleaning with a soft abrasive. It was prepared powder chalk in microcrystalline was and brushed on the ring surface with tooth brush (not effective), with a soft cloth or with the fingers (with glove), which was the most efficient method. The chalk hardness is enough to remove the layer of silver chlorides, but, since the ring suffer a fire, the corrosion products got harder. This method was done three times interleaved with the chemical treatment with the same solution as before mentioned with no cellulosic gel. Still, the tarnishing wasn't possible to be removed completely, but it was removed great corrosion products quantity and ended with a more homogeneous surface.

The application of thiourea solution was made in few earrings. After the application of a 5% concentration of this solution in methyl hydroxymethyl cellulose gel the earrings surface got a silver homogeneous lustre. But, after 24h in distilled water the earrings changed the patina to a light yellow patina. The application of thiourea was stopped and not done in more earrings. The removal of the yellow patina in these earrings was done by the application of a 10% solution of EDTA dissodic and a 10% solution of formic acid in water [Annexes IV, table 4.4].

After and during the chemical treatment all the earrings were placed in a glass with distilled water for two weeks, and renewed the water once and a while (hot water) to remove solution impurities. After this step they were cleaned with ethanol and dried in an air chamber at 50°C for 48h.

The earrings made from pure silver were placed in an inhibitor solution of 3% chlorophyll in ethanol and left there for 3 hours [Annexes IV] [24, 39], then with ethanol and dried in an air chamber at 50°C for 48 hours. Finally the earrings were varnished with an acrylic resin of 10% Paraloid B72[®] in acetone. For assembly the lost fragments and granules it was used a solution of 10% Paraloid B72[®] diluted in acetone, under the binocular. Only one earring (Earring 13) was needed to be assembled with a stronger adhesive as cyanoacrylate adhesive, Super Glue Alteco[®], since both fragments were always disassemble. The fragments and granules not assembled were storage in indented eppendorfs.

The state of preservation of the earrings after the conservation and restoration treatments in general was satisfactory [figure 3.1]. The metallic surfaces now are homogeneously with less tarnishing and more glossy. In some cases it wasn't possible to remove all the black corrosion products, mainly copper oxide (CuO), so there are remains of localized blackening. The earrings are now consolidated and protected with an inhibitor and a layer of an acrylic resin. However, the objects are still brittle and fragile so they should be handled carefully.



Figure 3.1 – Silver artefacts after the intervention.

For removal of the Paraloid B 72[®] used in the assembly and protection of the earrings can apply acetone. The Super Glue Altec[®] used in the earring E13, can also be soften with acetone, and dissolved in nitromethane, dimethyl sulfoxide, methylene chloride and gamma-butyrolactone.

3.3 Maintenance Proposal

The silver artefacts were storage in Minigrip[®] bags wrapped in silver inhibitor paper, Silver Saver[®] from Daubert VCL, INC. The assembled earrings were storage in a

polypropylene box with a polyethylene foam base and wrapped in a Japanese paper parcel, covered with a silver inhibitor paper, Silver Saver[®] [Annexes V, fig 4.72].

The inhibitor paper must be renewed every two years once for a new tarnishing-inhibitor tissue or cloth. The Minigrip[®] bags can also be renewed or changed to a polyethylene hermetic box.

It must be stored in stable conditions of relative humidity, in dry environments. It is recommended to add silica gel and active charcoal inside the cupboard where the objects will be stored. These earrings can't be stored in contact with any sulphur-containing material, as cloth, rubber, paint, casein glue, wool and certain wood.

The artefacts should be controlled regularly to check for any signs of active corrosion that may appear, as for example copper carbonates. And the acrylic resin varnish should be renewed regularly (every five years).

In the case the earrings are going to exhibition, they must be placed in a showcase also without any sulphur-containing material and with a controlled environment of relative humidity and temperature.

3.4 Discussion and Conclusion

In general, the earrings are now in a better conservation state and with a homogeneous patina. Nevertheless, this silver set has a particular feature since they suffered a fire, resulting in corrosion products that have hardened. Furthermore, intercrystalline corrosion makes the earrings very brittle, so the intervention procedure was chosen first by cleaning with ethanol and a wooden stick to remove the maximum of dirt. It was minimized the cleaning with scalpel and ultrasonic needle, since it was not appropriate for these brittle objects. The chemical cleaning was the main cleaning procedure for this set. Methyl cellulose combined with the chemical solutions was used to avoid deep penetration in the objects' core. The corrosion products were very hard to remove (which their removal could damage even more the objects) and it wasn't suitable to use higher solution concentrations since they contain risks for the objects, so some earrings still have slightly tarnished. Though, the objective was to remove dirt and eventually corrosion products covering details of the earrings. The silver sulphide layer is protective and therefore is not absolutely necessary to remove. The object will always tarnish back, so the tarnishing layer removal will slowly erode the object. Therefore, the better option for archaeological silver conservation is preventive conservation.

Chemical cleaning with thiourea can be very dangerous for archaeological silver if used in incorrect application, as was the case. Thiourea can dissolve silver chlorides even in the

metallic core. However, after the thiourea application, the earrings were placed in hot water and dried in an air chamber, which wasn't the correct procedure, since it should have been dried in ethanol and air dryer, then varnished with the acrylic resin. Due to this, it leaves a slightly yellow tarnishing which was removed with EDTA disodium and formic acid.

4. Annexes

4.1 Annexes I

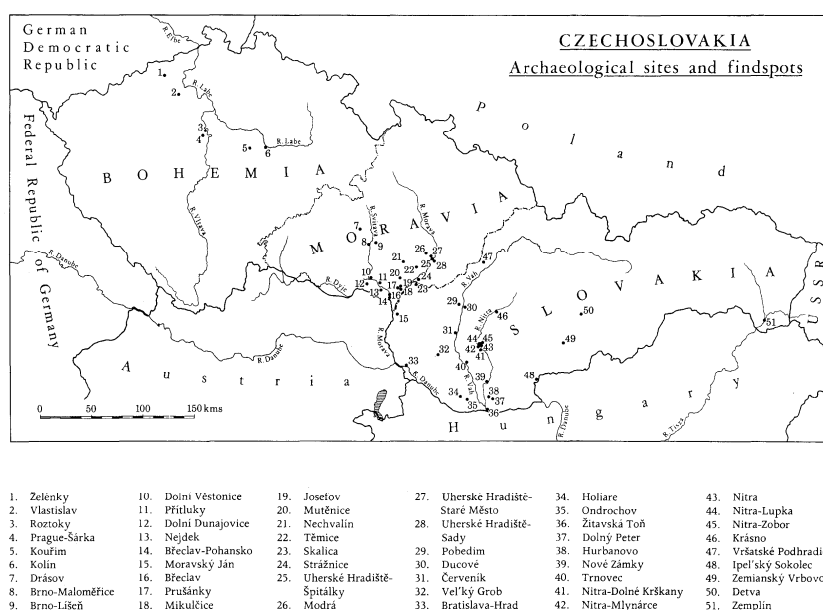


Figure 4.1 – Archaeological sites from the Great Moravia Empire [1].



Figure 4.2 – Washing away the debris from the fire with the aim to save some minor findings (Photo: Martin Frouz) [2].



Figure 4.3 – Box with some silver earring found in the debris (Photo: Martin Frouz) [2]



Figure 4.4 – Woman with temple rings in her ribbon [6].



Figure 4.5 – Girl with jewellery from the Naszacowic deposit, Małopolskie, Poland [5].

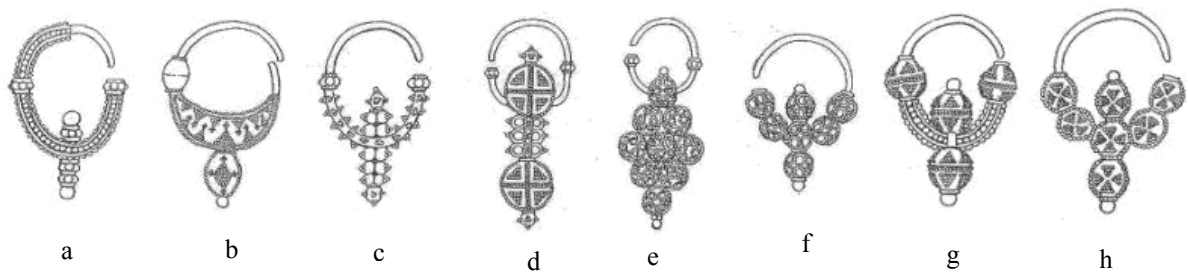


Figure 4.6 – Great Moravia earrings typology according to B. Dostála [8]: a – Earrings decorated on the upper arch²; b – Moon shaped earrings; c – Earrings with „grapes” shape; d – Column earrings; e – Nine cups’ earrings; f – Seven cups’ earrings; g – Four drum’ earrings; h – Seven drum’ earrings

² Note that the earring shape suggests that can not be placed in the ear since the lock is too narrow. However, it is possible to be hanging on a hair ribbon.

4.2 Annexes II

Table 4.1 – Standard reduction potentials, E° , for some reduction reactions relevant to silver corrosion. The standard conditions are: 25°C, 1 atmosphere pressure, and concentrations of 1 mole per litre for dissolved species [19, 23].

Reaction	E° (volts)
$\text{AgO}(s) + 2\text{H}^+ + e^- \leftrightarrow \text{Ag}^+ + \text{H}_2\text{O}$	+1.77
$\text{Au}^+ + 1e^- \leftrightarrow \text{Au}(s)$	+1.69
$\text{Ag}_2\text{O}_3(s) + 6\text{H}^+ + 4e^- \leftrightarrow 2\text{Ag}^+ + 3\text{H}_2\text{O}$	+1.67
$\text{Au}^{3+} + 3e^- \leftrightarrow \text{Au}(s)$	+1.50
$\text{Cl}_2 + 2e^- \leftrightarrow 2\text{Cl}^-$	+1.36
$\text{Ag}^+ + 1e^- \leftrightarrow \text{Ag}(s)$	+0.79
$\text{O}_2(g) + 2\text{H}^+ + 2e^- \leftrightarrow \text{H}_2\text{O}_2(aq)$	+0.70
$\text{Cu}^+ + 1e^- \leftrightarrow \text{Cu}(s)$	+0.52
$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \leftrightarrow 4\text{OH}^-$	+0.40
$\text{Ag}_2\text{O} + \text{H}_2\text{O} + 2e^- \leftrightarrow 2\text{Ag} + 2\text{OH}^-$	+0,34
$\text{Cu}^{2+} + 2e^- \leftrightarrow \text{Cu}(s)$	+0,34
$\text{AgCl} + 1e^- \leftrightarrow \text{Ag} + \text{Cl}^-$	+0,22
$\text{AgBr} + 1e^- \leftrightarrow \text{Ag} + \text{Br}^-$	+0,07
$2\text{H}^+ + 2e^- \leftrightarrow \text{H}_2(g)$	0
$\text{Ag}_2\text{S} + 2e^- \leftrightarrow 2\text{Ag} + \text{S}^{2-}$	-0,71
$\text{Cu}_2\text{O} + \text{H}_2\text{O} + 2e^- \leftrightarrow 2\text{Cu} + 2\text{OH}^-$	-0,36
$\text{SO}_4^{2-} + \text{H}_2\text{O} + 2e^- \leftrightarrow \text{SO}_3^{2-} + 2\text{OH}^-$	-0,92
$2\text{SO}_3^{2-} + 2\text{H}_2\text{O} + 2e^- \leftrightarrow \text{S}_2\text{O}_4^{2-} + 4\text{OH}^-$	-1,12

Example of an electrochemical reaction that can occur in the corrosion cell of a silver object in aerobic conditions [14]:

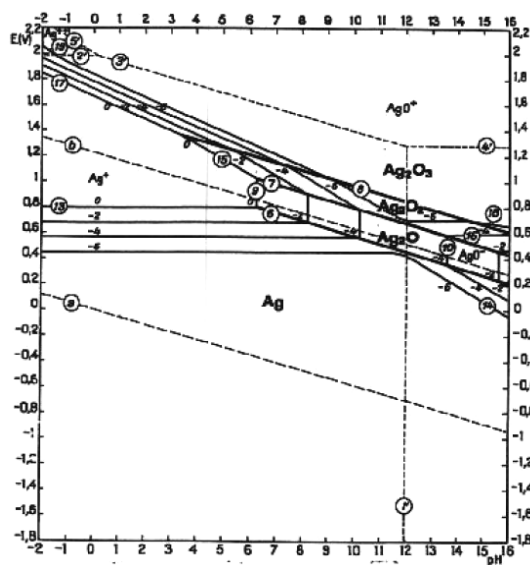
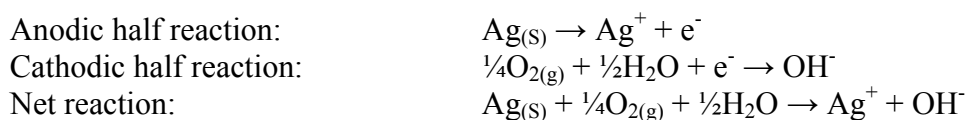


Figure 4.7 – Pourbaix diagram for silver in water at 25°C.

Table 4.2 – Most common silver corrosion products found in tarnished objects [14, 18].

Mineral name	Chemical Name	Chemical Formula	Colour
Acanthite	Silver (I) sulphide	α -Ag ₂ S	Black
Argentite	Silver (I) sulphide	β - Ag ₂ S	Black
Chlorargyrite	Silver (I) chloride	AgCl	White
Bromargyrite	Silver (I) bromide	AgBr	Yellow
Chalcocite	Copper (I) sulphide	Cu ₂ S	dark-grey

4.3 Annexes III

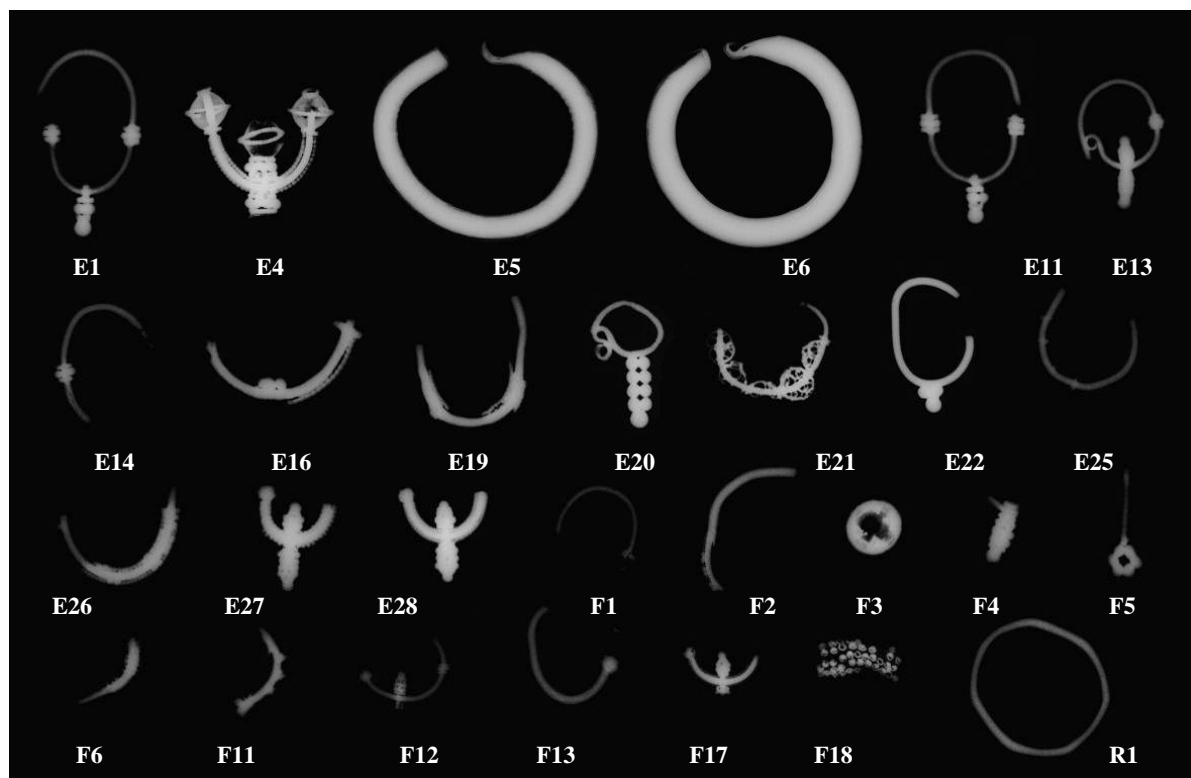


Figure 4.8 – Radiography of the set of the silver artefacts from Mikulčice. The earrings with substantial degree of mineralization are: E1, E4, E11, E13, E14, E25, F1, F2, F5, F6, F11, F12, F13 and F18.

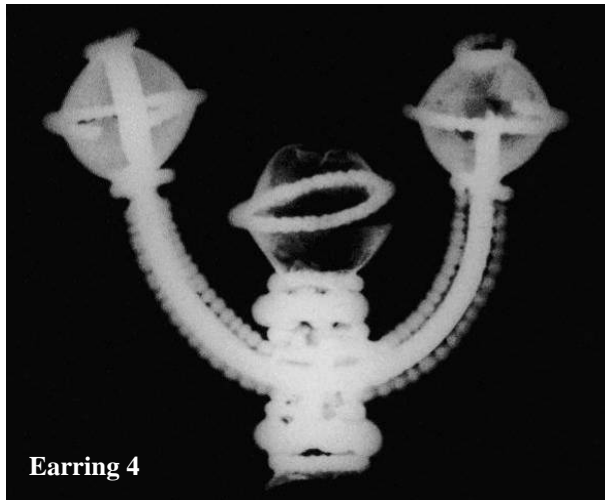


Figure 4.9 – Earring with granules in decoration and metallic deformed structure. The central sphere is more mineralized and fragile than the other side spheres. It is also possible to observe a support inside the side spheres.

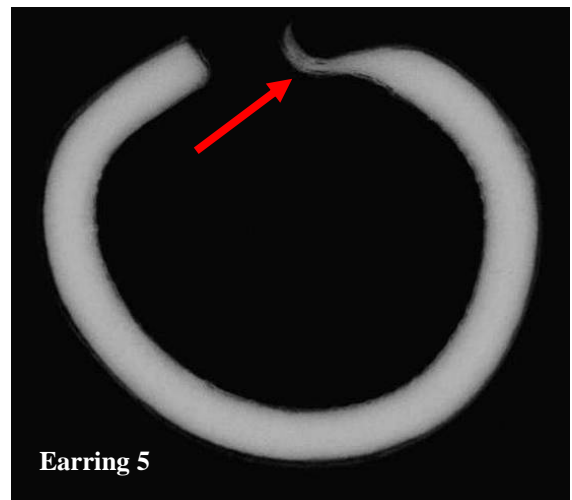


Figure 4.10 – Temple earring with foil around the base metal.



Figure 4.11 – Earring with dark grey and red corrosion products on the metallic surface (silver chlorides and cuprite), 25x.



Figure 4.12 – Earring with dark spots on the metallic surface, 15x.



Figure 4.13 – Earring with rusty patina, due to iron corrosion products contamination, 10x.



Figure 4.14 – Earring with rusty patina, due to iron corrosion products contamination, 20x.



Figure 4.15 – Earring with yellow and dark grey patina, respectively, tarnishing and silver chlorides, 25x.



Figure 4.16 – Earring with yellow patina, due to slightly tarnishing on the surface, 30x.

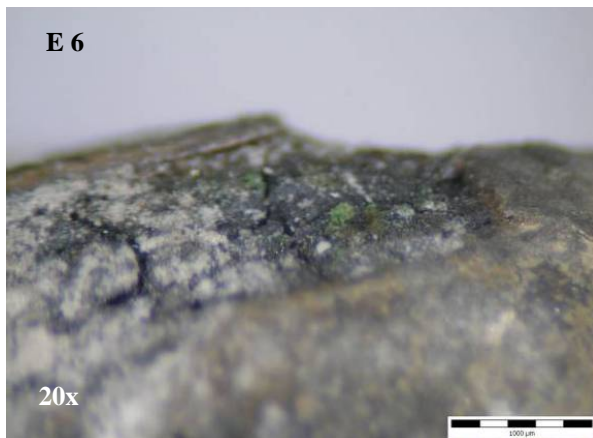


Figure 4.17 – Earring with green patina, of copper corrosion products, as copper carbonates and chlorides, 20x.



Figure 4.18 – Earring with bluish patina of copper corrosion products, 10x.



Figure 4.19 – Earring with fractures and cracks along the metallic surface, 10x.



Figure 4.20 – Temple earring with fractures and silver foil loss, 12x.

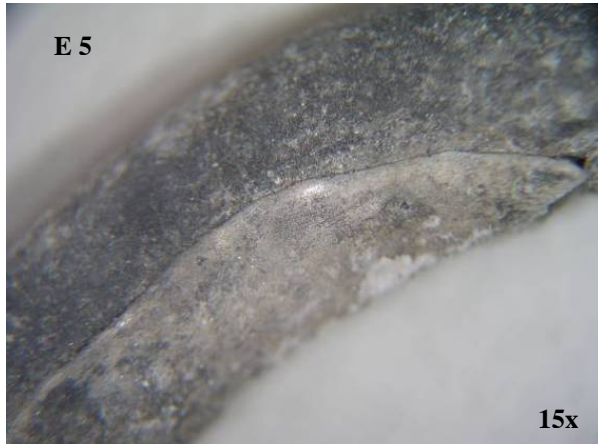


Figure 4.21 – Temple earring with silver foil,



Figure 4.22 - Earring that has a gilded layer well preserved, 20x.

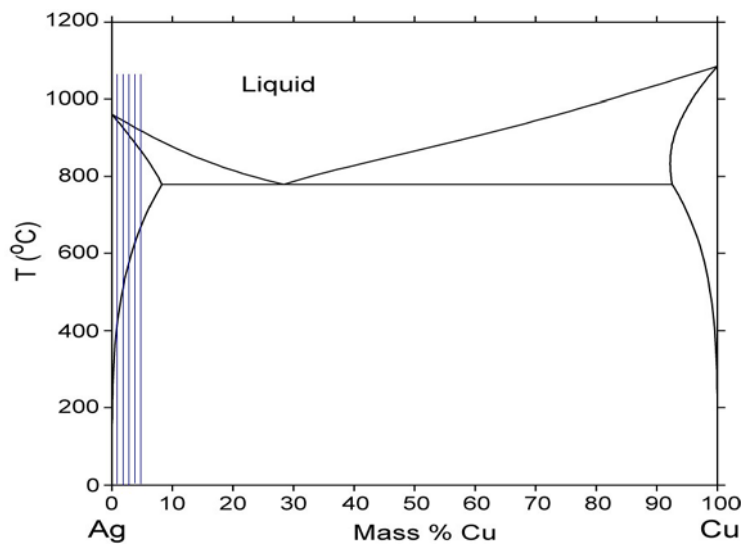
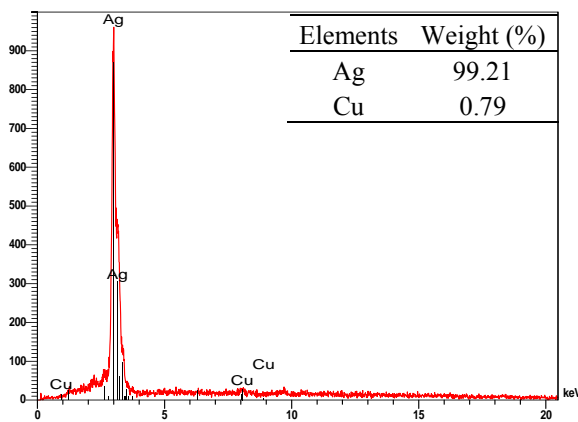
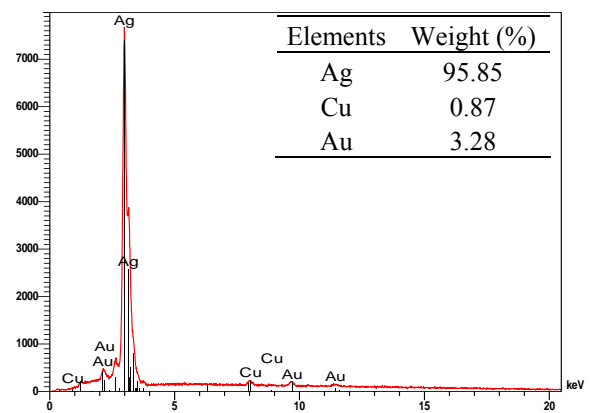


Figure 4.23– Phase diagram of Ag-Cu alloys.



Graphic 4.1 - Elemental analysis made in a point of the fracture surface or the Fragment 12.



Graphic 4.2 - Elemental analysis made in a point of a scratched surface of the Earring 26.

Table 4.3 – Metal alloys and decoration methods for the 28 earrings analyzed in microprobe.

	Copper plated with silver	Binary silver alloy gilded with Ag-Au alloy	Pure Silver
E1			X
E4			X ^{3 4}
E5	X (silver foil)		
E6	X (silver foil)		
E11			X ⁴
E13		X	
E14			X ²
E16			X ²
E19			X ²
E20	X		
E21			X ^{3 5}
E22			X
E25			X
E26			X ¹
E27		X ⁶	
E28		X ⁷	
F1			X
F2			X ¹
F3			X ²
F4			X
F6			X ¹
F11			X
F12			X ¹
F13			X ¹
F17			X
F18			X ¹
R1			X



Figure 4.24 – Base of the five granules circle from the central wire of the Earring 16, 15x.

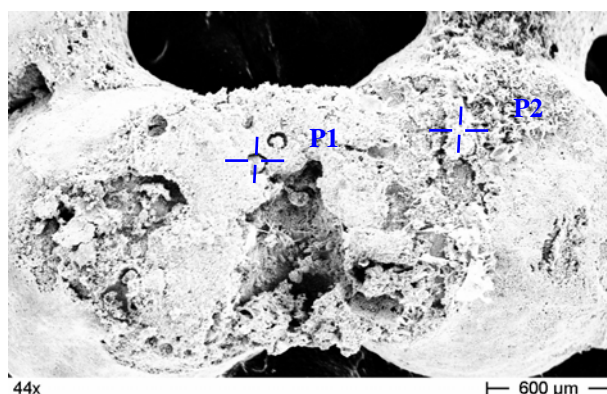


Figure 4.25 – Base of the five granules circle from the Earring 16, SEI – 60x.

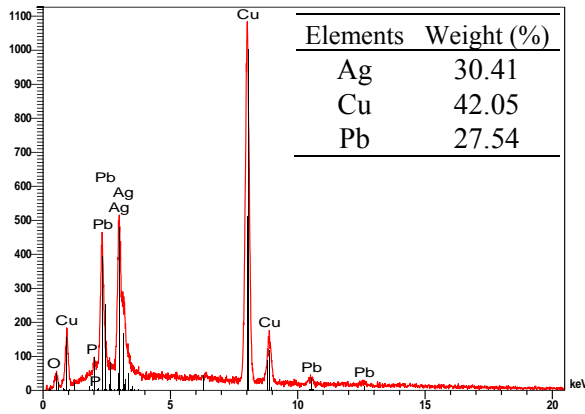
³ It has traces of gold

⁴ It has traces of lead

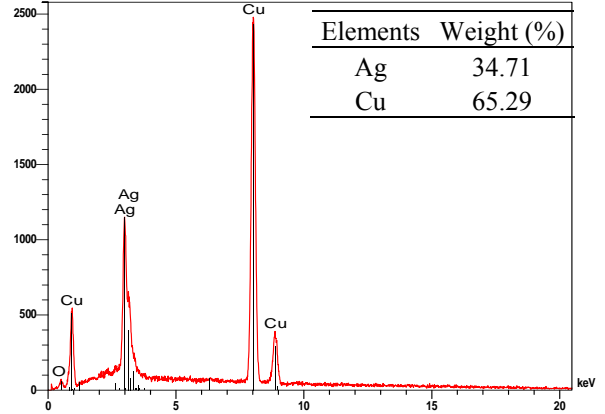
⁵ It has traces of zinc

⁶ Lower content of gold – white gold layer

⁷ Base with high silver content, and gilding layer with high gold content



Graphic 4.3 - Elemental analysis made in a point of the granule solder of the Earring 16 – point 1 figure 25.



Graphic 4.4 - Elemental analysis made in a point of the granule solder of the Earring 16 – point 2 figure 26.

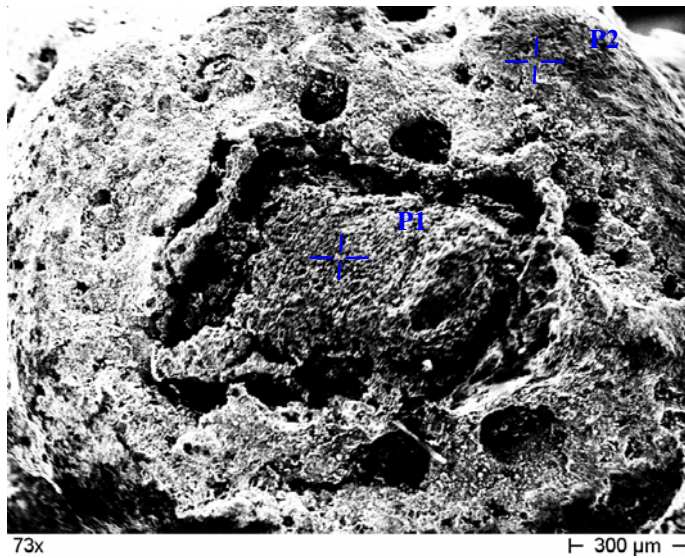
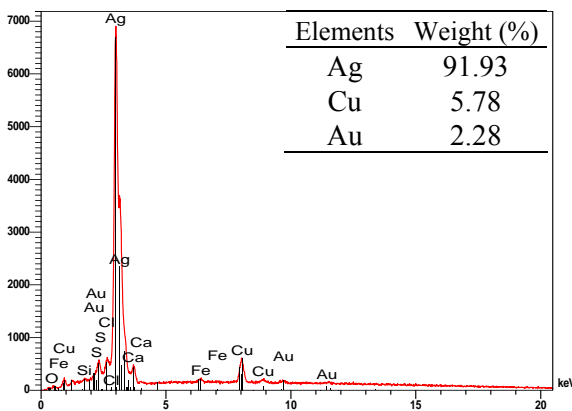
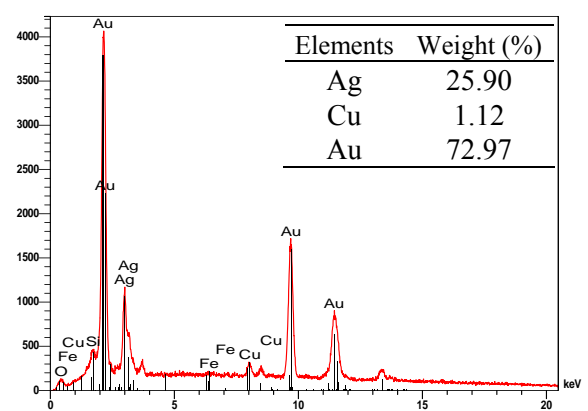


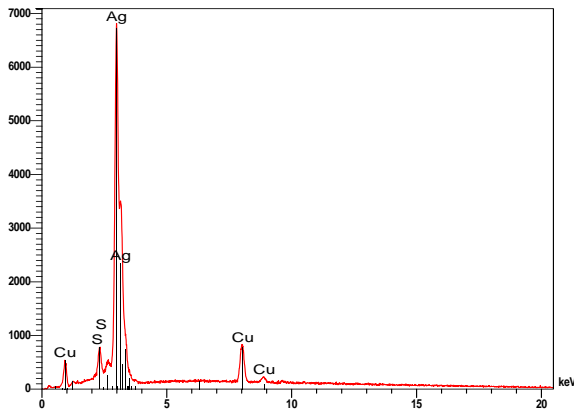
Figure 4.26 – Wire fracture of the gilded Earring 28, corresponds to figure 21, SEI - 100x.



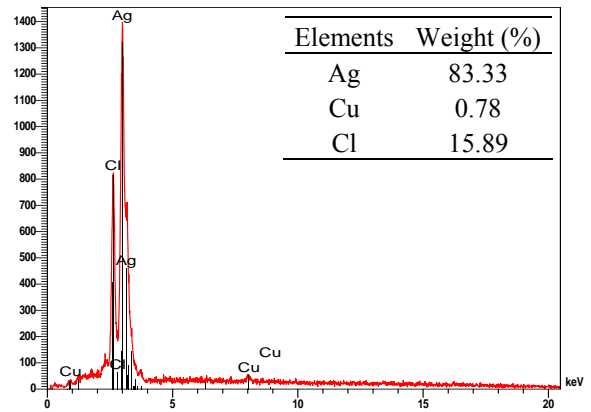
Graphic 4.5 - Elemental analysis made the Earring 28 wire fracture metal base - point 1 of figure 26.



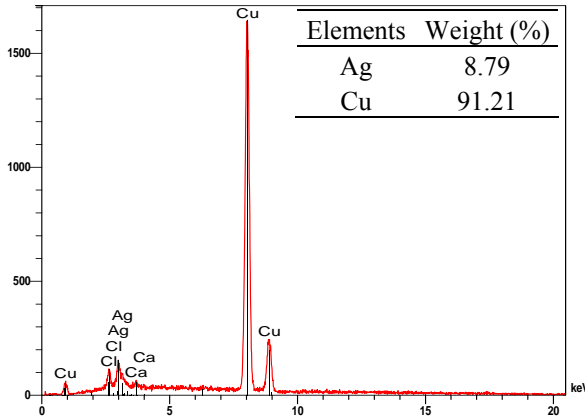
Graphic 4.6 - Elemental analysis made the Earring 28 wire fracture gilding layer – point 2 of figure 26.



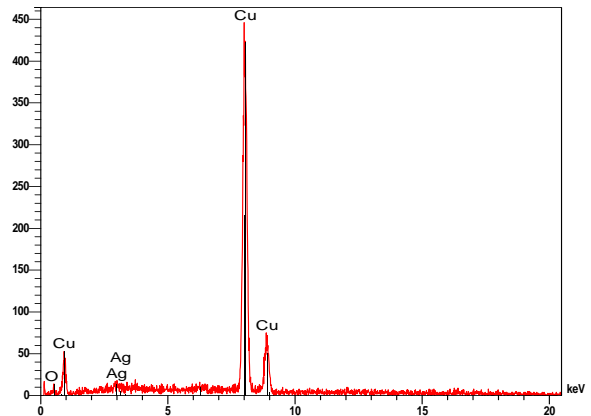
Graphic 4.7 – Elemental analysis made in a point of the central wire of the Fragment 17.



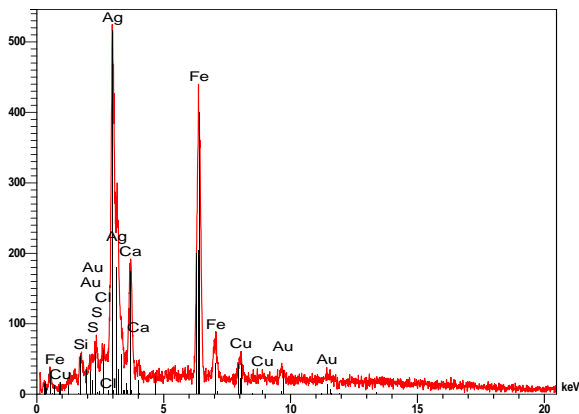
Graphic 4.8 – Elemental analysis made in a point of the central wire end of the Earring 25.



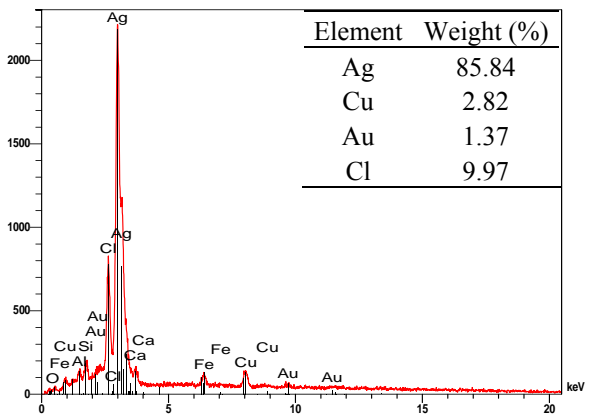
Graphic 4.9 – Elemental analysis made in a point of the dark red patina of the Earring 1 wire end.



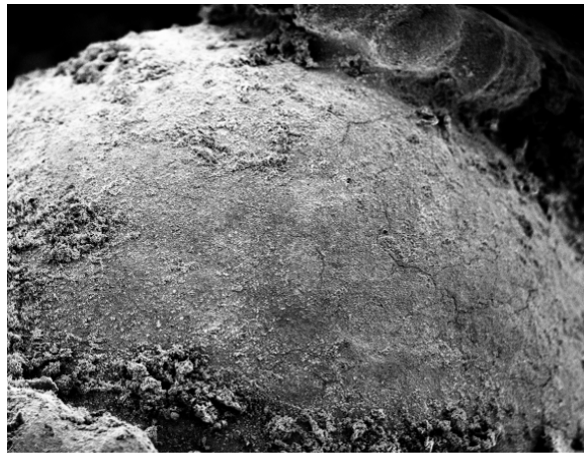
Graphic 4.10 – Elemental analysis made in a point of the base metal of the Temple earring 6.



Graphic 4.11 – Elemental analysis made in an area of the rusty patina of the fragment 18.

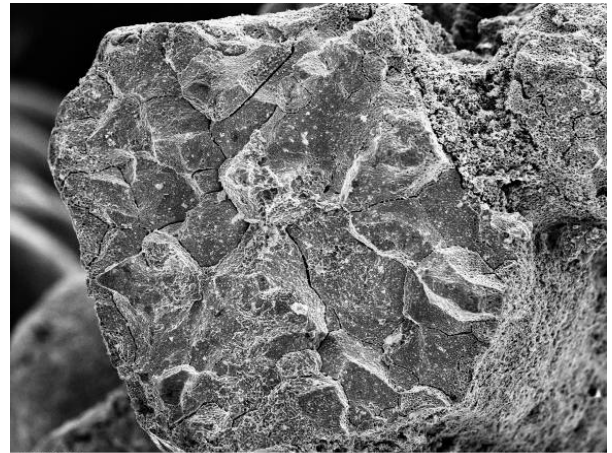


Graphic 4.12 – Elemental analysis made in a point of the yellowish patina of the Fragment 6 surface.



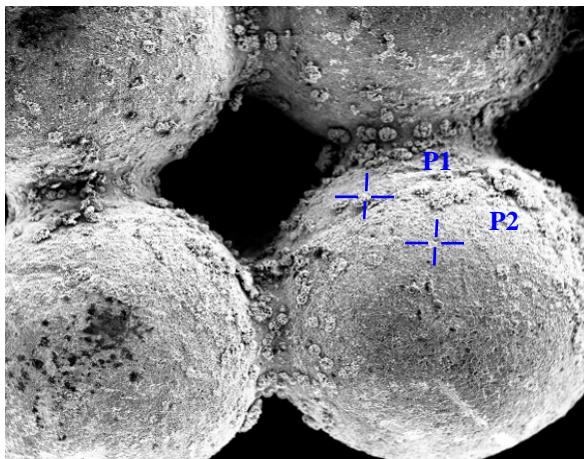
37x 700 μm

Figure 4.27 – Microcracks on the surface of one decorative sphere from the Earring 4, SEI - 50x.



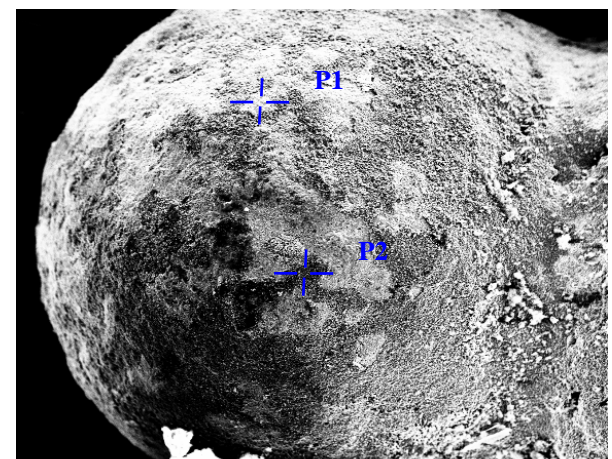
1,1E002x 200 μm

Figure 4.28 – Wire fracture of the F6, SEI - 120x.



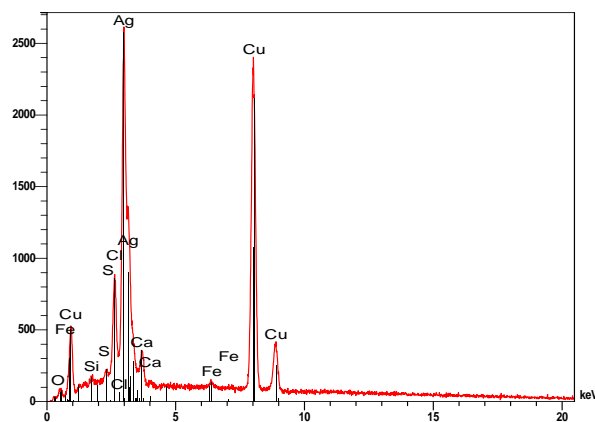
37x 700 μm

Figure 4.29 – Localized segregation of copper corrosion products on the surface of the granules of the Earring 20, SEI - 50x.

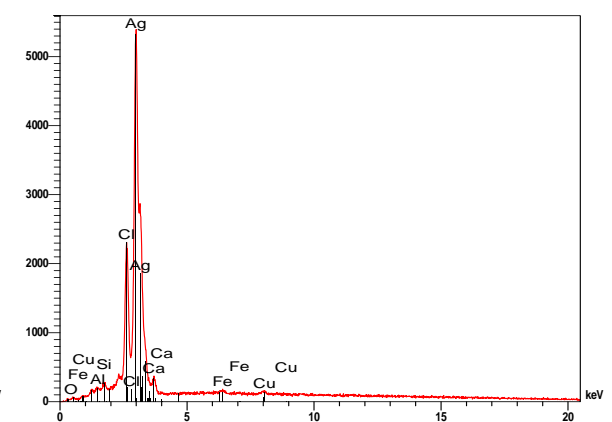


73x 300 μm

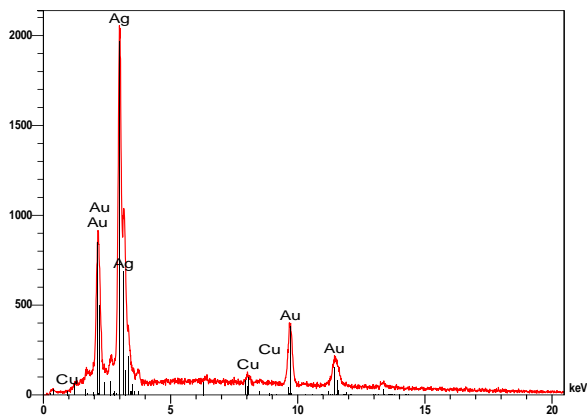
Figure 4.30 – Uniform segregation of copper corrosion products above the gilded layer of the Earring 13 granule, SEI - 100x.



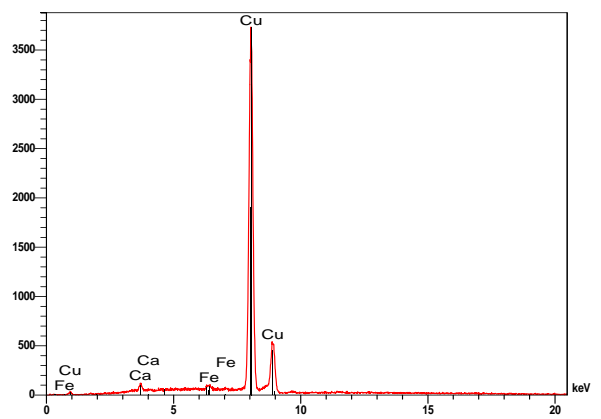
Graphic 4.13 – Elemental analysis made in a point on a dark spot of the Earring 20 – Point 1 of figure 29.



Graphic 4.14 – Elemental analysis made in a point on the metallic surface of the Earring 20 – Point 2 of figure 29.



Graphic 4.15 – Elemental analysis made in a point on the gilding layer of the Earring 13 (bright area) – Point 1 of figure 30.



Graphic 4.16 – Elemental analysis made in a point on the copper segregation layer of the Earring 13 (dark area) – Point 1 of figure 30.



Figures 4.31 – F6 earring fragment before the metallography.



Figure 4.32 – Macro-photo of F6 after break up with fragments identification.



Figures 4.33 – Photos of the all sides of the F6' fragment n° 2, 15x.



Figure 4.34 – Cross section of the F6' fragment n° 2, where is possible to observe the yellow patina only around the metallic surface.

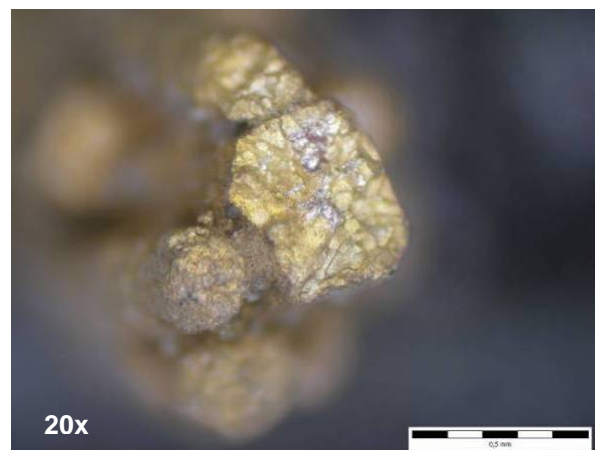


Figure 4.35 – Fracture surface from the earring fragment 6.

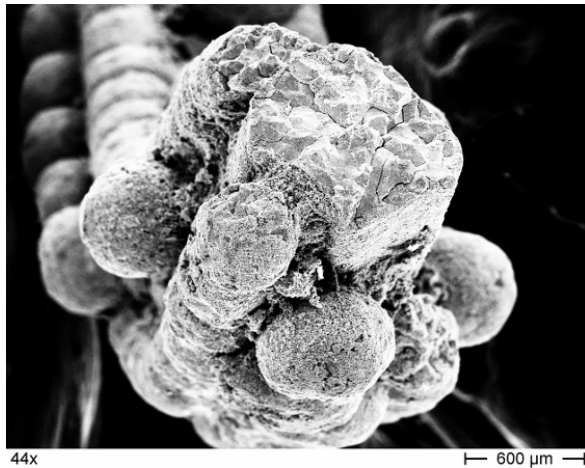


Figure 4.36 – Detail of the fracture surface from the earring fragment 6, SEI - 60x.

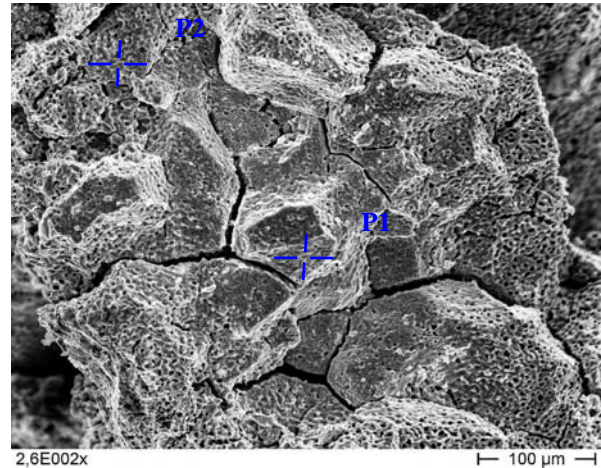
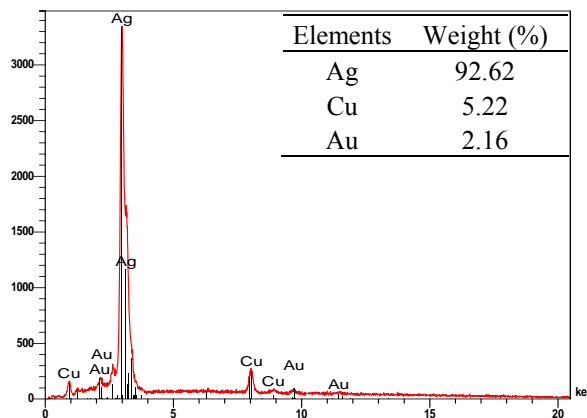
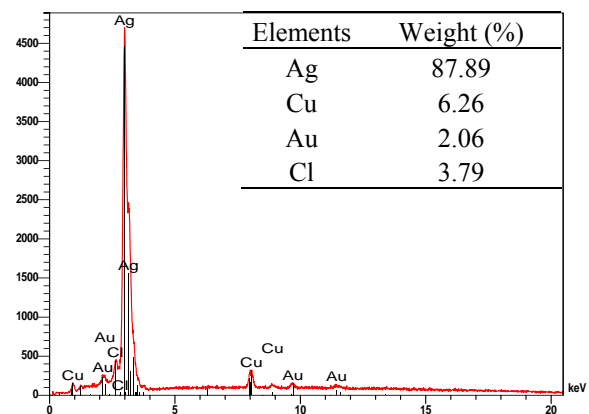


Figure 4.37 – Close-up view of the fracture surface of the earring fragment 6. Heavy intergranular corrosion damage resulting in separation of individual grains and corrosion pits on grain surfaces, SEI - 350x.



Graphic 4.17 - Elemental analysis made a point of the fracture surface - point 1 of figure 37.



Graphic 4.18 - Elemental analysis made a point of the fracture surface - point 2 of figure 37.

Preparation of the earring fragment 6 sample for metallography

Firstly the sample was cleaned with acetone to degrease and remove any dust, dirt and carbon resin from the microprobe analysis. Then it was placed in a cylindrical form in the vertical position. It was mixed a portion of 5:1 by weight of epoxy resin and hardener Buehler® Epoxicure™ Resin, and mixed very well and waited for 5 min to all the air bubbles come out. Then, the prepared resin was cast in the cylindrical form and left to harden for 24 hours.

The preparation of metallographic sample was performed in two steps. The first step was grinding on silicon carbide sandpapers under the water. It was used different sandpapers

grains size, starting with the bigger to the smaller grain sizes (P400, P800, P1200, P2500, and P4000). The paper was paced on a rotating plate, and every time which was changed the polishing paper, the sample was placed in the perpendicular position with respect to the last grinding step (to remove the scratches from the last grinding paper). The second part of the preparation was polishing with the diamond paste, also with different diamond grain sizes (D3, D2, D0,7), under the wetting with solution of glycerine and ethanol. When the samples was enough polished, it was washed in water with detergent, and then dried with pure ethanol and with the hair-drier.

However, after the first step it was seen that it was some air bubbles next to the sample, which can accumulate grind and damage the sample surface in the polishing procedure. So, it was add more resin with hardener in the bubble gaps by syringe as explained before.

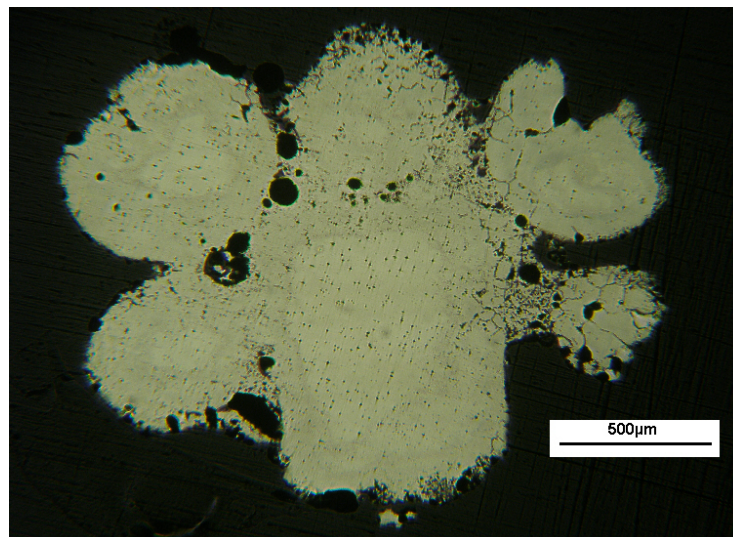


Figure 4.38 – Cross section of F6' fragment n° 2 after polish, 50x.

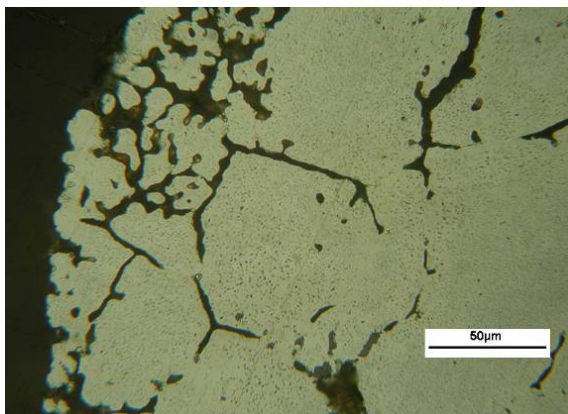


Figure 4.39 – Detail of a granule border with severe intergranular corrosion damage, 500x.

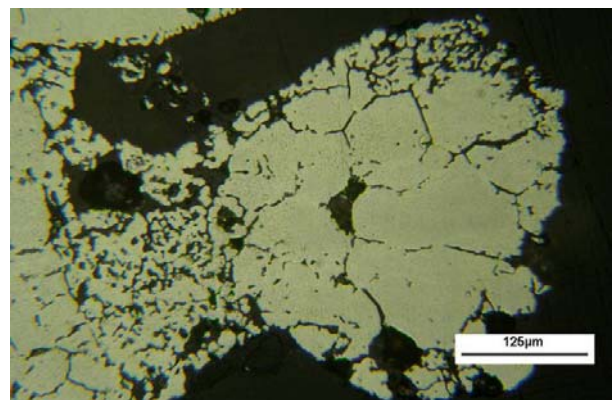


Figure 4.40 – Granule of the earring fragment 6, 200x.

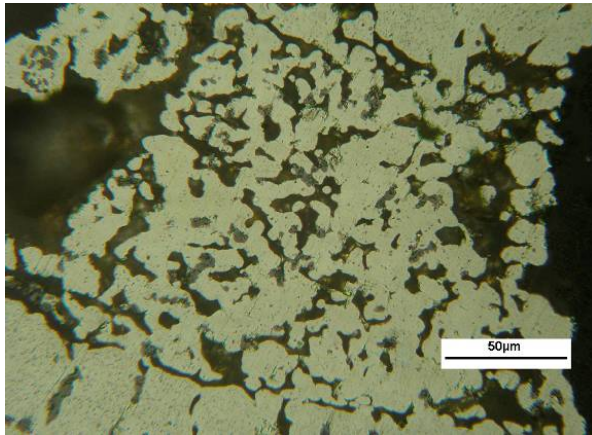


Figure 4.41 – Detail of the granule solder area, 500x.

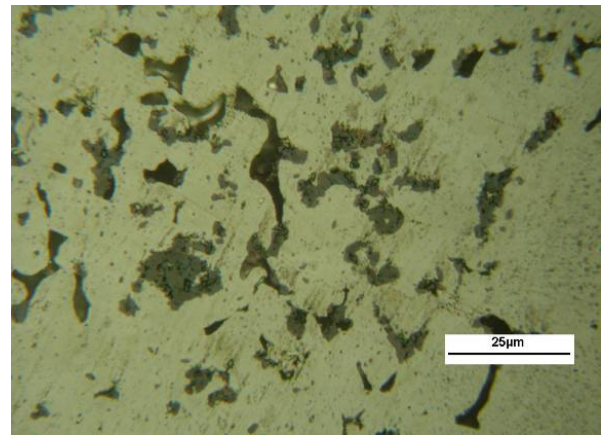


Figure 4.42 – Detail of the granule solder area grey compound, 1000x.

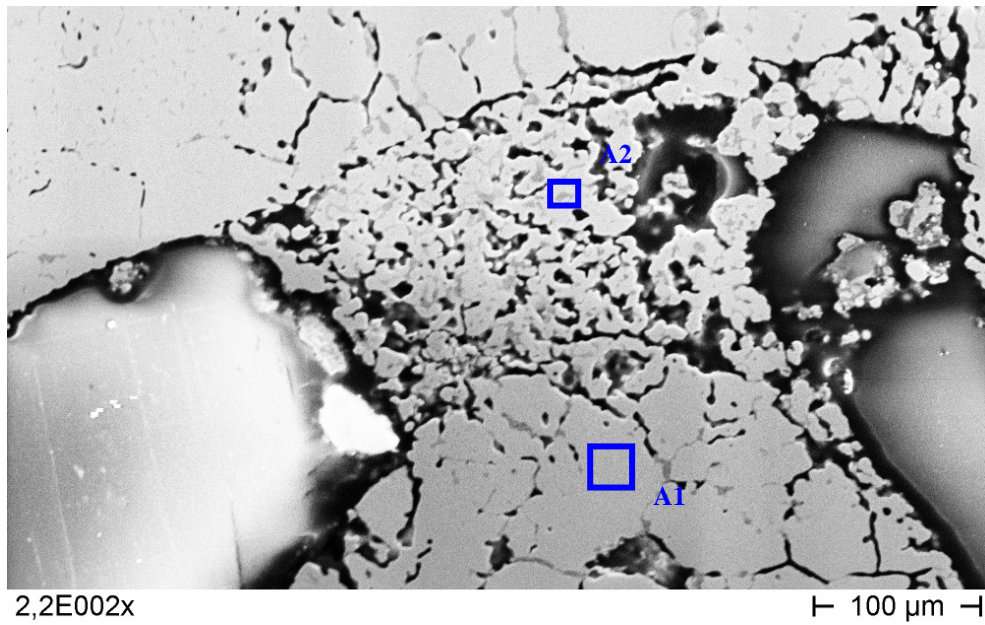
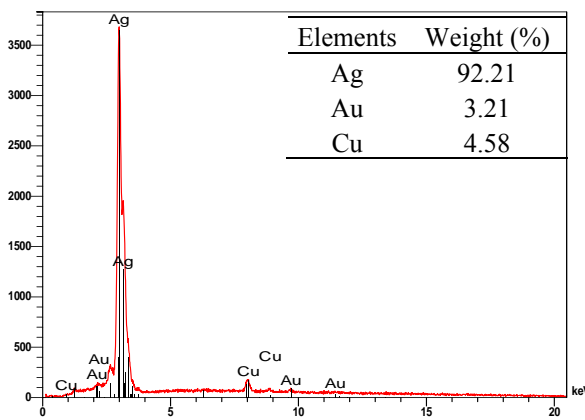
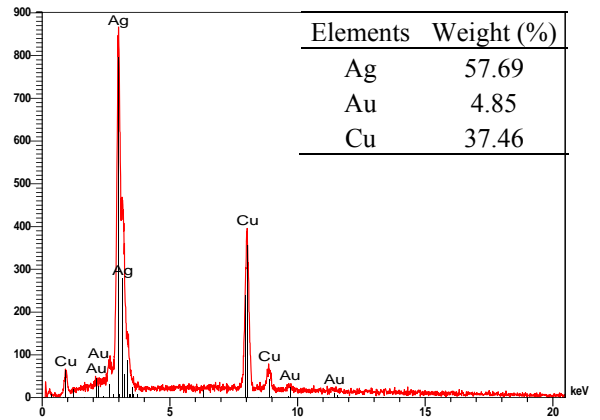


Figure 4.43 – Detail of the analysed solder area, SEI - 300x.



Graphic 4.19 - Elemental analysis made a solder area of the granule surface – area 1 of figure 43.



Graphic 4.20 - Elemental analysis made a solder area of the granule surface – area 2 of figure 43.

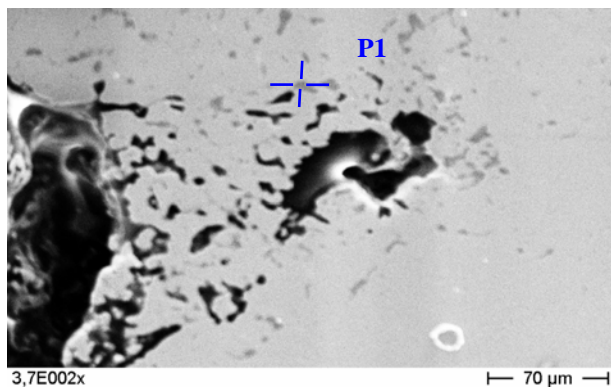
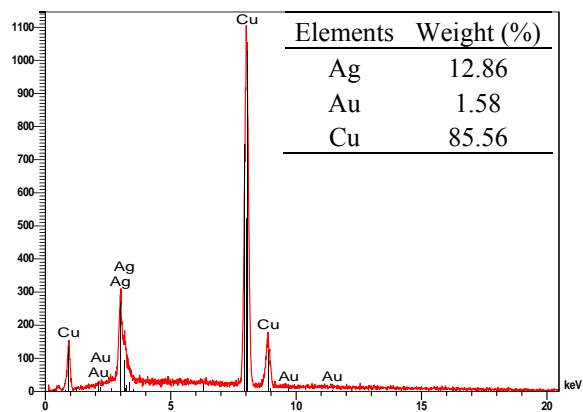


Figure 4.44 – Detail of a solder area, SEI - 500x.



Graphic 4.21 - Elemental analysis made in a dark grey spot next to solder area, from figure 44.

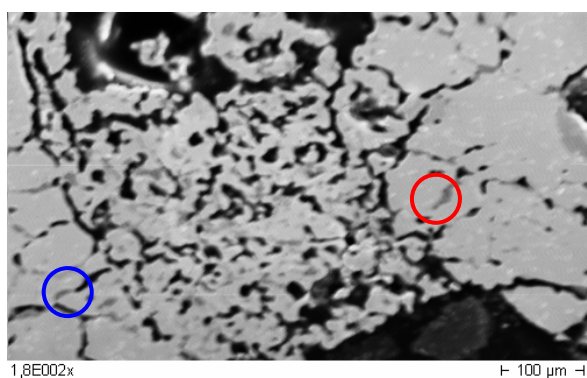


Figure 4.45 – Solder area of the small granule of the earring fragment 6, SEI – 500x.

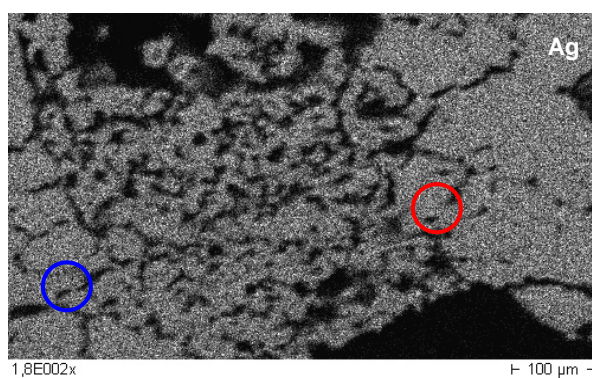


Figure 4.46 – Elemental distribution of Ag map, 500x.

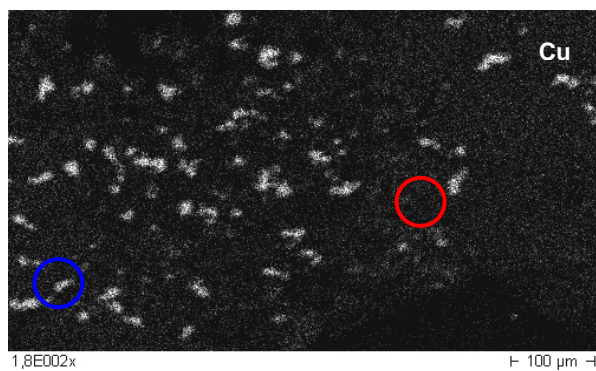


Figure 4.47 – Elemental distribution of Cu map, 500x.

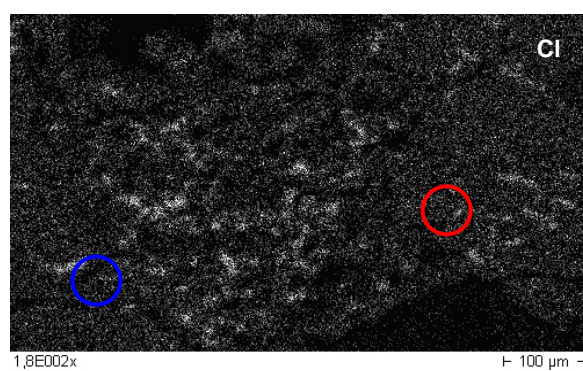


Figure 4.48 – Elemental distribution of Cl map, 500x.

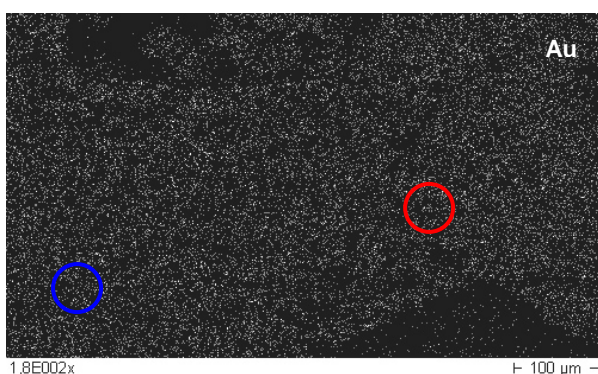


Figure 4.49 – Elemental distribution of Au map, 500x.

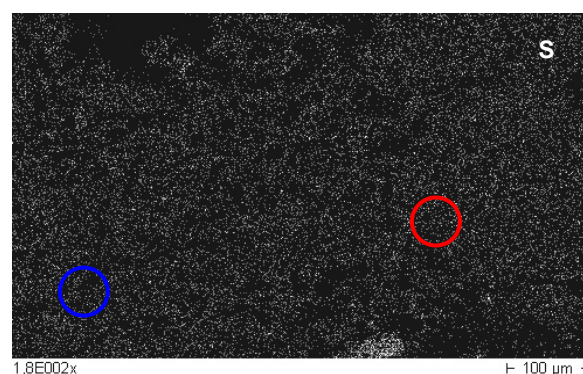


Figure 4.50 – Elemental distribution of S map, 500x.

Etching of the earring fragment 6 sample

Firstly the sample was degreased with ethanol, and then applied during few seconds in a freshly mixed solution of 5% Ammonium Persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and 5% of Potassium Cyanide (KCN) in water [29]. Then it was clean in current water for 10 minutes to remove all etchant and residues.

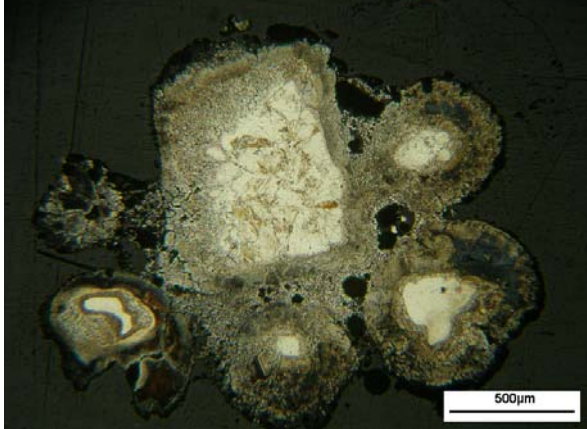


Figure 4.51 – Cross section of F6' fragment n° 2 after etching, 50x

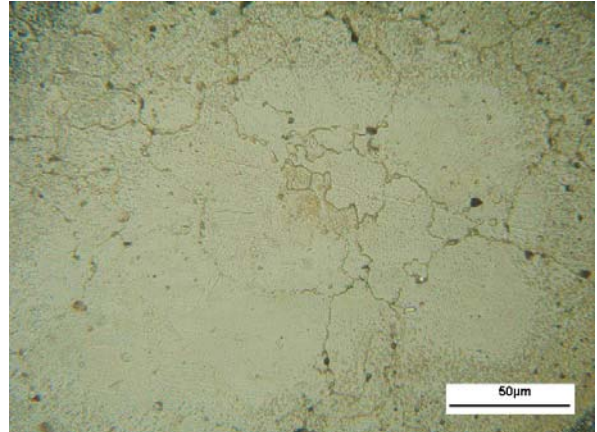


Figure 4.52 – Central wire metallic core after etching, 500x.

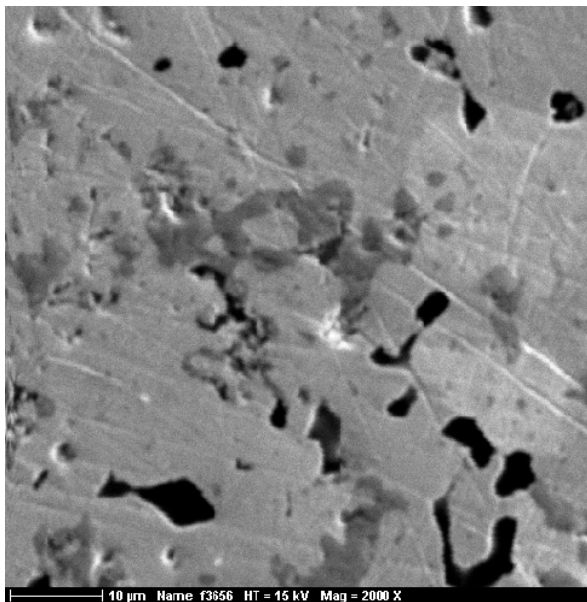


Figure 4.53 – Solder area of the small granule of the earring fragment 6, SEI – 2000x.

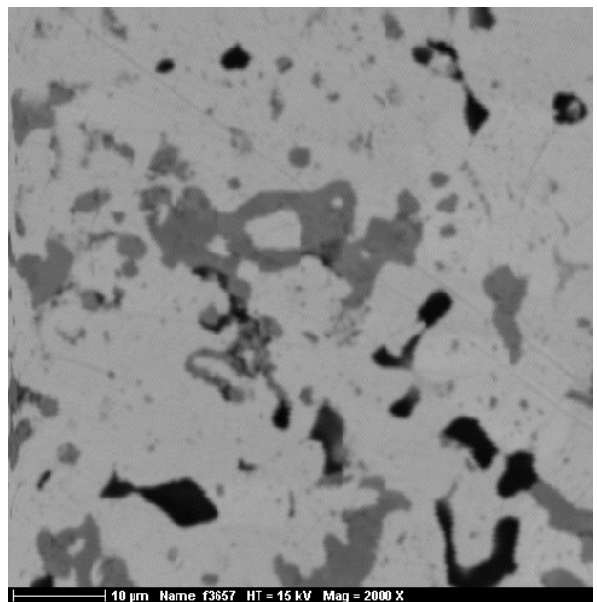


Figure 4.54 – Solder area of the small granule of the earring fragment 6, BSE – 2000x.

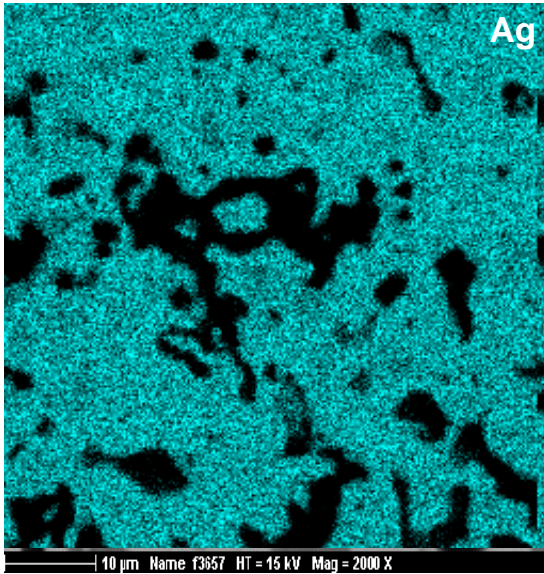


Figure 4.55 – Elemental distribution of Ag map, 2000x.

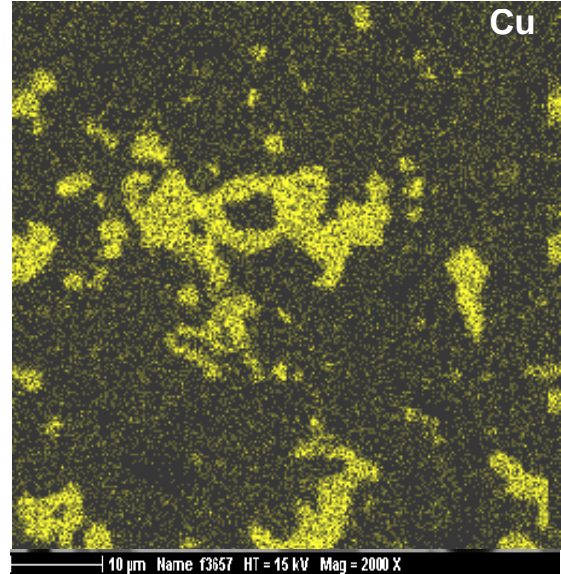


Figure 4.56 – Elemental distribution of Cu map, 2000x.

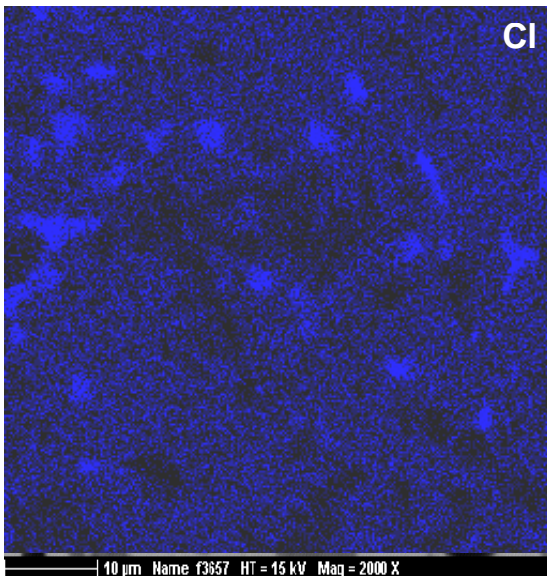


Figure 4.57 – Elemental distribution of Cl map, 2000x.

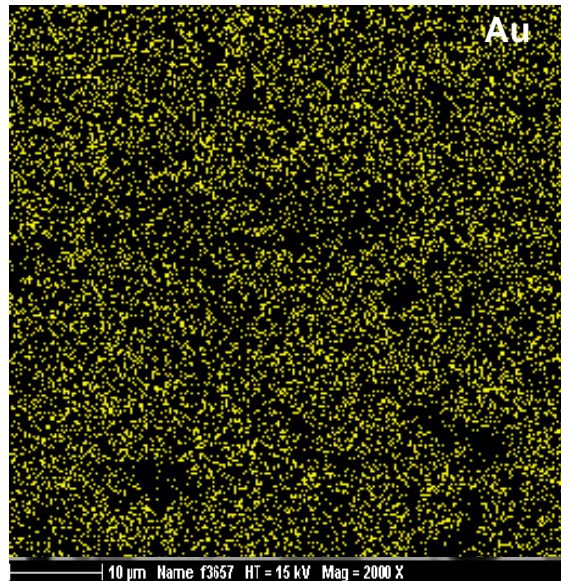


Figure 4.58 – Elemental distribution of Au map, 2000x.

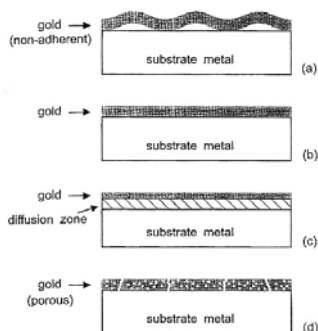


Figure 4.59 - Scheme of various gilding layer types (a) poorly secured, e.g., mechanically attached foil, (b) weakly secured, e.g., burnished or glued gold leaf, (c) strongly secured, e.g., diffusion bonded by heating burnished gold leaf, and (d) strongly secured but porous, e.g. fire-gilded or depletion gilded [23].

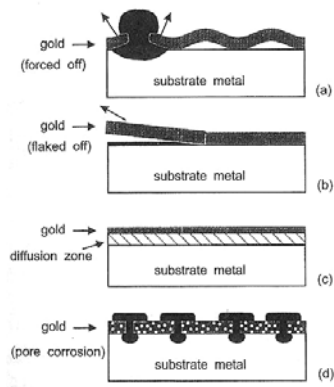


Figure 4.60 - Scheme of possible corrosion damage of the various gilding types (a) gilding layer forced off by corrosion of underlying metal, (b) flaking of gilding after deterioration of glue or corrosion of underlying metal, (c) no corrosion as long as is continuous and well secured, and (d) corrosion products of underlying metal passing through pores in gold [23].

4.4 Annexes IV

Silver samples installation in the exhibition room *Stories of Materials Treasury*, of the Museum of Decorative Arts, Prague.



Figure 4.61 – Sample n° 20 was placed inside a showcase, behind a chandelier.



Figure 4.62– Sample n° 33 was placed inside a showcase, behind a silver dish.



Figure 4.63 – Sample n° 69 was placed inside a showcase, behind a mirror.

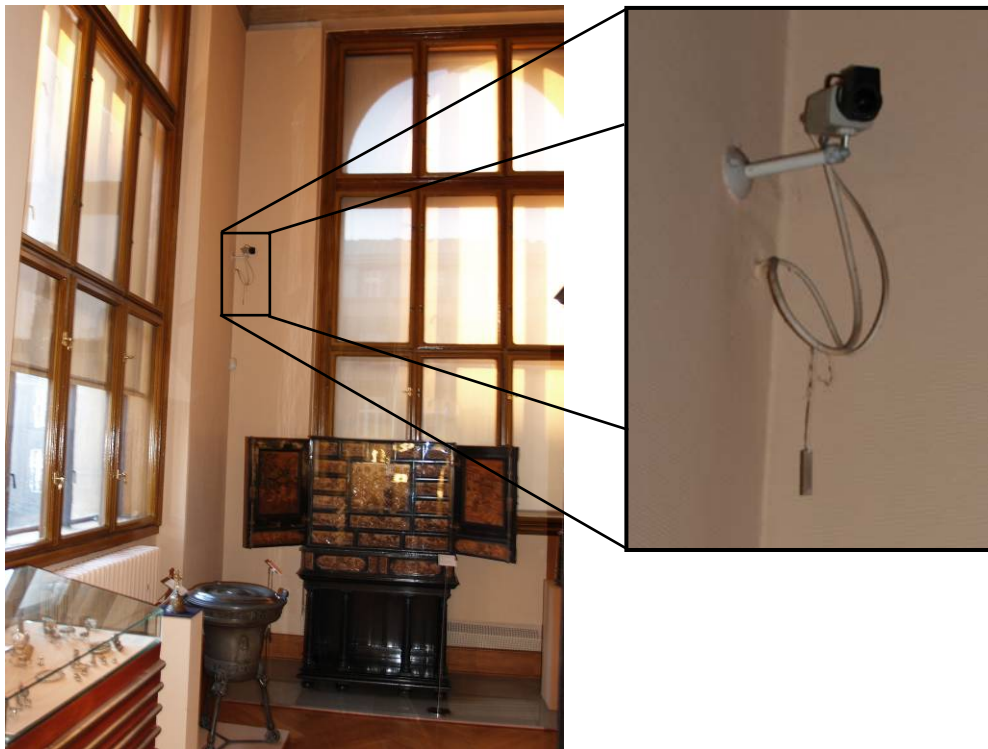


Figure 4.64 – Samples n° 71 and n° 72 were both placed in the two surveillance cameras of the exhibition room.

Silver samples installation in the storage room of the National Gallery Reservation, from the National Museum of Prague.



Figure 4.65 – Sample n° 18 was placed in the middle of the room.

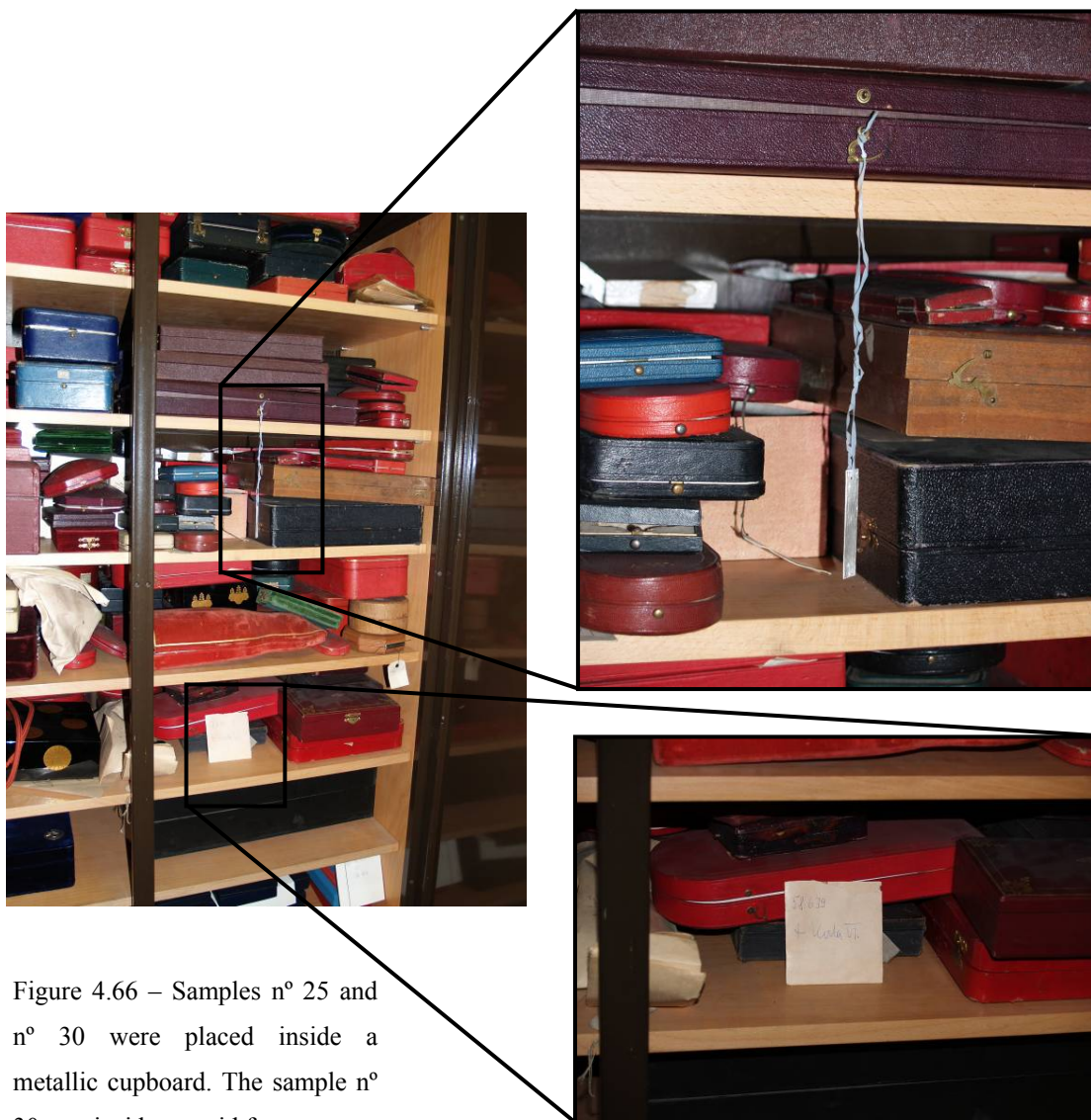


Figure 4.66 – Samples n° 25 and n° 30 were placed inside a metallic cupboard. The sample n° 30 was inside an acid free paper.



Figure 4.67 – Sample n° 68 was placed inside an acid free paper on a wooden cupboard.



Figure 4.68 - Sample n°27 was placed in inside a wooden cupboard without protection.

The silver samples installation in the exhibition room, *Decorations and Medals of European Countries in the 19th and 20th Centuries*, of the National Museum of Prague: it was placed six samples in the exhibition room: four inside the exhibition showcases (samples n° 8, 10, 16 and 32) and one outside, in the middle of the room (samples n° 29). It was not made photo-documentation of this samples exposition sites.

Table 4.4 – Minimum, maximum and average values of the humidity and temperature of the Museum of Decorative Arts and National Museum exhibition and storage rooms, during the six months of silver samples exposure time.

Museums	Humidity (%)			Temperature (°C)		
	Min.	Max.	Average	Min.	Max.	Average
MDA – Exhibition Room (02.12.2008 – 02.09.2009)	28,0	64,0	48,36	17,0	29,5	22,14
NM – Exhibition Room (24.02.2009 – 08.09.2009)	21,5	51,8	34,9	20,5	27,1	24,1
NM – Storage Room (12.12.2008 – 08.09.2009)	20,3	48,7	31,74	17,6	23,1	20,22

Galvanostatic Measurement Technique

The equipment used for the galvanostatic measurement technique was a gas tight corrosion cell with dissolved oxygen free electrolyte. The dissolved oxygen is removed from

electrolyte by purging with nitrogen for 2 hours before each electrochemical measurement. The traces of oxygen from the nitrogen were removed by passing through washing bottle with solution of vanadous chloride and zinc amalgam. During purging the electrolyte was stirred with electromagnetic stirrer. Before the samples measurements, firstly it was done blank test with clean pure silver sample to confirm the absence of oxygen in the electrolyte. The electrolyte used was a solution of 0,1M potassium chloride (KCl). The measuring circuit consists from measured silver samples as working electrode connected as the cathode and electrode from activated titanium as the anode. For monitoring of the potential of working measured electrode Ag/AgCl reference electrode was used. These three electrodes were connected to electrochemical corrosion measurement device GAMRY PC4 in galvanostatic measurements regime. It was applied a constant current density of $-0,12 \text{ mA/cm}^2$ at each silver sample, and time change of potential was monitored and recorded in the form of potential (E) versus time (seconds) relationships.

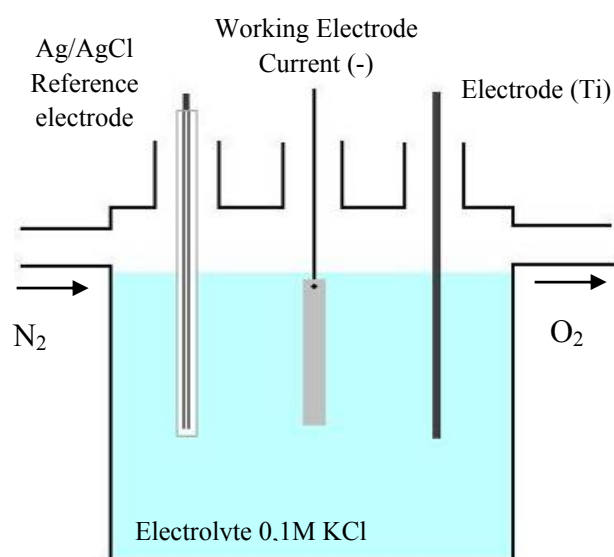
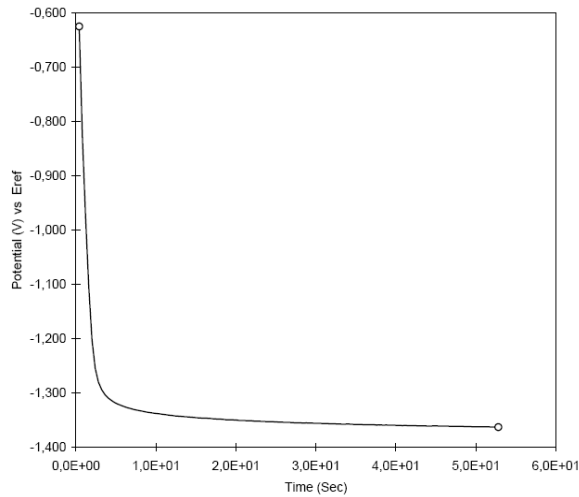
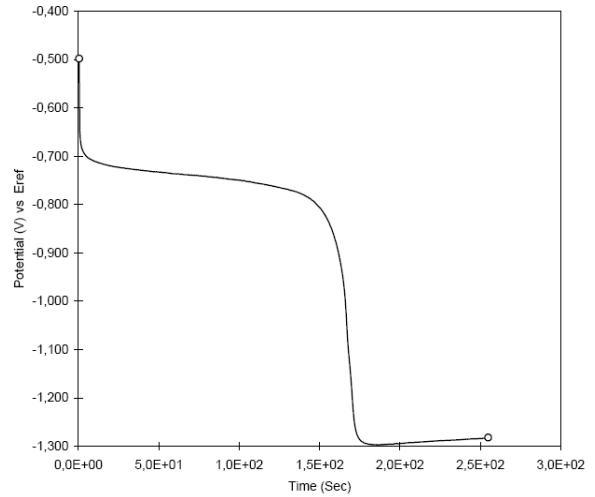


Figure 4.69 – Sketch of the galvanostatic measurement equipment.

Figure 4.70 – Galvanostatic measurement equipment.



Graphic 4.22 - Galvanostatic measurement on a pure silver sample.



Graphic 4.23 - Galvanostatic measurement on the sample n°71 from the Museum of Decorative Arts.

From potential vs time curves the time for silver corrosion product reduction in seconds at each sample was determined as the time from the beginning to end of plateau at potential around $\sim 0,7\text{mV}$. With this values and the exposure time in years it was calculated the corrosion rate of each silver sample.

Equations from Draft International Standard ISO/DIS 11844-2 to calculate the corrosion rate and film thickness [30]:

$$r_{\text{corr}} = \frac{i \cdot t_{\text{red}} \cdot M}{n \cdot F \cdot t}$$

$$f_{\text{thick}} = \frac{r_{\text{corr}} \cdot M_{\text{film}} \cdot t}{M \cdot \delta_{\text{film}}}$$

r_{corr} - Corrosion rate in $\text{mg}/\text{m}^2 \cdot \text{year}$

f_{thick} - Thickness of the corrosion film in nm (10^{-9} m)

i - Current density in mA/m^2

t_{red} - Total time for reduction of corrosion products in seconds

M - Molecular weight in grams (107,87g for Ag)

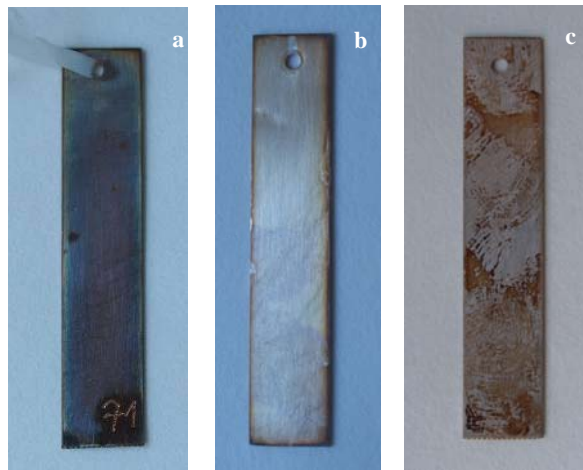
M_{film} - Molecular weight of the corrosion film in grams ($\text{Ag}_2\text{S} = 247,8\text{g}$)

n - Valance state (+1 for silver)

F - Faraday's constant = 96 485 C/mol

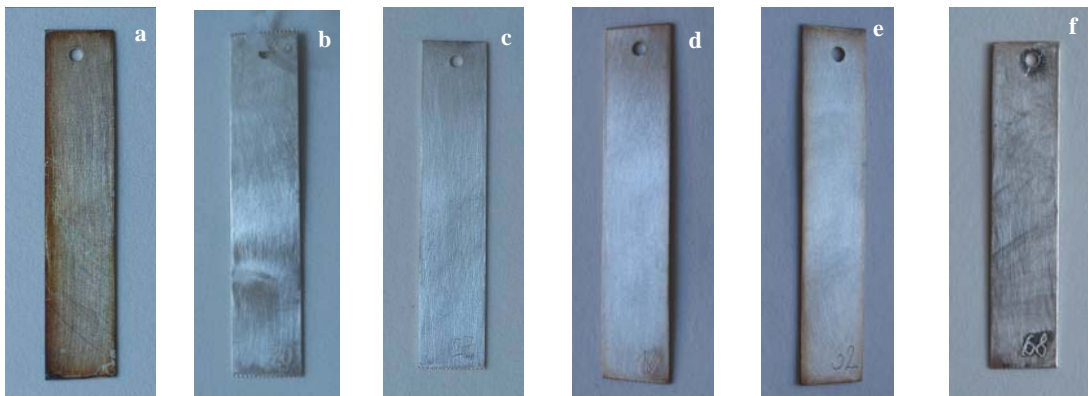
t - Exposure time in years

δ_{film} - Density of the corrosion film in g/cm^3 ($\text{Ag}_2\text{S} = 7,32$)



Figures 4.71 – Silver samples which were in external environment:

- a. sample n° 71 (MDA exhibition room);
- b. sample n° 18 (NM, storage room);
- c. sample n° 29 (NM, exhibition room).



Figures 4.72 – Silver samples which were inside showcases, cupboards and acid free paper:

- a. sample n° 25 (NM storage room, inside a metallic cupboard);
- b. sample n° 27 (NM storage room, inside a wooden cupboard);
- c. sample n° 68 (NM storage room, inside an acid free paper);
- d. sample n° 20 (MDA exhibition room, inside a showcase);
- e. sample n° 10 (NM exhibition room, inside showcase);
- f. sample n° 32 (NM exhibition room, inside showcase).

4.5 Annexes V

Table 4.4 – Intervention procedures applied on each earring and earring fragment.

	Cleaning dirt with wood stick and scalpel	Degrease with ethanol	Use of Ultrasonic Needle	Cleaning with formic acid	Cleaning with EDTA dissodic	Cleaning with thiourea	Application of Chlorophyll inhibitor	Varnish with Paraloid B72	Assembly with Paraloid B72
E1	X	X	X	X	X		X	X	X
E4	X	X		X	X		X	X	X
E5	X	X		X	X		X	X	X
E6	X	X		X	X		X	X	
E11	X	X	X	X	X		X	X	
E13	X	X	X	X	X			X	X
E14	X	X		X	X		X	X	
E16	X	X		X	X	X	X	X	X
E19	X	X		X	X	X	X	X	X
E20	X	X		X	X		X	X	
E21	X	X		X	X		X	X	X
E22	X	X	X	X	X		X	X	
E25	X	X	X	X	X		X	X	
E26	X	X	X	X	X	X	X	X	
E27	X	X		X	X			X	
E28	X	X		X	X			X	
F1	X	X		X	X		X	X	
F2	X	X		X	X		X	X	X
F3	X	X		X	X		X	X	
F4	X	X	X	X	X		X	X	
F5	X	X		X	X		X	X	
F6	X	X		X	X		X	X	X
F11	X	X		X	X		X	X	X
F12	X	X		X	X		X	X	
F13	X	X		X	X		X	X	
F17	X	X		X	X		X	X	
F18	X	X		X	X		X	X	X
R1	X	X		X	X	X	X	X	

Chlorophyll inhibitor solution preparation [24, 39]

- 3g of green leaves
- Ethanol

Leaves were smashed in a mortar and pestle. Then, they were mixed with 100ml of ethanol and macerate in the ethanol for 12 hours. After this time, the rest of the leads pulp was removed from the solution with a strainer.

To apply the chlorophyll solution in the silver objects, they must be immersing in this solution for 3 hours, and then dry it in ethanol and in a dry air chamber.



Figure 4.73 – Box with the assembled earrings.

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