



On surface analysis and archaeometallurgy

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Abstract

The tasks and problems which the study of ancient artefacts involves are manifold and almost as numerous as the different classes of materials and objects studied by modern specialists. This happens especially because the conservation of artefacts depends not only on their material and manufacturing techniques, but also very much on the environment and the type of soil in which they were deposited, sometimes for millennia. A number of archaeological materials and objects, dated to different periods, from the earliest use of metals to historical times, and also coming from very different geographical contexts in the whole Ancient World are discussed in this paper. The most common surface analysis methods will be evaluated and discussed in the framework of different applications.

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1. Introduction

Experience in archaeometallurgy of the last five decades and research carried out on archaeological materials in general have by now shown which problems can be solved by applying different particular methods, and which methods are more likely to give good results. In this paper several applications of surface analysis techniques such as XRF or SEM/EDS are presented. It is suggested that, in the main, the same good results

can be achieved by using PIXE. In cases where past surface analysis has been shown to be unsuitable for solving specific problems, the application of PIXE would, with all probability, encounter the same difficulties, while it might represent an excellent solution in some other cases.

Recognizing the original appearance and often even the original composition of archaeological artifacts is not always a simple task, as the surface of the item is almost always altered by age and, more especially, by long deposition in the soil. Because of corrosion phenomena, the appearance of the items is often so different from the original, that the nature of the material is almost never

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recognizable without the help of chemical analysis. The task of determining the material of inlays, applications and decorative layers, such as gilding, silvering or tinning, can also be rather difficult, because of the various techniques in use in antiquity.

Various non-destructive analytical methods can be employed to determine the production techniques of complex objects and to distinguish repairs from original parts. A further field of application for surface analysis is the identification of fakes.

2. Corrosion and oxidation phenomena

The best known corrosion and oxidation phenomenon on Cu-based objects is the formation of a patina [1]. When Cu-based alloys are kept in a damp oxygenated environment the Cu dissolves first along the grain boundaries and forms red cuprite (Cu_2O), which in the upper layers is subject to reaction with the soil and forms carbonates and sometimes chlorides.

The so-called noble patina, a compact and often aesthetically very attractive layer which develops on Cu alloys in general, consists normally of green malachite, basic Cu(II) carbonate ($\text{CuCO}_3 \cdot \text{Cu(OH)}_2$) or, in drier environment and less commonly, blue azurite, a different basic Cu(II) carbonate ($2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$). The colour can be darkened by the presence of sulphides of Cu and Pb, or become lighter because of the presence of Cu carbonates or of cassiterite, Sn oxide (SnO_2).

The consistency and the colour of the layer which forms on Cu and its alloys depends on the environment in which the archaeological object is found, and not on the kind of Cu-based alloy. There is no optical differentiation between the patina which forms on Cu and those developing on bronze and brass [2]. However, it has to be noted that the patina which forms on some Ag alloys is very often impossible to distinguish from the patina on Cu alloys, as it can take the same green colour. This happens particularly in a base Ag alloy, when the Cu corrodes preferentially and develops its corrosion products on the surface and between the crystals of the alloy, but it has also been noted in the case of Ag alloys containing only 2% or 3% Cu [3].

If the question is as simple as distinguishing bronze, leaded bronze, brass, leaded brass and Ag alloys, PIXE would give an appropriate answer, but because of the presence of corrosion layers, the results would be semiquantitative only and there would always be the danger of measuring extraneous elements absorbed from the environment. The same results can be (perhaps more cheaply) achieved by XRF.

Differences in the patina structure can occur, when parts of an object have been treated in different ways. For example, the parts of objects left in the as-cast condition tend to develop a spongy, more friable, often 1–2 mm thick, whitish patina, while hammered parts present a compact, shiny and smooth patina of a darker colour. Non-destructive surface analyses can help to recognize different alloys. However, for precise quantitative analyses of objects with corrosion layers, “destructive” methods, such as ICP or AAS, are certainly the best solution.

2.1. Artificial patina on copper alloys

Artificial patinae on Cu alloys are by now well known in the archaeological literature [4,5]. The most famous artificially patinated alloys are the Roman corinthium aes alloys, i.e. Cu alloys, containing small amounts of Au (ca. 1%) and often also Ag (ca. 1%) and As and Fe (ca. 0.5%), which, after a treatment in a chemical bath, achieve a purple, black or blue patina. However, the most ancient objects of this material, identified up to now, come from Egypt and are dated to the 19th century B.C. [6]. These alloys seem to have completely disappeared from the Mediterranean world after the fall of the Roman Empire and survived only in the east of the Old World: in Japan, with the name of shakudo, and in China, with the name of wu tong.

The example shown in the present paper comes from Kun Ming, the capital of Yun Nan in China, and is an opium pipe, most probably locally made in the 19th century A.D. It is a small, but rather complex object which has been analysed by SEM/EDS to avoid destructive sampling (Fig. 1).

The pipe head is made of a good Ag alloy, while the internal tube is made of common brass. The



Fig. 1. Opium pipe from Kun Ming, Yun Nan, China 19th century A.D. The head is of Ag, the tube is of brass covered by a wu tong sheet of Cu, with 0.6% Au, 1.8% Ag, 1.9% Zn and 0.4% Fe, black patinated by sweaty hands.

real patinated wu tong alloy is a sheet of Cu, containing around 0.6% Au, 1.8% Ag, 1.9% Zn and 0.4% Fe, soldered on the internal brass tube. The analysis of some traces of solder near the join, has shown that it is a Sn/Pb alloy with a low melting point. The rings which keep the wu tong sheet in place at its ends are made of a cupro-nickel alloy, i.e. of a Cu alloy of a very shiny and silvery colour with 18.8% Ni and 10.9% Zn.

The sheet was engraved with the decorative motif first. The Ag alloy used for the inlays (containing 15.3% Cu and 7.5% Zn), was then poured on and filed away after cooling, so as to reveal the engraved lines now filled with the silvery alloy. This is shown by the structure of the inlays, as seen in the SEM micrograph (Fig. 2): the alloy shows a clear dendritic structure, impossible to explain if the decoration had been carried out by inserting thin wires into the keying as was done in antiquity.

The different parts were then mounted and the object was finally patinated, by the typical Chinese method of handling the wu tong with sweaty hands for several hours. Recent experiments have shown, that this method, on which some doubts were expressed in the past, works perfectly well [7]. Ancient objects in the west and Japanese metalwork were treated instead in an aqueous solution containing various Cu salts.

Experience with non-destructive analyses carried out on original and experimental patinated layers have shown that, with XRF and EDS, the Au percentages are mostly far too high compared with the ICP or AAS analytical data. PIXE might

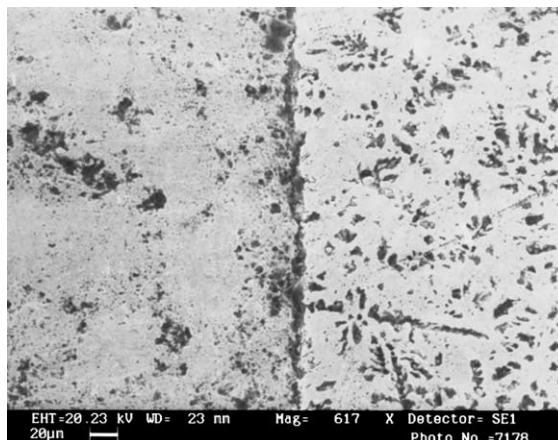


Fig. 2. SEM micrograph of the pipe inlay. The Ag alloy, with 15.3% Cu and 7.5% Zn, was poured on the engraved sheet and the excess metal filed away after cooling, as shown by the dendritic structure.

possibly represent a better solution to this problem, because of its larger penetration depths, (allegedly up to around 20–40 μm [8] or with high-energy PIXE for qualitative analysis even to several mm [9]) and should be tested with different experimental set-ups on different patinated alloys. However, it must be kept in mind that ancient metal objects are never homogeneous and that, besides corrosion problems, also internal segregation phenomena of different kinds represent a problem which can be easily solved by taking a “destructive” sample of a few milligrams. Therefore AAS and ICP are for the moment still recommended whenever samples can be taken.

2.2. Inclusions and voids in metal corrosion

Iron tends to corrode by loss of metal from the surface due to oxidation phenomena and can either disappear in the soil or, with alkaline or neutral soils, can deposit as iron oxides and iron carbonates, noticeably increasing its volume. It becomes a bulky lump, in which it is difficult to find any relationship with the original shape of the object. In some cases, X-rays can reveal the original shape as a void in a thick corrosion layer, without any metal remains. With SEM it is often possible to identify the traces left by organic material within the mass of oxides. In several cases, it

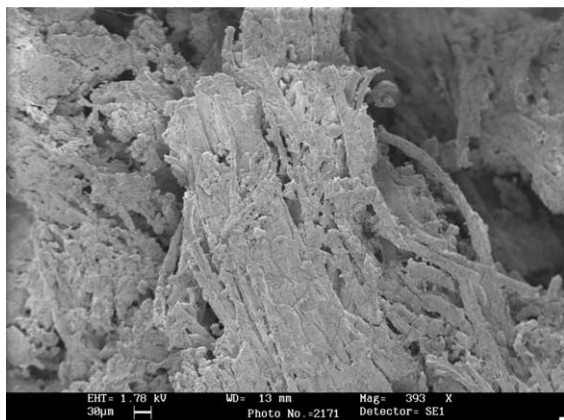


Fig. 3. SEM micrograph of coloured linen fibres, preserved in tin oxides, from a Villanovian necropolis, 8th century B.C. The EDS analysis identified the pigment as Fe oxides (pompeii red or red bolus).

has been even possible to retrieve information on the weave of textiles inside the corrosion of iron or of other metals and on the mineral pigments employed on the fabric.

The example shown here is a tiny fragment of metal from a Villanovian grave in a necropolis (8th century B.C.) in the Apennines (Fig. 3). The fragment of sheet, made of a Sn and Cu alloy, on one side shows an incrustation, in which it was possible to recognize the remains of a textile made of linen fibres. The SEM/EDS analysis showed that the linen was most probably treated with uric acid, because of the presence of the typical rounded formations [10], and coloured with iron oxides, which gave it a reddish colour. Remains of the inorganic pigment (pompeii red or red bolus) were identified in the yarn of the textile.

3. Repairs and inlays of various materials

Using SEM/EDX, XRF and of course also PIXE, it is possible to identify decorative materials, repairs or functional parts of different materials, without taking samples for destructive analyses, as required by AAS or ICP. Instances of these applications are myriad and here only two examples are given. For instance, a bronze situla, dating from the Roman period, most proba-

bly from Flavian times, and belonging to a hoard found in the Po Plain hidden in a well, was examined by XRF before carrying out quantitative analyses by ICP, for a detailed determination of the alloys employed for the artefact and for identifying the trace elements. The XRF analyses, confirmed later by “destructive” ICP analyses, showed that two of the patches are made of the same bronze alloy and are contemporary, while the others are different and were applied at different times.

The second instance of non-destructive identification of different materials on the same piece concerns a pendant of uncertain but rather recent date (ca. 19th–20th century A.D.) from Thailand, made of a Ag-like metal, locally called “Laotian silver” or “silver from Laos”. The SEM examination revealed that this material is a cupro–nickel alloy, with some Zn (2–3%) and ca. 20% Cu, similar to the alloy of the finishing rings on the wu tong pipe described above. The black decorative material, with which the pendant is inlaid, was identified as a Cu/Pb niello, a black decorative material consisting of metal sulphides, known in the Mediterranean since classical antiquity. However, for the moment not much is known about its use and history in Asia.

The earliest examples of niello scientifically identified, at least up to now, are already extremely sophisticated and are dated to the classical period, i.e. to the 4th–5th century B.C. As it appears at this stage of the research, they came most probably from the regions around the Black Sea [11].

3.1. Organic decorative materials on metal

A field of particular interest is the study of organic materials employed on metals. Some of these look rather similar and cannot be recognized without the aid of SEM/EDS, in this case certainly the best solution with small objects or if a sample can be taken.

The inlays can be made of ivory of elephant tusk, ivory of boar tusk, white (or altered) coral, various antler types, bone or shell. They consist of calcium compounds, of course contaminated with elements absorbed from the soil and from the surrounding objects, and the different materials

can mostly only be recognized with certainty by their structures. In some cases, it is possible to do this even with a strong magnifying lens. Elephant ivory, antler and bone are easily identifiable, due to their typical structure, and are more commonly found on decorative objects and have been better studied [12]. Both antler and bone are osseous materials and rather similar, but antler grows very quickly, is shed every year and has a typical honeycomb-like medulla, while the inner surface of long bones shows irregularly distributed perforations. Lamellae and vascular channels can be distinguished under low magnification. In the case of ivory, the lines of the blocks of curving dentine tubules are the most characteristic feature [13,14].

However, without tackling the problem of more exotic materials, such as mammoth, walrus, hippopotamus or narwhal ivory, even the structures of common materials, such as ivory of boar tusk or sea shells, employed as inlays on ancient metals in different European and non-European archaeological contexts, are less well known.

It is important to note that on a SEM micrograph the structure of a boar tusk can considerably change in different areas of the same material. Further, in some areas, the layered structure of a sea shell fragment can also look very similar to that of a boar tusk or even to the lamellae of elephant ivory [14]. These materials have been used since earliest times in all European contexts and can give valuable information on the trade routes at different times. They are often in a very fragmentary state or are found as pieces inlaid in other materials, so that identifying them is often impossible without taking a sample which, for examination in the SEM, has to be made conductive with a thin Au/Cu layer.

4. Decorative layers on metals: gilding

Various kinds of gilding techniques [15] can be identified by XRF, even better by SEM/EDS and, of course, by PIXE too. The earliest gilding method can be easily recognized, as it involved the plating of objects with a relatively thick Au foil applied on the surface, by inserting its margins

into grooves. There are some rare instances of the use of this method still in Roman times.

However, even during the early times, thin Au leaf was applied on metals by burnishing it on any degreased metal without any solder. The extreme malleability of Au makes it easy for the leaf to adhere to the metal surface, particularly if it had been roughened beforehand. Remains of gilding can normally still be identified in the keying by any surface analysis method, even if the gilding has been scratched away to recover the precious metal. Leaf gilding can normally be recognized, because the Au layers are thicker (up to a few μ) where the edges of single pieces of leaf overlap. On Ag alloys, in some cases, the diffusion of Au into the Ag underneath was achieved by heating, to obtain a better bonding of the two metals. In these instances, the certain identification of the gilding method as diffusion can be rather difficult, if it is not possible to look at a section. The performance of PIXE has been tested on similar materials and might possibly help to solve this problem [8].

It has also to be noted that, in Egypt particularly, there are also instances of gilding by applying thin Au foil on a substrate of calcite or gypsum [15,17]. This is also common to later periods (for example in Hellenistic times) and in other regions of the Old World. If the objects are small enough for the SEM chamber, it is sometimes possible to distinguish traces of the tools used to insert the Au leaf or the Au wire into the keying. These were made of wood, bone or ivory, rather soft materials, which did not damage the thin gold leaf. To burnish and render shiny large portions of gilding on smooth metal surfaces, carefully polished stones, such as haematite or agate, were employed [16].

4.1. Fire or mercury gilding

Fire gilding seems to have been used on small objects already in Hellenistic times [18] and up to modern times (Fig. 4). The surface of the pieces to be gilded is first degreased and then covered with a paste-like amalgam, obtained by mixing Au filings or bits of Au leaf or wire and mercury. The object was then heated to over 352 °C to

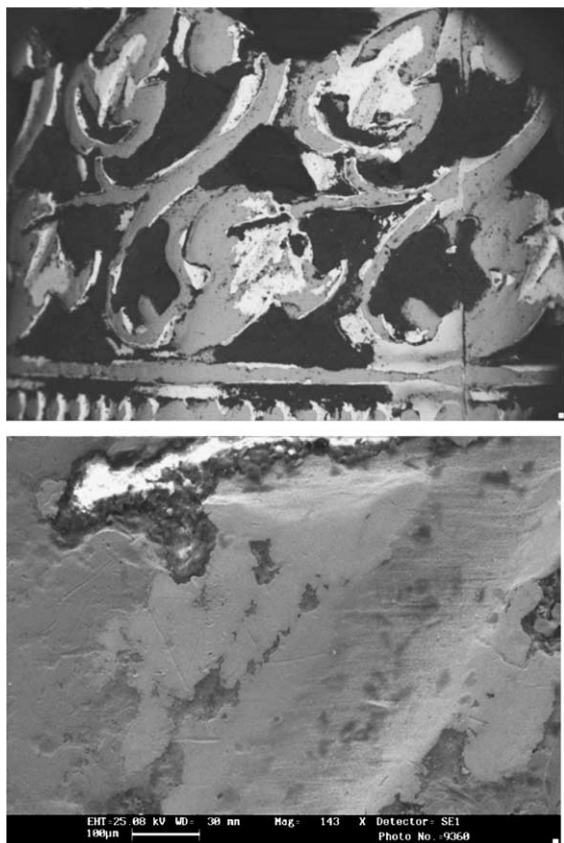


Fig. 4. SEM micrograph showing traces of fire gilding on copper, the keying filled with organic material. Writing pen, 18th century A.D.

evaporate the mercury from the amalgam. The thin and opaque layer of Au on the surface was finally burnished with haematite or agate.

Au amalgam was also applied on the surface of Cu items and left to “dry” for several weeks, until the mercury had evaporated, or mercury was applied to the surface and covered with Au leaf [19]. The presence of mercury residues can be easily determined with any surface analysis.

We also have to keep in mind that the presence of mercury in gilding, where the overlap of Au leaf is evident, does not automatically indicate that Au leaf was applied on mercury. There is also the possibility that gold leaf was applied on a previous layer of mercury gilding, during a later restoration.

Modern electroplating is rather different from ancient gilding: the alloys contain Au, Cu, Zn

and Ni, which can of course be easily identified, and the layer of gilding is only 0.10–0.15 μ thick. Clumsy fakes employ modern alloys, but, if an alloy similar to the ancient alloys is used, electroplating can still be recognized, because the thin layer cannot be polished and porosities and bubbles (which of course formed during the deposition of Au on the surface) are visible in the microscope [16].

5. Silver and silvery layers

In antiquity and up to the Middle Ages, rather than silvering, Ag plating was used. Several instances of the use of plating with a relatively thick Ag foil on coins and small objects are known [20].

The Roman republican coin of which a detail is shown on the SEM micrograph (Fig. 5), represents a new excellent example and shows the head of *C. Coelius Caldus* (r) and on the reverse the head of the sun-god *Sol* (v). The core is made of a rather pure, unalloyed Cu blank, which was wrapped in a thick leaf of a good quality Ag alloy with only 3% of Cu. The core wrapped in the Ag leaf was certainly heated to induce diffusion of Ag into the Cu and achieve a bond between the two metals. However, in the area where the Ag layer is missing, it is quite clear that the bond was only partial. The

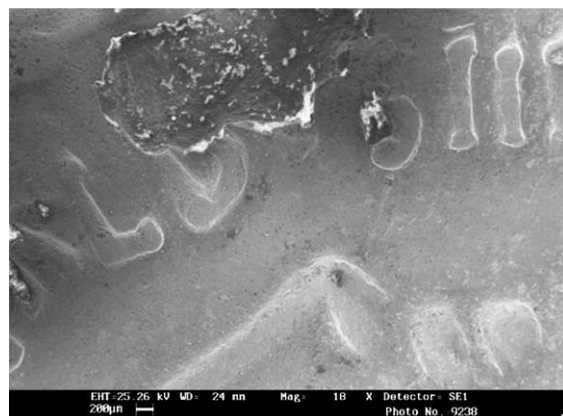


Fig. 5. SEM micrograph of a plated (subaerata) Roman coin of the republican period. The silver sheet contains 3% Cu, while the nucleus is unalloyed Cu.

eutectic alloy (72% Ag and 28% Cu) could be identified by EDS only on small areas on the unalloyed Cu. These coins are called *subaerata*, their technique is well known and has been studied since the 19th century [21,22].

5.1. The depletion technique

As already seen above with cupro-nickel alloys, silvery surfaces can be achieved in different ways. A good way of making a debased alloy look like Ag, is the use of surface treated debased Ag alloys, i.e. of the depletion technique, a selective corrosion technique, carried out by pickling a debased Ag–Cu alloy in organic acids, such as strong vinegar or fruit juices. The acids dissolve the Cu in the surface, leaving behind a much purer albeit porous Ag layer, which is then burnished and struck-like a normal coin blank. This technique was very common in the Roman Empire, to improve the look of the debased Ag denarii which, in particular in the period of inflation between 63 A.D. and 260 A.D., only contained 12–18% of Ag [23].

The coin presented here, however, shows a new instance of the application of this technique in the Middle Ages, on a Crusader coin from Jerusalem, dated 1190/1191 A.D. (Fig. 6). As shown by the SEM micrograph, the porosity of the surface in the areas not too heavily struck while minting the coin clearly demonstrates that the surface was depleted by some acid. The more heavily

struck recesses, where the spongy texture has been flattened, present a compact layer of rather pure Ag instead. For examination, the thin coin was polished on the edge, to reveal the internal structure. The sectional examination showed that the Ag layer is very thin and becomes very porous immediately under the surface. The internal core is much richer in Cu (probably also because of inverse segregation) and the less noble Cu increased its volume by oxidizing, thus breaking the Ag layer, which is flaking away in several areas.

5.2. Silver imitations and fakes

Several Ag imitations or Ag fakes, obtained without precious metals were known and used in antiquity. The most ancient one is arsenical Cu, the first Cu alloy employed by man, since the 4th Mill. B.C., when metallurgy had its beginnings. The first examples of arsenical Cu were probably produced by chance, by smelting mixed As and Cu minerals, but later, when bronze was already the established Cu-based alloy, arsenical Cu was still used to imitate Ag.

Because of the phenomenon of inverse segregation, which happens even with very low As concentrations in Cu, the eutectoid Cu–As (with 21% As in Cu), of a silvery colour, is pushed to the surface of cast objects during the cooling process, and forms a silvery layer [24]. Surface analyses of these alloys give very high As results, which do not correspond to the real bulk composition.

Antimony has a similar effect on Cu and both elements, As and Sb, greatly enhance the segregation phenomenon and the formation of the silvery surface layer on cast objects. High percentages of these elements in Cu render the metal fragile and hard and the objects cannot be hammered.

Apparently in the Late Bronze Age and in the Iron Age, natural As–Sb–Cu alloys, perhaps the result of smelting the mixed minerals occurring in several European deposits, traded as “special alloys”, with or without the addition of other “silvery” metals, such as Ag, Pb and Sn, were employed in particular for small decorative objects. Examined by SEM, these alloys show a characteristic enriched dendritic pattern on the surface, which represents a serious problem for EDS and

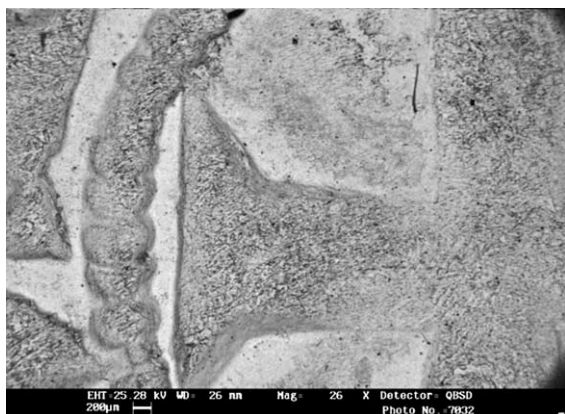


Fig. 6. Surface enrichment (depletion silvering) of debased silver alloy. Crusader coin from Jerusalem, 1190/1191 A.D.

XRF surface analyses, with enormous differences in the results, of up to 10–15%.

In the same period, also several instances of cheap ornamental objects made of simple Pb or of Pb–Sn alloys are known. A further rather easy way to obtain a silvery metal is that of casting high Sn alloys, which was employed at different times, for example in the Late Bronze Age, for the wheel-shaped pendants found in the hoard of Kanalski Vrh in Slovenia [25], but also at other contemporary sites [26,27].

These alloys, with around 20–23% of Sn, were also used in Roman times and later in other contexts, i.e. in China and Japan [28,29], especially for the production of mirrors with a colour, due to the formation of the intermetallic compound $\delta(\text{Cu}_{31}\text{Sn}_8)$ within the alloy. Roman mirrors were the prized production of the specialized artisans mentioned in the *Codex Theodosianus* (13.4.2) and in the *Codex Justinianus* (10.64.1) as specularii. The alloy for mirrors is hard and fragile and can only be polished, and indeed these artifacts are usually found in pieces. On the surface there occurs formation of the acicular structure of the α phase, together with the δ compound, which SEM can easily reveal, if a fragment of the mirror is available [3,30].

A cheaper version of the Roman mirror was made of “normal” leaded bronze with a tinned surface. This technique can be distinguished by examination in the microscope or, if possible, in the SEM. The layer of tinning is rather inhomogeneous and several components, going from metallic Sn, to intermetallic compounds of the ε (38.2% Sn = Cu_3Sn) and η (61.0% Sn in the alloy = Cu_6Sn_5) phases can be recognized [3,20,30].

6. Conclusions

As discussed above, surface analyses in general do not seem, at least up to now, to be suitable for quantitative analyses of ancient oxidized or corroded metals or of alloys prone to segregation phenomena, but analyses of precious metals were never a problem for methods such as XRF and EDS. The latter also has the advantage of showing details which are not visible with other magnifying

devices, giving the possibility of analyzing tiny inclusions and of distinguishing Sn segregation and tinning.

However, PIXE might represent the best method for the study of depleted precious alloys, natural or artificial, such as the South-American tumbaga, and perhaps also for artificially patinated and inlaid objects, such as hmyt km, corinthium aes, shakudo and wu tong. The application of PIXE analysis to artificially patinated alloys might be an interesting experimental field for the future.

A useful and interesting field for PIXE is also the quick identification of fakes: wrong alloys and false patina can easily be discovered by surface analysis and also in the case of other materials, such as glass and pigments, the presence of modern ingredients can be detected immediately.

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