An overview on the ancient goldsmith’s skill and the circulation of gold in the past: the role of x-ray based techniques

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From the study of coins and casted simple objects to intricate jewellery comprising many diverse parts joined together, analytical queries on ancient goldwork concern the description of the manufacturing techniques, the identification of the authenticity and the localisation of the exploited sources of gold. Through the examination of the objects by x-ray radiography and the non-destructive elemental analysis of the gold alloys – by XRF, SEM-EDX, PIXE and SR-XRF, x-ray based techniques have always played an important role in the study of cultural heritage and, in particular, of goldwork.

The aim of this article is to give a short overview of the use of the most established scientific-based techniques in the study of goldwork, with special outlining on the limitations, advantages and applications of x-ray based techniques. Two applications illustrate both the potential of examination techniques to identify the authenticity of gold jewellery and the importance of combining examination techniques and elemental analysis to describe the fabrication stages of goldwork. At last, a third example shows the significant socio-economical assumptions developed by determining the characteristic trace elements of gold when coinages are considered. Copyright © 2008 John Wiley & Sons, Ltd.

INTRODUCTION

Ancient goldwork comprises objects of simple production such as hammered plaques or struck coins; however, in a general way goldwork comprises different parts sometimes partially produced in other materials. Studies on iconography, style, date and period are sometime enough to understand the manufacturing techniques and the usage of an object. When these studies come together with research on the documents giving the 'pedigree' of an object without archaeological context, it is sometimes possible to attest whether it is genuine or a modern invention. However, by combining art history with scientific analysis-based research, fundamental information can be obtained on the making techniques of the objects and on the circulation of gold in the past.

To tackle such a large range of questions, the combination of examination of the object with the analysis of the constituent materials is necessary. Much information can be obtained using techniques such as macro-photography and optical and electron microscopies. Complementary information is obtained concerning the decoration and mounting techniques by x-ray radiography. Metallography (which can be rather interesting for the study of deterioration of gilded objects), and high-resolution surface profilometry and topography provide complementary information on the production techniques. However, only elemental analysis gives further information on certain manufacturing techniques (composition of a soldering or of a gilding foil, for example) and elemental analysis or—in few situations—isotopic analysis infer the circulation of gold in the past.

The most important requirement concerning ancient goldwork is the non-destructiveness of the analysis. For this reason, x-ray based analysis has always been a leader in this field of research. In spite of the large use of activation analysis in early archaeological science measurements, as evidenced by the first volumes of the Archaeometry journal (a review in Ref. 6), XRF (x-ray fluorescence), SEM-EDX (scanning electron microscopy with an energy dispersive x-ray system) and afterwards PIXE (particle induced x-ray emission) became, more or less rapidly, major techniques in the field of archaeological sciences. An increasing use of x-ray based techniques in archaeometry is at present illustrated by the attraction for synchrotron-based analysis despite the outstanding required facilities and the consequent difficult access to archaeologists and museum curators.

Although nowadays the more widely-used SEM-EDX and PIXE facilities in the field of Archaeometry, these techniques can hardly compete with XRF that turned into the most popular elemental analytical set-up for a large panoply of materials. From the simple identification of a more or less complex material, by the determination of major chemical elements, to the measurement of the characteristic trace elements in the raw material for the study of the circulation routes; from the traditional ED and WD (energy or
wavelength dispersion) systems to the small mobile systems with micro and macro analysis, this technique is easy to use for non-technical operators. However, in the case of gold alloys, XRF can hardly provide more than the surface concentrations of major elements (Au, Ag and Cu), being in most cases inadequate for gold fingerprinting as well as for the study of certain manufacturing techniques requiring particular analytical facilities.

The aim of this article is not to describe the features and innovations of the x-ray based techniques used for the analysis of ancient gold items, but to give a short overview of their limitations, advantages and applications among the techniques used to study goldwork.

**GOLD AND GOLDWORK**

Gold occurs in rocks and ores in many ways but, in the past, extraction from auriferous quartz or direct panning in alluvial deposits provided powder, pellets and nuggets that were melted and refined to obtain the necessary raw material to produce goldwork. Refining techniques changed over time. Separation of precious metals from other elements present in native gold was achieved by cupellation and parting. Documents dating mostly from the Middle Ages reveal very mystified processes of refining and processing that several authors have been trying to decipher and experiment.

Gold alloys were produced by addition of silver and copper to gold—native electrum was used before the control of the metallurgical processes—their colour and mechanical properties depending on the quantities of each added metal. A ruler defines the fineness of a coinage; a goldsmith chooses the alloy according to the required colour (reddish by the addition of copper; greenish by the addition of silver etc.) and the required hardness and tensile strength according to the purpose of the objects or of a part of it. These latter properties are increased by the addition of copper and silver, but also by annealing, quenching and hammering.

Goldwork comprises all the objects that are manufactured both totally and partially with gold along with golden objects obtained by the addition of a gold layer on the surface of an alloy of lower quality. Gilding is used either for a polychrome aim or in periods of lack of gold. Goldwork varies from very simple constructions, based on hammered plaques or casted forms, to very complex constructions comprising a large number of parts individually produced to be joined together. In the first situation, we can find coins which can be obtained directly by either pouring the alloy into a mould or by laminating and cutting of a plaque, processes that are followed by striking. A statuette can be obtained by lost-wax casting followed by polishing or burnishing the surface. For these types of objects, whose manufacture is revealed by observation, the origin and provenance of gold is the most pertinent and tricky question for the analyst.

An object can however be very complex, produced by hammering or casting and afterwards decorated by chasing, engraving, stamping or by addition of other materials—gems setting, gilding, niello inlaying, etc. Composite objects, such as intricate jewellery, which may comprise a large number of different elements of separate production joined together, involves more complex analysis. If gold fingerprinting can be carried out by elemental and in a few cases isotopic analysis—in the case of gold, only lead and osmium are achievable—the identification of the decoration, joining, mounting and surface finishing techniques requires accurate observation under different lights and radiations in order to obtain information on the surface morphology, which also reveal invisible details.

The study of an object as a whole allows tackling all the different aspects covering its production, from the exploitation of the ore to the finishing of its surface. The ability to recognise and identify different goldsmithing techniques and to understand the gold provenance is necessary for this purpose; however, a large number of scientific-based techniques must also be available in order to bring together all the complementary required information.

**SCIENTIFIC TECHNIQUES**

A large number of scientific techniques are available to study ancient gold objects. The choice of a sole technique or of a combination of techniques depends on the question and the type of object concerned. The study of goldwork comprises essentially two steps; examination and analysis. Observation under different lights and radiations is a paramount tool to describe an object. Optical microscopy, x-ray radiography, SEM and high-resolution surface profilometry and topography are the main examination techniques. To identify whether an object was casted, cold hammered or annealed, the removal of a sample, which is polished and etched before metallographic examination, is required, restricting the application of this technique in the case of gold objects.

Some authors avoid removal of a sample by using XRD directly on the surface of rare objects, but this belongs to sporadic applications.

Elemental analysis provides information on several goldsmithing techniques and, when trace element determination is carried out, on the origin and provenance of gold. Fingerprinting requires the use of elements, which are characteristic of the origin (primary or secondary deposits) or of the provenance (localisation of the deposit) of gold. The elements present in the last form of the production depend on the metallurgical steps; however, we remind the importance of platinum group elements (PGE) and Sn (characteristic of alluvial deposits) for fingerprinting gold.

Contrary to elemental analysis provided by a large number of techniques, isotopic analysis, connected to the formation of a geological deposit, also provides information on the gold provenance, but it can only be carried out either by TIMS (thermal ionisation mass spectrometry) or by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), a more recent development. Both techniques are destructive, because a sample is dissolved or chemically prepared and consumed during analysis. For lower precision, laser ablation removal of a sample is possible in the case of MC-ICP-MS, otherwise dissolution is necessary. However, we must note that
only the isotopic ratios of lead (element commonly present at very low contents in objects produced with native gold) or of osmium (found only in particular geo-chemical formations,\textsuperscript{25}) are useful for fingerprinting gold. For these reasons, elemental analysis, which can be totally non-destructive, is preferred.

**Examination techniques**

An important characteristic of goldwork is the absence of highly corroded objects except in the case of some gilded items (depletion gilding\textsuperscript{26} is usually excluded). Even though we are aware of surface enrichments caused by copper oxidation and removal during burial for low quality gold alloys and of surface effects caused either by silver corrosion\textsuperscript{2} or by pickling in an acidic solution for flux removal after soldering,\textsuperscript{27} in most cases gold objects show high-quality surfaces. In this situation, examination concerns mainly the study of the manufacturing techniques of the objects.

The observation of the objects under a binocular reveals many details of their fabrication and conservation. SEM can refine information on some details, such as the wire soldering of Fig. 1(a) While binocular reveals the presence of solder joins between two spiral beaded wires on a gold pendant from the beginning of sixth century A.D., SEM shows a bad temperature control of the materials during brazing. In fact, a part of the filler did not melt as shown by a pellet on the region of grain structure corresponding to the joint alloy (Fig. 1(b)).

Conversely, x-ray radiography gives information on the invisible parts of an object, as shown for a gold finger ring found in a male’s tomb dated from the second half of the sixth century A.D. The finger ring of Fig. 2(a) obviously comprises a ribbon-type hoop, a bezel and three spiral beaded wires whose joining and mounting can be discerned under the SEM: a gold plaque outlined by a filigree form the bezel. However, x-ray radiography reveals a new feature on the finger ring mounting: the bezel is oddly sustained inside the construction by an extra wire (Fig. 2(b)). This type of information can only be recovered by radiography.

Examination techniques can, in some particular cases, still provide assumptions on the origin of gold. A gold Hellenistic finger ring from the fourth century B.C., in addition to signs of use-wear, showed under the binocular the presence of PGE inclusions (Fig. 3(a)). With the SEM, we could quantify the diameter of these precipitates, which ranges from 20 to 120 µm (Fig. 3(b)). We can assume that an alluvial deposit is at the origin of this gold. We remind that alluvial gold placer deposits are formed in watercourses by erosion of primary gold deposits\textsuperscript{28}; being sedimentary deposits, they concentrate high-density minerals such as gold and PGE.\textsuperscript{29} In the case of our finger ring, only further elemental analysis of these precipitates, for instance, by SEM-EDS\textsuperscript{30} and comparison of the gold trace elements with published data can indicate the provenance of gold.

In addition to the previous examination techniques, we must still consider non-contact high-resolution surface topography analysis, which gives quantitative information on some goldsmith’s decoration techniques such as engraving, chasing, repoussé and stamping. Figure 4 shows the extracted profiles for a triangle, which was produced by three different techniques on a silver plaque. These profiles

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**Figure 1.** Wires joining by brazing on a gold plaque: (a) binocular image showing the joining region; (b) SEM SE image of the grain structure corresponding to the joining alloy with a filler pellet (source: M.F. Guerra, C2RMF).

**Figure 2.** (a) The medieval finger ring bezel (source: D. Bagault, C2RMF); (b) x-ray radiography of the bezel discovering the internal wire sustaining the bezel construction (source: T. Borel, C2RMF).
Figure 3. PGE inclusions on the bezel of a Hellenistic finger ring: (a) binocular image; (b) SEM SE image (source: M.F. Guerra, C2RMF).

Figure 4. Extracted profiles for a triangle produced on a silver plaque by: (a) engraving (with the ‘volcanic’ type border due to metal removal); (b) stamping (with slight deformation peak on the border); (c) chasing (regular valley without borders).

are characteristic of the type of deformation of the metallic plaque and show whether the technique involves metal removal (engraving) or not (others). The dimensions (distances, slopes and angles) of the extracted profiles give the depth and the penetration, which are characteristic of the employed technique and the tool as well as of the effect required by the goldsmith.

Elemental analysis
According to the equipment availability and cost, elemental analysis gives access to many types of non-destructive micro or macro analysis of an object or a sample. A large number of information is obtained by determination of the surface or the bulk composition, the determination of major, minor and trace element concentrations, and so forth.

The analysis of gold objects can be easily undertaken by non-invasive ED-XRF. E. T. Hall used this technique in the 1950s for the analysis of archaeological objects. Since then, a large number of technical developments allowed a wide application of this technique in the field of archaeological sciences. Nowadays, several set-ups are available for XRF analysis, including the use of small x-ray tubes to produce the incident beams (for example, Refs 33–35) as well as more complex systems including XRF and XRD. Some authors compare the results obtained by portable and non-portable XRF and a few use this technique in the case of gold alloys. When precious objects cannot be moved to the laboratory, the use of portable techniques is of most importance. We must, however, note that only major elements (gold, silver and copper) and sometimes one or two minor elements can be determined. Several books give an overview of the x-ray techniques, others combine archaeological and analytical approaches either in the case of x-ray techniques or in general.

We must, however, cite SEM-EDX that plays a very important role in the field of archaeometry. By combining elemental analysis with electron imaging, this technique provides the topography of the surface and the elemental analysis of the details. The most significant disadvantages of SEM-EDX in the case of gold objects are the volume limitation of the vacuum chamber and the poor detection limits; the low depth of analysis is a disadvantage in the case of plain gold objects but an advantage in the case of, for example, gilding. Contrary to TEM (transmission electron microscopy), which is used for archaeological materials containing nanoparticles, such as glass, is hardly used in the case of gold objects, as sampling is required.

Despite based on heavy and expensive equipments, the replacement of the x-ray incident beam provided by an x-ray tube by either a charged particle beam produced by particles accelerators or by synchrotron radiation makes available improved detection limits for the characteristic elements of gold. PIXE, usually with proton beams, and SR-XRF have the advantage of being totally non-invasive, providing microanalysis and elemental mapping facilities.
Overview on the ancient goldsmith’s skill and the circulation of gold

In addition to the x-ray based techniques, we can still consider activation analysis and inductively coupled plasma (ICP) with atomic or optical emission spectrometry (ICP-AES and ICP-OES) as well as with mass spectrometry (ICP-MS). In the case of gold alloys, activation analysis is usually carried out with proton beams, but its use largely declined during the last two decades for safety reasons. In the case of ICP-based techniques, ICP-AES and ICP-OES can only be achieved with the removal of a sample and only few applications are known for gold alloys. ICP-MS can be carried out, in some particular cases, by dissolution of a sample of a few milligrams or by laser ablation. (LA-ICP-MS) only a small number of applications to goldwork are known (for example, Refs 25, 56–60) as this technique is constrained by the volume of the ablation cell.

Figure 5 shows the comparison of detection limits in the case of gold analysis for all the cited techniques except XRF and SEM-EDX, which typically determine major elements in gold. Data was obtained with particular set-ups that were expressly developed for the analysis of trace elements in gold alloys. The main characteristics of these analytical developments are the following:

- PIXE was carried out with a 3 MeV external proton beam of 30 µm diameter and an intensity of 30–40 nA. Two Si(Li) detectors collected the emitted x-rays. The first measured major elements while the other, covered with a 75 µm selective filter of Cu to absorb the gold L-lines, improved the detection limits of trace elements in gold alloys by a factor of 10 to 100. Pt was measured by PIXE-XRF with an As primary target, that excited the Pt-LIII line (11.59 keV), and a 25 µm Zn filter on the Si(Li) detector that improves the measurement by reducing the Compton and Rayleigh lines of As along with the tailing of the latter. The contribution of the atomic resonant Raman effect of gold constrains the detection limit to 80 ppm. Acquisition times were typically 30 m for PIXE and 45 m for PIXE-XRF.
- Spatially resolved SR-XRF was carried out with an incident beam of 33 keV except for Pt, which was measured with a beam of energy first as above and afterwards below the Pt-LIII edge energy (11.564 keV). A Si(Li) detector and a 50 µm Cu filter lowered the limit of detection of Pt down to 20 ppm; calculations were performed by Monte Carlo simulation and subtraction of Au and Pt spectra obtained on pure standards. Acquisition times were typically 20 m at low energy and 5 m at high energy. Proton activation analysis (PAA) of gold alloys, developed in the 1960s by Meyers, is here considered in a 12 MeV beam of 2 µA intensity configuration. By interposition of a 3-mm thick lead sheet between the detector and the sample to absorb the γ-ray emission from the two Hg197 isomers produced in gold (<300 keV), γ-ray spectrometry could be carried out after irradiation. The short irradiation contrasts with the long acquisition times for the different half-life radioisotopes.
- ICP-MS was performed using pick jumping mode, 10.24 ms dwell time, 30 s acquisition time and three repeated runs for dissolved gold samples of about 2 mg. Indium was added for use as internal standard. The short acquisition time contrasts with the long chemical dissolution of the sample. LA-ICP-MS was performed with a 2-mJ pulsed VG Nd : YAG laser working on Q-switched mode and in the UV wavelength with a shot frequency of 6 Hz using pick jumping mode, 10.24 ms dwell time, 60 s acquisition time after 10 s of pre-ablation and 3 by 3 raster scan pattern. AuAr+ ion was used as internal standard and quantification was obtained by comparing peaks after subtraction of the background on the sample and the standards.

In Fig. 5 ICP-MS, with detection limits under the ppm level for almost all the elements of the periodic table, is irrefutably the only technique providing ultra-trace measurements. However, the removal of a sample and its dissolution is necessary. In the case of composite objects, the analysis of their different parts can hardly be performed. When coupled to a LA system, the sampling amount is largely reduced, but the size of the objects is constrained by the volume of the ablation cell and the quantitative analysis requires matrix effects corrections. Elemental mapping cannot be carried out.

PAA in non-routine conditions provides low detection limits for many elements, but induces radioactivity. In addition to this, point analysis and elemental mapping are inaccessible. SR-XRF has a gain factor of about 100 in relation to routine filtered PIXE and PIXE-XRF. Like the ion beam techniques, SR-XRF allows point analysis and elemental mapping but it requires heavier and more expensive equipments. The choice of the analytical technique for the analysis of goldwork must be strongly considered according to the query.

APPLICATIONS

The aim of this section is to show different situations where the study of gold and golden objects needs the combination of examination with elemental analysis or just the use of the latter. According to the type of object and the information, queries at different levels of research can be undertaken.

Authenticity of an Etruscan fingering

Examination techniques are adequate to identify the authenticity of gold objects such as Etruscan gold finger rings with...
cartouche produced in the second half of the sixth century B.C.\textsuperscript{63} Fig. 6(a) shows the x-ray radiography of a cartouche finger ring that consists of a ribbon-type hoop, a repoussé gold plaque placed on the top of a gold bezel and ornamental wires and granules (Fig. 6(b)). The presence of gold plaques placed inside the bezel to reinforce the assemblage cannot be attributed to an ancient goldwork. These plaques can be seen through the gold plaque rip illustrated in Fig. 7(a).

Several other details on wire and granules\textsuperscript{64} that point out a modern production could be observed under the binocular and the SEM: (1) the use of modern drawn wires, characterised by their symmetric grooves on the surface\textsuperscript{17} and the thick solder joining (Fig. 7(b)); (2) the strong pickling;\textsuperscript{27} (3) the addition of sets of granules and wires. Nevertheless, the ‘in repoussé plaque’, which seems ancient, is enclosed in a first plain beaded wire, produced with a square in section wire which was not achieved (Fig. 6(b)). If the production of this wire could be assumed as modern by observation, elemental analysis seems to show its authenticity.

Figure 6. Etruscan gold finger ring with cartouche: (a) x-ray radiography of the bezel (source: T. Borel, C2RMF); (b) binocular image of the ‘in repoussé plaque’ and of the filigrees on the bezel (source: M.F. Guerra, C2RMF).

Table 1. Base-alloys of the different parts of the bezel by PIXE: ancient parts are of higher quality (about 22 carats) than the modern parts (about 18 carats)

<table>
<thead>
<tr>
<th></th>
<th>Au %</th>
<th>Ag %</th>
<th>Cu %</th>
</tr>
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<tbody>
<tr>
<td>Plaque</td>
<td>92.6</td>
<td>4.5</td>
<td>2.6</td>
</tr>
<tr>
<td>Plaque wire</td>
<td>91.3</td>
<td>4.7</td>
<td>3.8</td>
</tr>
<tr>
<td>Bezel</td>
<td>79.6</td>
<td>17.8</td>
<td>2.5</td>
</tr>
<tr>
<td>Bezel wire</td>
<td>75.7</td>
<td>20.9</td>
<td>3.4</td>
</tr>
<tr>
<td>Bezem granule</td>
<td>75.1</td>
<td>20.7</td>
<td>3.7</td>
</tr>
<tr>
<td>Hoop</td>
<td>78.0</td>
<td>19.4</td>
<td>2.5</td>
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<tr>
<td>Hoop wire</td>
<td>78.5</td>
<td>17.9</td>
<td>3.2</td>
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<tr>
<td>Hoop granule</td>
<td>75.9</td>
<td>21.4</td>
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Manufacture of a pair of brooches from the late antiquity

A pair of silver-based triangular head brooches produced with the lost-wax technique at the end of the fifth century A.D. (Louviers necropolis, Eure, France\textsuperscript{65}) were finished by the use of gold foils. Fire-gilding, using the gold amalgam process, became the standard gilding technique in Europe after the third century A.D.\textsuperscript{66} Used under the Romans (as referred by Pliny,\textsuperscript{67}) till the medieval period,\textsuperscript{68} it consisted on the application of either a mixture of hot mercury where gold was dissolved on the objects or of gold foils on the top of a layer of mercury.\textsuperscript{15} We could point out by SEM-EDS the expected presence of variable amounts of mercury on the brooches (corresponding to the heating variation to evaporate off mercury) as well as the presence in both the objects of both the techniques (Fig. 8). Mercury-gold mixture was the first to be applied on the surface of the brooches. Later, certainly as a repair (maybe for funerary purposes), gilding was obtained by application of gold foils.

High-resolution surface analysis gives the dimensions of the details of engraved, stamped, chased, and in repoussé designs. A set of profiles can be represented as a 3D image corresponding to the volume of the tool mark obtained by micro-topography analysis. With a non-contact micro-measure STIL facility, based on the chromatic-coded optical principle of quasi-confocal imaging\textsuperscript{69} and an optical sensor with a measurement field of 3000 \( \mu \text{m} \), a spatial resolution of 10 \( \mu \text{m} \) and a working distance of 38 mm, data on the brooches decorations was obtained with 100 Hz of acquisition frequency and 5 \( \mu \text{m} \times 50 \mu \text{m} \) quantisation step. Figure 9(b) illustrates the 3D image of a selected region on the head of one brooch (Fig. 9(a)) and an extracted profile (Fig. 9(c)). This profile, obtained with a resolution of 0.1 \( \mu \text{m} \) and a precision of 1 \( \mu \text{m} \), corresponds to the use of engraving on the mould and polishing after casting. The quantification of the distances and slopes estimates the dimensions of the goldsmith’s tool.

The composition of this pair of brooches (named A) obtained by PIXE was compared in Table 2 to two pairs of brooches of the same type, period and culture: pair B is from the same necropolis as pair A and pair C from another necropolis. Contrary to pair B, which seems to come from a different type of production, pair A has a rather homogeneous composition that can derive from a simultaneous fabrication. Brooches A and B, with 70–87\% silver contents, are made with an alloy of lower quality than brooches C; brooches C could have been produced simultaneously. The lower quality of the alloys is caused not only by the presence of higher Cu contents, but also by the presence of high Pb, Sn and Zn contents. We note that
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The presence of Pb and Sn in the silver alloy is rather common for this period. In the case of silver coins struck in the French territory, Pb attains 2% and Sn 5%. The presence of Zn is less usual at such high quantities, but we must notice that this element attains 2.3% in a few French coins issued in the sixth century A.D. and 2.1% for English silver-base brooches from the sixth century A.D. We can assume that the lower quality of brooches A and B and the presence of high quantities of Sn, Zn and Pb is caused by re-melting and reuse of assorted objects. Re-melting and reuse practices increase with the decrease of precious metals supplying, like in late antiquity, and are the basis of the large number of fire-gilded jewellery items found in necropolis from this period instead of plain gold jewellery from other wealthier periods.

Provenance and circulation of gold in the kingdom of Portugal

The Age of Discoveries is the wealthiest period of the Portuguese history: in 1482, the Castle of Elmina was built in the coast of Ghana to control the routes of West African gold; in 1498, India was reached and access to the Asian trading route was available; in 1507, the gold routes of the
Table 2. Composition of the different pairs of brooches by PIXE

<table>
<thead>
<tr>
<th>Brooches A</th>
<th>Ag %</th>
<th>Cu %</th>
<th>Pb %</th>
<th>Au %</th>
<th>Sn %</th>
<th>Zn %</th>
<th>Sb %</th>
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<tr>
<td>Brooch 1</td>
<td>85.1</td>
<td>3.3</td>
<td>2.0</td>
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<td>4.3</td>
<td>2.6</td>
<td>0.05</td>
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<tr>
<td>Brooch 2</td>
<td>86.0</td>
<td>5.6</td>
<td>1.3</td>
<td>1.9</td>
<td>2.3</td>
<td>2.8</td>
<td>0.04</td>
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<table>
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<tr>
<th>Brooches B</th>
<th>Ag %</th>
<th>Cu %</th>
<th>Pb %</th>
<th>Au %</th>
<th>Sn %</th>
<th>Zn %</th>
<th>Sb %</th>
<th>As %</th>
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<tr>
<td>Brooch 1</td>
<td>87.0</td>
<td>8.8</td>
<td>1.5</td>
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<td>1.6</td>
<td>1.0</td>
<td>0.08</td>
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<td>Brooch 2</td>
<td>69.8</td>
<td>16.6</td>
<td>3.8</td>
<td>0.4</td>
<td>4.4</td>
<td>5.0</td>
<td>0.10</td>
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<tr>
<th>Brooches C</th>
<th>Ag %</th>
<th>Cu %</th>
<th>Pb %</th>
<th>Au %</th>
<th>Sn %</th>
<th>Zn %</th>
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<td>Brooch 1</td>
<td>96.6</td>
<td>1.8</td>
<td>0.3</td>
<td>1.2</td>
<td>0.04</td>
<td>0.03</td>
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<td>Brooch 2</td>
<td>95.0</td>
<td>2.1</td>
<td>0.6</td>
<td>1.3</td>
<td>0.5</td>
<td>0.4</td>
<td>0.04</td>
<td>0.01</td>
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Mwanamutapa kingdom in Mozambique were controlled; in 1500, Brazil was found and later the famous gold mines of Minas Gerais. If between 1248 and 1438 only one Portuguese king struck gold coins, after 1438 gold issues proliferated. How far does the gold come from these new worlds?

A small set of gold coins, made accessible by the Portuguese Numismatic Association and issued from 1139 to 1865 where analysed by PAA and LA-ICP-MS. The Pd and Pt contents of the coins in Fig. 10 evidence three chemical groups corresponding to precise periods: the first group corresponds to the dynasty that reigned after the expulsion of the Arabs from the Iberian Peninsula and the subsequent dynasty; the second group corresponds to the beginning of the Age of Discoveries; and the third group corresponds to the exploitation of Brazilian gold.

The gold struck in Portugal from 1139 to 1211 comes from the re-cycling of gold coins issued by the last Islamic dynasties reigning over the Iberian Peninsula, the Almoravids and Almohads. The similar chemical characteristics of these coins and of the gold struck between 1483 and 1521 is explained by the arrival of the Portuguese to the West coast of Africa and the production in this region of about 500 kg of gold per year. This African gold arrives from the geo-chemical regions previously exploited by the Almoravids and the Almohads. In 1521–1523, a crisis emerges in Elmina, causing the decrease of the exported gold. Simultaneously, the arrival of gold from Portuguese India is said to increase and the gold from Peru, Mexico and Antilles is said to reach Lisbon. To test these assumptions, monetary gold from Portuguese India and South America was analysed. Both the Portuguese Numismatic Association and the National Library in Paris made the ingots and coins available for this study.

Figure 10 shows the Pd and Pt contents for gold coins struck in India from 1495 to 1557 together with the groups 2 and 3 of Fig. 10. Two chemical groups are observed for the Indian gold. However, none of these groups have the same characteristics of the gold issued in Portugal.

The group of Fig. 11 issued in India from 1495 to 1557 corresponds to a period of installation in the coast of Mozambique (since 1507). The Portuguese established in the valley of the river Zambezi after 1530 and controlled the regions with gold mines. The first coins struck in India were certainly issued with a local gold, but the second group could have been produced with an Eastern African gold, as in 1629 the Portuguese controlled the whole gold trade and commercial exchanges with India. However, this does not seem to affect the Portuguese economy.

Furthermore, the groups of Fig. 10 were compared with coins struck in Portugal, Spain, Peru, Mexico and India. Figure 12 shows that the Peruvian and Mexican gold form a detached group. Despite the documents, Peruvian and Mexican gold do not affect the Portuguese economy. It is a Colombian gold that is used to produce the Spanish issues but in Portugal, the monetary gold seems to be a mixture of Colombian gold with a West African gold. The latter is exploited till 1638 but it could also have entered in the new issues by re-cycling. The same type of gold is struck in Brazil before the discovery of gold in Minas Gerais.

After the discovery of gold in the state of Minas Gerais in Brazil, the composition of all the coins struck by the

![Figure 10. Ratios of Pt and Pd concentrations in ppm to gold content in % for the coins struck in Portugal from 1139 to 1865.](image_url)

![Figure 11. Ratios of Pt and Pd concentrations in ppm to gold content in % for the coins struck in Portuguese India and in Portugal from the 16th to the 19th century.](image_url)
last Portuguese dynasty (group 3 of Fig. 10), characterised by high contents of Pd and lower contents of Pt, fit with the gold coins and ingots produced in Brazil80 of Fig. 12.

CONCLUSION

Ancient goldwork comprises many sorts of objects from simple hammered gold foils to complex items containing different parts, which can at times be partially produced with other materials and gilded. The study of goldwork concerns many questions connected to the manufacture techniques of the objects and to the circulation of gold. Such different issues may require the use of many scientific-based techniques, which are restricted by the non-destructiveness requirement. This requirement together with several specific facilities essential in the case of some objects—such as point analysis, elemental mapping, good accuracy and sensitivity—has always established the importance of x-ray based techniques in this field of research.

X-ray radiography and SEM-EDS are main tools for jewellery studies. X-ray radiography gives unique information on the mounting and assembling of objects. This information can be complemented by optical and electron microscopies. Under different lights or radiations, invisible details on the surface and in the interior of the objects are revealed. SEM-EDS is nowadays the only technique that couples for small gold objects, non-destructive elemental analysis and imaging with x-rays. However, only the composition of base-alloys, of surface layers, and of PGE inclusions can be determined and in-situ analysis is not possible.

When in-situ analysis is required, a good compromise is made by coupling portable x-ray radiography to optical microscopy and portable XRF. In this case, again, only the concentration of major and a few minor elements is available. Other techniques may complement XRF such as LIBS (laser-induced break-down spectroscopy80) or XRD.5

PIXE and PIXE-XRF (the latter barely applied to the analysis of gold81,82) and more recently SR-XRF give information on the concentration of major, minor and some characteristic trace elements that give crucial information on certain manufacturing techniques and sometimes on the origin and provenance of gold. Totally non-destructive, accurate and sensitive SR-XRF has a large potential for the analysis of goldwork. The main drawback of this still emerging technique in this field of research is the availability and the heavy expensive equipment. Ion beam analysis that also requires expensive equipment is easily available.

When the detection limits of those and other established techniques in the field of gold analysis are appraised and compared, only ICP-MS in liquid and LA modes appears to be available nowadays for a nearly non-destructive measurement of ultra-trace elements. However, this type of analysis is restricted by: (1) the reduced number of queries on gold provenance requiring such low detection limits, which concern mostly coins; (2) the size of the laser ablation cell; (3) the gold objects allowing sampling; (4) the possibility to consume the sample during analysis.83 However, when a multi-collector (MC) configuration is used, ICP-MS is the only technique providing elemental and isotopic analysis in liquid and LA modes (the accuracy of the latter depending on the element content).

Through three different examples we could show the importance of the choice of the analytical technique to recover enough and correct information in order to be able to appreciate the ancient goldsmith’s skill and explore the authenticity of goldwork. Moreover, the combination of examination with elemental analysis showed to be of singular importance when dealing with intricate jewellery and particular manufacturing technologies, such as gilding and non-authentic objects. Studies on the circulation of gold in the past, requiring a good expertise on the historical documents and an accurate choice of the analysed objects, suffer from the complexity of the ancient socio-economical situations and from the re-melt and reuse of gold. In some particular cases, such as periods of exploitation of huge gold supplies, we could show that the evolution of the concentration of the characteristic trace elements of gold allows inferring the commercial exchanges in large regions and periods of time.

REFERENCES

Overview on the ancient goldsmith’s skill and the circulation of gold


