Elemental Analysis of Coins and Glasses

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Many historical questions can be solved by the elemental analysis of archaeological objects. Each archaeological material is a special case: in contrast to ceramics, metals and glasses are often remelted. For coins we can study their fineness, debasement and adulteration and for both coins and glasses their fabrication and provenance. To solve these questions we must define criteria determining the method of analysis to be adopted in each historical case.

1. Introduction

The elemental analysis of coins and glasses is a characterization study in the field of archaeometry. Dealing with several scientific areas, archaeometry is a quite new domain (the review journal Archaeometry was produced in Oxford first in 1958) concerning the study of a wide variety of archaeological artefacts and art objects. However, we know that the study of archaeometry started a long time before, at the beginning of the 19th century, when David himself made a chemical analysis of a Roman painting pot and Roentgen an x-ray analysis of a painting by Dürer.

The evolution during the 1950s of atomic and nuclear techniques for non-destructive testing opened vast possibilities of analysis of museum objects. Several techniques have so been developed and applied to the elemental analysis of archaeological artefacts (as Ambrosino and Pindrus, 1953; Emelius, 1958; Kraay, 1959). During the 1960s and 70s the development of the “milliprobe” and of the “isoprobe” (Hall et al., 1973), the technical evolution of solid-state detectors (avoiding chemical separation), the development of fast neutron activation (Meyers, 1969), of the PAA method (proton activation analysis, Barrandon and Debrun, 1976) as well as of IBA techniques (the most used are PIXE, PIGE and RBS), gave rise to new research areas in archaeometry [a compilation of the first archaeometry publications was made by Sayro and Meyers, (1971)]. They included: the surface enrichments and depletion effects for certain alloys (Condamin and Picon, 1972; Carter et al., 1983; Beauchesne and Barrandon, 1986) as well as the manufacturing technology and the origin of the archaeological materials [for example, Friedman et al. (1966), Gordus (1971), Meyers et al. (1973) and Guerra et al. (1991)].

Perhaps the attribution of ceramics is one of the most productive areas in archaeometry. Metals might have been remelted and reused in new minting or for producing other objects and so may glass, which is a rather difficult matrix to be analyzed. Each archaeological material has to be considered by itself as an analytical problem which poses different historical questions. Several analytical methods have so been developed and applied to the elemental non-destructive analysis of archaeological artefacts (Bird et al., 1983). Here we discuss, using typical questions in archaeometry, the characterization methods connected to coins and glasses, their applications and limitations. For coins we are able to solve problems such as fineness, debasement, recasting and forgery and for both matrices, manufacturing technology and provenance. We must define criteria for the elemental analysis of coins and glasses in order to use the most appropriate technique for each historical case.

2. Elemental Analysis and Historical Problems

2.1. Numismatics

Among all the metallic objects, coins are the most studied in archaeometry as they provide the most fruitful results. In fact, we can say that in general they are stuck with a well controlled alloy by a known mint (sometimes with a date of issue); references can be found in ancient documents and their typology, metrology and chronology have been well studied. However, cases exist where the lack of written documentation brings about experimental difficulties.

One of the most important analytical problems in archaeometry concerns the patina: the corrosion and oxidation layer. Gold, electrum and pure silver coins, without corrosion and oxidation, may be analyzed by all sampling (as NAA or AAS) and surface (as XRF
or PIXE) methods, but “billon” (silver/copper/alloy) and copper alloy coins present “surface phenomena” limiting the analyses. The inhomogeneity of the samples, due to surface enrichment and depletion effects, may give random results. Condamin and Picon (1972) showed that the results obtained for silver, zinc, tin and lead concentrations on the surface of several copper alloy coins do not correspond to the interior composition [see also Demortier et al. (1981)].

A recent work (Beauchesne et al., 1988) compares the results obtained on Roman copper alloy coins by PIXE, PAA and FNAA (fast neutron activation analysis using a cyclotron, Beauchesne and Barrandon, 1986); SEM has also been used to study the patina. Figure 1 shows a depth profile for copper, tin and lead on a lead–bronze roman coin. For certain coins the patina may attain a thickness of more than 100 μm and the tin and lead precipitates are often observed up to a 300 μm thickness. These facts explain the differences found in the compositions obtained by PIXE (first μm), PAA (about 300 μm) and FNAA (global). This example clearly shows that surface analytical methods can only be used after a surface treatment, as proposed by Carter (1964). Bulk analytical techniques like FNAA (or γ-activation spectrometry) are in fact the most suitable ones for this kind of matrix.

The determination of gold and silver content in, respectively, gold and silver coins, gives their fineness as well as other major and minor elements which may give coins debasement. In most cases, with time, the devaluation corresponds to the replacement of the noble metal by a less expensive one. The study of fineness itself, connected to metrology and typology, may per se define a difficult chronology. A good example is the chronology proposed by Oddy and Munro-Hay (1980) for the Aksumite kings’ gold coinage, using in situ specific gravity analysis.

However, as well as confirming a chronology, the study of fineness may reveal other problems. A good example is the determination of the silver content of the 1st Portuguese dynasty “dinheiros” (Guerra et al., 1989) using XRF (Gil et al., 1989). Figure 2 shows the fineness evolution during all the 1st dynasty, which means from 1128 to 1383. We can say that until 1367, that is from Afonso Henriques (AFH in the diagram) to Pedro I (P in the diagram), the average fineness corresponds to the legal one, but for Fernando I (F in the diagram), the last reign (1367–83), the difficult economical situation of the country is well demonstrated by the fact that the silver content of 0.17% does not correspond to the legal one: 2.78%. In the same diagram we can see the unexplained existence of two sub-groups for Sancho I (SI in the diagram). This latter discovery led to other analyses as we will see later on.

The change in the composition which we call debasement has two possible reasons: official debasement and forgery. In the first case, the devaluation corresponds to economical difficulties during the period; in the second case, we may have two types of phenomena: recent forgeries, recognized by the lack of trace elements (like gold in silver) only possible by the use of new technologies, and ancient forgeries with a different minting technology as silver-plated coins, which are copper blanks covered with a silver foil (as ancient forgeries we shall also consider the remelting and alteration of current coinage).

Both debasements might be differentiated by a combination of a surface with a bulk technique, the first one giving surface composition and the other the average one. However, we can use a single technique like DP-PIGE (Beck et al., 1991); with a variable incident beam energy, this non-destructive method determines the composition of each layer of the coin as well as the thickness of the plating surface.

Another silvering technique is blanching (Florowski and Stos, 1975), a quite usual procedure during the Middle Ages; the billon “dinheiros” being a typical example. The SEM analysis being a destructive technique for coins, silver depth profile was done on two coins, showing that the blanching surface is of about 1–2 μm. Also, an attempt to explain the second sub-group of the Sancho I reign, found by XRF analysis (Fig. 2), was made using FNAA for the determination of the trace elements. Figure 3 shows,
for the typological groups of all the reigns, the silver content in function of the ratio As/Cu, taken in % (arsenic being a characteristic element of the copper ore). This diagram provides evidence of different copper supplies to the different mints working under several reigns, leading to a new chronology by the attribution of the sub-group HSII, attributed by typology to Sancho I, to the second mint striking at the transition between a debasement by the use of copper supply; however its origin was not yet possible to be determined.

An example of the first and more successful case concerns the metals of the New World. Geochemical data shows that Andean silver is characterized by germanium and indium together with gold. To determined gold and indium concentration (germanium can not be determined without chemical separation) in silver coins with ppb detection limits, a global non-destructive analytical technique was developed: TFNAA [thermalized fast neutron activation with a cyclotron, Guerra and Barrandon, (1988)]. If we compare indium concentration (in ppm taken in function of silver content in %) determined by TFNAA in both Spanish and Potosi silver coinages (Guerra et al., 1991) from the 16th and 17th centuries (Fig. 5), we can clearly see that the Potosi silver arrives in Spain at the end of the reign of Philip II (the approximate date because coins do not present a date of issue) and that it suffered with time a dilution in others silver ores (followed using the ratio

by means of a certain characteristic element (not affected by refinement) and in the second case to find several “tracers” or determine its lead isotope (Budd et al., 1993) which are characteristic of each vein.

We cannot find in the literature a great number of provenance studies for metals. We can refer to some attempts made by Friedman et al. (1966) on copper artefacts, Meyers et al. (1973) on the Sasanian silver, Gordus (1971) on Sasanian and Islamic coins and Morrison et al. (1993) on lead Byzantine stamps. Unfortunately, not all examples of the second case have not so far been successful. A good example is the analysis of the Roman gold coins struck from 198 to 491 (Poirier and Barrandon, 1982). In the same way as lead in silver ores, platinum is not affected by the gold purification, therefore being a characteristic element in this metal. As for Constantinople’s coinage, PAA is the best analytical technique because it determines, for a gold matrix, platinum with a detection limit in the order of the ppb. If we consider the evolution of the platinum concentration with time we can see that it remains around zero until about 346AD when it suddenly attains about 1000 ppm. The study of ancient documents shows that this increase of platinum corresponds to a change in the gold supply; however its origin was not yet possible to be determined.

Fig. 3. Silver content in function of the As/Cu ratio for the “dinheiro” typological groups.

Fig. 4. Evolution of the Pb content with silver for the Byzantine coinage.
Au/Ag for gold contents). For French and Italian silver coinages of the same period we obtained the same type of diagrams. It was possible to date the arrival of Potosi silver in those countries as well as follow its dilution with time. Also the relative amount of Potosi silver arriving at the European mints was calculated.

A similar study for Brazilian, Portuguese, English and French gold coinages allowed the dating, by the determination of palladium concentration (Brazilian gold tracer) using PAA, the arrival and dilution of Brazilian gold in Europe during the 18th century (Barrandon, 1994). We can say that the study of the arrival in Europe of the silver from Potosi in the 16th century and of the gold from Brazil in the 18th century remains one of the most rich in answers to the historical and economical questions posed to the analyst.

2.2. Glasses

Glass is a generic term in which we can include glass as we understand it nowadays, obsidian (natural glass) and vitreous phase materials like faience, Egyptian blue, glaze... Glass appeared in the Middle East about 3000 BC and one thinks that its manufacturing technology came either from the glassy slags from copper and lead ore smelting or from an evolution in ceramics technology. Only the invention in Roman times of the glass blowing technique developed a glass industry.

Glass is basically made of a source of silica, of a compound to lower the melting point such as soda, potash or lead, of a stabilising agent such as lime or alumina, to avoid the solubility in water, and of additives, such as colourings (copper, manganese, cobalt) and opacifying agents (tin, antimony). The impurities present in the raw materials may give light-coloured glasses, but they may also be obtained by the intentional addition of metal salts and oxides. Deliberately coloured glass may be red, blue or other deep colours. Colourless glasses are also deliberately produced.

The study of glassy materials has problems similar to those of numismatics: when studying the raw materials and the additives we want to determine the manufacture technology and the provenance. The connection to numismatics is well shown by a very interesting work done by Gratuzé and Barrandon (1990) on the Islamic glass weights and stamps. The determination of 12 elements by FNAA defined four chemical groups by means of the variation of raw materials ratios. The evolution of this ratios with time (Fig. 6) defines a chronological classification allowing a relative dating and to explain the manufacture technology used during the past 500 yr.

Although most of time the same sampling techniques as for ceramics can be used, the analysis of glasses is similar to the analysis of metals: either we look for major and minor elements or for trace elements. The high corrosion suffered by this material may inhibit the use of surface techniques; the reuse of glass, for lowering the melting point during production makes the provenance harder to determine.

Sometimes elemental analysis identifies the glass workshop if we are dealing with very different geographical origins; in this case simple analysis may determine commercial trades. Often we differentiate glass in function of the used raw material other than silica: soda, potash, lime and lead. For example, soda–lime–silica glass (made with natron) were used in ancient times and potash–lime–silica glass (made with plants and tree ashes) characterize medieval times. A more detailed classification is used by authors like Turner (1959) and Sayre (1961). Other minor types can be defined in function of the geographical area.

Most of the intentional colourings are easily found in nature, except for deep red and blue glasses. Blue glass may be obtained by the addition of copper compounds (e.g. for Egyptian blue) or cobalt oxides or others cobalt and copper ores. Copper sources being very common are very difficult to trace. However cobalt having rare extraction veins might be easier to recognize. The determination of trace elements correlated to the cobalt colouring may allow...
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Preciousness and corrosion must be considered when studying archaeological materials: we have to look at the conservation of the object and for the representativity of the analysis. The technological development of the analytical methods avoids sampling as well as the contribution of the patina, which means that the analyst tends to use bulk non-destructive techniques in archaeometry.

In order to solve simple problems like the fineness of coins all the recent techniques, together with metrology and typology, can define a chronology for noble pure metals. If we consider the case of a matrix containing a high concentration of copper alloys (for example devaluation procedures) we must be careful with the results. Let us take an obvious example. The analysis of six Roman billon coins from the British Museum (BM) gives by XRF, for the three radiate head type coins and for the three head with a laurel wreath type coins, the following fineness:

<table>
<thead>
<tr>
<th>Type of Coin</th>
<th>Radiate head (%)</th>
<th>Radiate head (%)</th>
<th>Radiate head (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>42</td>
<td>34</td>
<td>47</td>
</tr>
<tr>
<td>Laurel wreath head</td>
<td>32</td>
<td>46</td>
<td>28</td>
</tr>
</tbody>
</table>

The analysis made by XRF, PAA, \(^{252}\text{Cf}\) activation and FNAA at the Centre Ernest Babelon on three Bibliothèque National (BN) coins of the same types gave the following silver contents:

<table>
<thead>
<tr>
<th>Type of Coin</th>
<th>XRF (%)</th>
<th>PAA (%)</th>
<th>(^{252}\text{Cf}) (%)</th>
<th>FNAA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiate head:</td>
<td>58.4</td>
<td>36.7</td>
<td>26.4</td>
<td>28.0</td>
</tr>
<tr>
<td>Laurel wreath head:</td>
<td>46.4</td>
<td>30.5</td>
<td>22.7</td>
<td>23.2</td>
</tr>
</tbody>
</table>

If we compare the XRF results obtained for the BN coins with the BM results, we might think that the radiate head BM type corresponds to the head with a laurel wreath BN type. However if we take PAA results, the same comparison leads to the same attribution. If we look at both neutron activation results we cannot say that (considering the measurement uncertainty) there is a different fineness for each type. Here we face a typical problem of patina. If global methods are not used we risk a wrong historical conclusion.

The study of composite objects need precise, accurate techniques and plated objects need techniques using variable beam energies. Archaeometry can easily answer, using non-destructive techniques, to this kind of question, if only major and minor elements are required. In the first case we may use, for example, PIXE/PIGME microbeam analysis and in the second case DP-PIGE analysis. However if for some composite objects, like glasses and some metallic objects, we need to determine trace elements, we see further that we can only with difficulty solve some types of questions.

The most difficult cases presented to the analyst concern the manufacture technologies and the determination of provenance. In fact to solve these kinds of problems we need to determine the trace elements characterising the alloy. We have seen that most of the manufacturing technology questions may be solved (about 80%) by nuclear activation techniques together with the study of the documents and statistical analysis. Most of the time we can find some trace elements which allow the origin of the raw material to be determined.

Provenance determinations are the hardest in archaeometry. Trace elements and lead isotopes ratios provide the only possible answer to this type of question. Lead isotopes ratios were expected to give a very good database on the sources of ores; a simple lead isotope ratios determination on the objects would therefore rapidly give the ores' origins. Unfortunately it seems that lead isotopes analysis is so far quite limited for provenance studies of archaeomaterials.

At the moment non-destructive trace elements determination is performed mostly with global nuclear activation analysis to determine the provenance of an object or of an ensemble of objects. There are two types of provenance problems. We want to determine which mine was exploited to make the objects or we know the mine and we want to correlate the objects to it. There are no successful studies for the first case, however for the second one we were able, with the activation techniques, to follow the Potosi silver and the Brazilian gold arrival and dilution in Europe. However, we know that Mexican mines started to be exploited by the Spanish at the end of the exploitation of the Potosi mines, but we were unable to recognise the Mexican metal.

The same problems exist for glassy materials. Although the Bingöl and Nemrut Dagh obsidian sources in Turkey are known and may so be
characterized, the activation analysis of the obsidian artefacts from those regions (Gratuze et al., 1993) shows that Nenrut Dagh and one of the Bingöl sources have similar compositions, which means that differentiation could not yet be made.

We can say that nuclear activation methods and IBA techniques are well defined and have attained the best detection limits as well as the maximum of elements determined, at least in the archaeometry domain. At present we can continue to solve a great number of historical and economical problems, but for provenance studies the future seems to be the use of non-destructive techniques, like LA–ICP–MS, which determine a large number of elements reaching lower detection limits.

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