Chemical Analyses And Archaeometallurgy: Problems and Possibilities

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ABSTRACT
The tasks and problems, which the study of ancient artefacts involves, are complex and manifold and almost as numerous, as the different materials and objects, studied by modern specialists. This happens especially because the conditions of the artefacts depends on their material and on the production techniques, but also on the environment and on the type of soil in which they were deposited, sometimes for millennia. A number of archaeological objects, dated to different periods and from very different geographical contexts in the Ancient World are discussed in this paper. The most common analysis methods are going to be evaluated in the frame of different applications, from the point of view of an archaeometallurgist, who does not usually employ PIXE, but “destructive” analyses, such as AAS and ICP and, only in particular cases, XRF and SEM/EDS.

Keywords: Chemical analyses, ancient metalwork, archaeological finds, XRF, SEM/EDS

1. INTRODUCTION
Recognizing the original appearance or even the original composition of archaeological artifacts is not always a simple task, as the surface of the item is altered by age and, especially, by the long permanence in the soil. The nature of the material is almost always optically not recognizable without the help of chemical analyses. The task of determining the material of inlays, applications and decorative layers, such as gilding, silvering or tinning, can also be difficult, because of the various techniques, which might have been applied in antiquity. Different methods can be employed to determine the production techniques of archaeological objects and, for instance, to distinguish repairs from original parts. In the next paragraphs several examples will be given for each of the instances listed above.

2. CORROSION AND OXIDATION PHENOMENA
The simplest corrosion phenomenon is the formation of patina on metal objects. The so-called noble patina, a compact and aesthetically attractive layer, consists of malachite or azurite. There is no optical differentiation between the patina, which forms on copper, and those developing on bronze and brass [1]. The layer, which forms on silver alloys is often impossible to distinguish from the patina on copper alloys, as it can take the same green colour [2]. Corrosion layers and segregation phenomena represent a serious problem for any kind of surface analyses (XRF, EDS, EPMA, PIXE etc.). Up to now, the only way of getting precise results is that of taking drill samples for “destructive” analyses (ICP or AAS), by carefully discarding the upper layer and removing any corrosion under the microscope before dissolution. Ancient artificial patinae on copper alloys containing small amounts of precious metals, such as the Egyptian hmy km or the Roman Corinthium aes are by now well known[3]. With these materials XRF and EDS give distorted, usually enhanced Au results and PIXE might possibly represent a better solution.

2.1 Corrosion and oxidation on iron
By oxidation Fe corrodes by loss of metal from the surface and can disappear in the soil or, with alkaline or neutral soils, deposit as Fe oxides and Fe carbonates, increasing its volume, and becomes a bulky
lump, without any relationship with the original shape of the object. X-ray radiography can reveal the original shape as a void in corrosion, without any metal remains. The only way of determining the production and working techniques of Fe and its alloys is by destructive metallography. With SEM/EDX, it is possible to identify traces of organic material within the oxides. In some cases it has been also possible to retrieve information on disappeared organic materials, for instance on the weave of a textile inside the corrosion layers of iron or of other metals, and on the colouring agents (Fig. 1).

**FIGURE 1.** Example of ancient linen fibres, preserved in Sn oxides, from a Villanovian necropolis, 8th c.BC.

### 3.1 DECORATIVE LAYERS ON METALS: GILDING

Various gilding techniques can be easily and cheaply recognized by XRF and, if the object size allows it, even more easily, by SEM/EDS. The most common ancient techniques were foil gilding, diffusion gilding and fire (mercury or amalgam) gilding [4]. PIXE can of course be particularly useful for the identification of natural or artificial depletion (such as *tumbaga*).

**FIGURE 2 A, B.** Traces of fire gilding on copper. In this case the mercury was easily identified by EDS. The keying was filled with organic material. Details of a writing pen, 18th c. AD.
3.2 Silver and silvery layers.

In antiquity, rather than foil- or amalgam silvering, Ag plating with Ag foil was used (Fig.3). Several silver imitations or ancient silver fakes are known, for example surface treated debased silver alloys (depletion by acids Fig.4), copper-based alloys with As and Sb, high Sn alloys, tinned copper-based alloys [5]. The materials can be recognized by various surface methods: the most flexible and the cheapest is for sure EDS, but often only metallography can solve the problem.

![Figure 3](image1.png)  
**FIGURE 3.** Plated (*subaerata*) Roman coin, The silver foil contains 3% Cu, the nucleus is unalloyed Cu.

![Figure 4](image2.png)  
**FIGURE 4.** Surface enrichment (depletion) of debased silver alloy. Crusader coin from Jerusalem, 1190/1191 AD. (All photos by A.Giumlia-Mair)

4.1 INLAYS OF VARIOUS MATERIALS

Using SEM/EDS on small objects or XRF on larger ones, it is possible to (cheaply) identify decorative materials or the alloys used for composite objects, as for example vessels, with body, handles, bottom and small parts, such as rivets (important to determine differences in metal quality for minor items).

4.2 Organic decorative materials on metal.

A field of particular interest is the identification of organic materials used as decoration on metals. Some of these look rather similar, have the same composition (calcium carbonates) and cannot be recognized without the aid of SEM/EDS. This is for example the case with inlays made of ivory of elephant tusk, ivory of boar tusk, white (or altered) coral, bone or shell, which can only be identified by their structure.

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REFERENCES