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Authentication and analysis of goldwork

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A new approach to the authentication of goldwork using combined Scanning Electron Microscopy and External-beam PIXE

*Une nouvelle approche pour l'authentification des objets en or
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Olivier BOBIN* and Hervé GUEGAN**

Abstract: The study of goldwork encompasses several large fields of investigations. Scientific analyses can respond to questions concerning production techniques, provenance and preservation. However, what about authentication? This type of works of art generally has very high prices, leading to an increase in the number of forgeries. Today, fakes can imitate artworks produced by most civilisations and with different origins. Moreover, most of the objects we analyse cannot be submitted to destructive sampling. That is the reason why we employ external-beam PIXE for the analysis of such objects, a method able to offer reliable and non-intrusive scientific investigations. Our methodology consists of two steps, which, in their combination, provide information about the chronological compatibility of the objects with their presumed period. First, an optical and electronic microscope investigation allows us to identify tool marks, weathering features, to reveal traditional or fraudulent surface treatments, and to characterise superficial deposits. This first approach is able to identify bad quality fakes. However, these analyses are generally insufficient to establish the authentication of the objects. That is why we also perform external-beam PIXE analyses on goldwork. Thus, the qualitative and quantitative studies of trace elements are able to provide insights into metallurgical methods and the fineness of alloys. This paper describes our methodology and presents different examples of its application, including the discussion of specific problems encountered in the analysis of this type of objects.

Résumé : Les objets en or sont étudiés par des approches très diverses, et parmi celles-ci les analyses scientifiques répondent généralement à des problématiques concernant la recherche des techniques de fabrication ou l'étude de provenance et de conservation. Mais, qu'en est-il de l'authentification? Ce type d'objets d'art étant en effet d'une valeur marchande élevée, ils sont de plus en plus souvent sujets à des contrefaçons, qui imitent aujourd'hui la plupart des styles et des civilisations. Les investigations scientifiques doivent être absolument non destructive et la technique PIXE en faisceau extrait est alors idéale pour ce type d'expertise. Nous avons ainsi développé une méthodologie qui nous fournira un faisceau d'indices qui sera compatible ou pas avec l'ancienneté présumée de l'objet. En premier lieu, l'examen par microscopie optique et électronique permet d'identifier les traces d'outils, les figures de corrosion, de révéler si l'objet a subi des traitements de surface anciens ou modernes et de caractériser la nature des dépôts superficiels. Ce premier niveau d'investigation permet d'écartier les faux flagrants ou de mauvaise qualité. Toutefois, cette étude est généralement insuffisante pour établir l'ancienneté d'un objet en or. C'est pourquoi, nous réalisons en complément une étude par PIXE en faisceau extrait qui détermine la composition en éléments traces, eux-mêmes révélateurs des méthodes métallurgiques et de la pureté des alliages. Ce texte décrit cette méthodologie et présente différents exemples d'application en précisant les problèmes auxquels nous avons été confrontés sur les différents types d'objets rencontrés.

Keywords: gold, analysis, Scanning Electron Microscope, Particle Induced X-ray Emission, external beam, trace elements, authentication, fakes.

Mots-clés : or, analyse, Microscopie Électronique à Balayage, PIXE faisceau extrait, éléments traces, authentification, faux.

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1. INTRODUCTION

The analysis of goldwork interests archaeologists, art historians, or museum curators. The aims of such investigations are to study the style, the iconography, and the techniques of manufacture, to establish a hypothetical period and provenance of these objects, and to develop a strategy of conservation. To these purposes, scientists can contribute useful information regarding the composition of the alloy, the analysis of deposits, and the weathering degree. Most of the studies on gold artefacts aim to define the origins, trade and provenance of the ores based on the trace elements composition (Guerra and Calligaro, 2003; 2004; Bugoi *et al.*, 2003; Demortier *et al.*, 1999; Ontalba Salamanca *et al.*, 1998).

Generally, few methodological studies exist about the authentication of gold (Craddock, 2009; Guerra, 2008). First of all, gold objects are very resistant to long time corrosion. Thus, we cannot establish our conclusions on the weathering degree of the gold alloy or the nature of the corrosion products, as for copper alloys (Craddock, 2009; Robbiola and Portier, 2006). Thermoluminescence tests, performed on casting cores, can provide interesting chronological information for bronze objects, for example (Craddock, 2009). However, goldwork does not typically contain residual cast cores. In addition, gold forgeries have become progressively flawless, as the falsifiers became aware of the scientific tools used in the authentication of works of art. It is quite easy to use ancient gold shreds to re-create a new and fake artefact, following an ancient style, and with a typical ancient trace elements composition. In this case, a single scientific approach, which only uses trace elements to distinguish fakes from original ancient goldwork, is no longer sufficient to discriminate all the forgeries. In order to improve the authentication of gold objects, this paper presents a combined approach, including as the first step an investigation of the surface by scanning electron microscopy (SEM-EDX) to observe tool marks, superficial deposits, the microstructure of the alloy, and eventual weathering features. As the second step, a quantitative analysis of the alloy by external-beam PIXE is employed, in order to define its trace element composition.

2. METHODS

The study of the surface and the chemical composition of the deposits were carried out with an energy-dispersive X-ray spectrometer (EDS), using a 20 keV electron beam, coupled with a scanning electron microscope (SEM) Jeol JSM 840.

These analyses were performed on the surface without pretreatment or metallization. We employed both back-scattered electron (BSE) and secondary electron (SE) images.

External beam PIXE (Particle Induced X-Ray Emission) is a non-destructive method of analysis which allows determining the concentration of major, minor and trace elements. For this purpose, we used a 3 MeV H^+ ion beam produced by the singletron accelerator of CENBG (Centre d'Etudes Nucléaires de Bordeaux Gradignan). Due to the limits of the accelerator, this energy optimizes the ionisation cross-section for interesting elements, such as Sn, Sb, Cd, Ru, and Rh. In front of the dedicated external beam-line, artefacts can be analysed without sampling or limitations in terms of size. Two detectors are used in the experimental setup, and allow the measurement of emitted X-rays under the interaction with the incident ion beam, which constitute a spot size of 1 mm in diameter on the sample.

3. RESULTS

SEM-EDS investigations

The micrographs of the surface provide information on the manufacturing techniques employed. We also searched for tools marks, such as those as a result of hammering, burnishing or polishing. Finally, we also investigated the decoration methods and analysed the superficial deposits. The small objects (less than 5 cm) can be placed in the specimen chamber of the SEM. This allowed us to directly determine their composition (major and minor elements) and observe their microstructure. For the bigger objects, we worked on surface replications (cellulose acetate film), which reveal the fingerprint of the surface and remove superficial deposits (Funga and Sanipelli, 1982).

This first step allows identifying the noticeable fakes, which show fundamental anomalies, such as modern tool marks or traces of acid attack.

Figure 1 shows a surface replication of a gold statuette presumed to originate from the New Kingdom of Egypt (1580-1085 BC). On the surface, we can observe very thin and unidirectional ridges, which cannot correspond to restoration or cleaning phases. They correspond to burnishing tool marks. This polishing technique was traditionally performed with a burnisher, a type of little hammer with a perfectly polished head (Ogden, 1993; Arminjon and Bilimoff, 1998; Scott, 1991). Nowadays, the burnishing is carried out with a mechanical burnisher using thousands of rotating micro-balls. The thinness and the regularity of the marks observed on the surface of this object are clearly a result of this modern technique.

Figure 1: SEM SE image of a surface replication from a gold statuette. We observe thin and unidirectional ridges, which correspond to the use of modern tools and techniques.

Figure 1 : Image MEB de la reproduction de la surface d'une statuette en or. Les stries fines et unidirectionnelles correspondent à l'utilisation d'outils modernes.

Following the SEM-EDS study, we also detected silver chloride micro-particles, which are not mixed with the mineral deposits. In addition, we did not detect any silver sulphide micro-particles, which are usually also found in naturally corroded gold-silver alloys (Gusmano *et al.*, 2004). As a consequence, it can be inferred that the silver chloride micro-particles originate from a deliberate chemical attack, carried out in order to simulate the natural weathering of the material. *Aqua regia* treatment leads to a partial dissolving of the metal and to the formation of numerous silver chloride micro-particles. Finally, we observed superficial cupules, which are also characteristic of an acid attack. This result is consistent with the large quantity of chlorine contained in the deposits. The presence, on the entire object, of modern tool marks and characteristics of chemical attack is inconsistent with the presumed period of this piece. It is thus easily understandable that, in this case, a complementary PIXE analysis is not necessary.

The second example concerns a gold earring from China, presumed to be from the Shang Dynasty (11th-10th centuries BC). The SEM observation of the superficial deposits shows an amorphous to non-crystalline material, which is composed of iron, chloride, calcium and silicated phases. The

association of iron and chloride, and the microstructure of these deposits indicate that they correspond to residues of an acidic solution, such as ferric chloride (Perego, 2005). The contents of iron and chloride are too high to correspond to natural clay or 'earth'. This indicates that the object underwent a surface treatment to modify the surface aspect of the object and to simulate mineral deposits and/or presence of copper corrosion products.

We can see that SEM surface analyses represent a powerful tool for discriminating the obvious fakes, which show formal traces of modernity. These investigations are necessary, but not sufficient, to establish an object's authenticity, because it is easier to attest that an object is a forgery than to establish its authenticity (Robbiola and Portier, 2006).

External-beam PIXE

The external-beam PIXE developed at CENBG is one of the five beam-lines of the AIFIRA platform. Four of them are dedicated to macro-, micro-, and nano-analysis by nuclear techniques. AIFIRA is a brand new facility built in 2006 using the 40 years old experience of the CENBG in Ion Beam Analysis.

While some other external-beam PIXE facilities exist in the world, for the present study we have developed an experimental setup dedicated to the analysis of gold items. For this purpose, two types of information are interesting: the composition of the gold alloy and the trace elements. However, it is not possible to obtain both at the same time, with the same detector.

In our experimental setup, we simultaneously used two Si(Li) detectors with different shields in order to optimize the different types of investigated information. We will describe below the obtained spectra and the errors in interpretation which could occur if we did not pay attention.

The quantitative data corresponding to Figures 2 and 3 are not included in Table 1. The first spectrum reported is obtained from a gold necklace presumed to date from 1500 BC, with the detector equipped with a 315 µm carbon filter before the silicon crystal (Fig. 2). This setup was used to stop the backscattered proton beam and the low energy X-rays (especially M-lines from Au and L-lines from Ag, Sn, Cd, etc.). This spectrum allowed the determination of the Au/Ag/Cu composition (98.1/0.7/0.9%), and the detection of trace elements Fe (620 ppm) and Ni (114 ppm), because of their large X-ray emission cross-section. In addition, we had to move the detector away from the target to prevent pile-up effects, due to the fact that the counting rate was so high as compared to the frequency of the multi-channel analyser. Nevertheless, we observed on the spectrum four

Figure 2: PIXE spectrum of a gold necklace collected with a 315 µm carbon filter. We identified the composition of the alloy as 98.1% Au, 0.7% Ag, and 0.9% Cu, and we detected Fe and Ni as trace elements.

Figure 2 : Spectre PIXE d'un collier en or dont l'acquisition est réalisée avec un filtre de 315µm de carbone. La composition de l'alliage a été définie (Au 98.1, Ag 0.7, Cu 0.9) et le Fe et le Ni ont été détectés au niveau d'éléments trace.

little sum peaks due to this phenomenon, which prevent the detection of important elements in the process of authentication, like Pd and Cd. Furthermore, the little solid angle in this configuration is not suitable for the detection of other trace elements, like Sn and Sb, due to their low X-ray emission cross-section, and the only interesting trace element which could be detected is Pb, due to its $L\gamma_1$ line at 14.762 KeV with a limit of detection (LOD) of 300 ppm. Detection of other trace elements, such as Hg or Pt, is not possible due to the high level of Au L-rays. At this stage of the study, we were only able to determine the composition of the alloy. Even if this information is important, it is not sufficient for providing reliable chronological information about the object.

The second experimental setup was thus necessary in order to obtain data on other trace elements. In this configuration, an absorbing copper foil (75 µm thick) is placed in front of the detector. The reason we used copper is because its edge of absorption will neutralize especially the energy of the gold L-rays. This setup prevents the pile-up and allows us to move the detector closer in order to improve the LOD down to 60 ppm for the elements Ru, Rh, Pd, Cd, Sn, and Sb. On the resulting spectrum (Fig. 3), we can observe the energy range where the L-lines of gold are very low in intensity, the lack of pile-up in the region under consideration, and

Figure 3: PIXE spectrum of a gold necklace collected with a 75 µm copper filter. This configuration allows detecting the presence of tin (1762 ppm) and antimony (123 ppm) in the alloy as trace elements.

Figure 3 : Spectre PIXE d'un collier en or dont l'acquisition est réalisée avec un filtre de 75 µm de cuivre. Cette configuration permet de déterminer l'étain (1762 ppm) et l'antimoine (123 ppm), éléments présents dans l'alliage à l'état de trace.

the presence of trace elements Sn (1762 ppm) and Sb (123 ppm). On the same spectrum, we can also observe the peak of xenon, which is present in the air on the path of the incident proton beams.

This result indicates the fact that the refining of this gold alloy is quite poor and consistent with ancient processes. Nevertheless, an old alloy could also be used by a forger to manufacture a modern item. Thus, we have to corroborate these analyses with an investigation of the surface of the alloy by SEM in order to identify eventual corrosion microstructures and surface treatments.

Combined methods: SEM and PIXE

Example 1

The observation of the surface of a European gold ring presumed to date from the 5th century AD indicates that the decorations have been performed with a hand-tool (Arminjon and Bilimoff, 1998). The surface of the metal is smooth with irregular microstructures. The edges of the engraved designs are not raised. However, we did not observe clear weathering features, such as micro-pitting or corrosion of grain boundaries (Fig. 4). From these results, it is difficult to provide formal information about the chronological compatibility of this object with its presumed antiquity.

Figure 4: SEM SE image of a gold ring. The surface and the edges of the engraved designs are smooth and not raised.

Figure 4 : Image MEB d'un anneau d'or. La surface et les bords des dessins gravés sont lisses et non saillants.

In such a case, PIXE analysis of the trace elements composition of the alloy is necessary. The analysis showed a very pure gold (99.6 to 99.9 wt% Au), with silver, copper, iron, nickel, calcium and chromium as trace elements (Table 1). The last four elements probably originate from the contribution of a mineral deposit. Thus, silver and copper would be the only constituting trace elements of this metal.

The ancient gold alloys contained many trace elements, such as lead, tin, platinum, palladium, zinc, bismuth, and

antimony (Bugoi *et al.*, 2003; Craddock, 2009; Demortier *et al.*, 1999; Guerra, 2008; Guerra and Calligaro, 2003; 2004; Ontalba Salamanca *et al.*, 1998; Ott and Schindler, 2001). The absence of a significant set of trace elements in this alloy is abnormal. This aspect suggests that the metallurgical methods employed in the making of this object do not correspond to ancient traditional ones. Its composition indicates that modern extraction and refining (thermal or electrolytic) were used (19th or 20th century AD).

Example 2

The analysis of a Middle East gold dagger presumed to date from the 4th-3rd century BC required a combination of the SEM and PIXE approaches to verify its authenticity. The material was a gold-silver-copper alloy. The concentration of the gold was in the range of 84 to 86%. It corresponds to 20.5 carat gold.

The three analysed areas contain iron, nickel and tin as trace elements (Table 1). The presence of tin and nickel should indicate an ancient metallurgical method. However, their concentrations are relatively low, and we did not detect any other trace elements, such as lead, antimony or platinum, for example. Yet, we also did not observe any formal evidence of modernity, such as the presence of aluminium by SEM (more than 0.1 wt%) or of cadmium by PIXE, for example (Scott, 1991; Craddock, 2009). From the PIXE results, it was difficult to draw a definite conclusion regarding the authenticity of this dagger.

The SEM micrographs of the gold indicate it has a smooth surface with irregular features and numerous pits (Fig. 5). It presents a rounded microstructure, and the profiles of depression are not sharp. We also observed an important micro-porosity. The microstructure of the surfaces appears to correspond to prolonged and natural weathering pro-

Object	Point	wt %	wt % or ppm		ppm										
		Au	Ag	Cu	Fe	Cr	Ca	Ni	Zn	Ru	Rh	Cd	Sn	Sb	Pb
Gold ring (presumed from 5 th century AD)	1	99.9	1000	270	105	nd	nd	93	nd	nd	nd	nd	nd	nd	nd
	2	99.9	716	193	100	nd	nd	125	nd	nd	nd	nd	nd	nd	nd
	3	99.6	815	580	980	230	3400	110	nd	nd	nd	nd	nd	nd	nd
Gold dagger (presumed from 4 th -3 rd centuries BC)	1	86.1	8.0%	5.0%	7723	nd	nd	152	nd	nd	nd	nd	100	nd	nd
	2	84.9	9.0%	6.0%	735	nd	nd	238	nd	nd	nd	nd	200	nd	nd
	3	83.6	8.6%	6.0%	16000	nd	nd	216	nd	nd	nd	nd	230	nd	nd
Gold belt (presumed from 6 th - 3 rd centuries BC)	1	97.8	0.99%	6780	1140	nd	3614	94	nd	nd	nd	nd	250	30	nd
	2	98.1	1.1%	4610	1310	nd	1450	105	nd	nd	nd	nd	2700	134	nd
	3	97.8	0.96%	6630	1440	nd	6630	85	nd	nd	nd	nd	1430	60	nd
	4	96.0	3.2%	7730	520	nd	nd	130	nd	nd	nd	nd	485	60	nd

Table 1: Compositions of the alloys of different objects. The major and minor elements are expressed in weight percent and trace elements in ppm. Even if the limits of detection are not presented, they are evaluated for each element and each analysed point. The non-detected elements or those whose for which the detected levels are less than or equivalent to the detection limit are indicated as 'nd'.

Tableau 1 : Composition des alliages des différents objets. Les éléments majeurs et mineurs sont exprimés en % et les éléments traces en ppm. Malgré l'absence de limites de détection, ces valeurs ont été déterminées pour chaque élément et pour chaque analyse. Les éléments non détectés ou dont la concentration est égale ou inférieure à la limite de détection sont indiqués « nd »

Figure 5: SEM SE image of a gold dagger. The surface of the metal has a smooth surface with irregular features and numerous pits. We can also observe a rounded microstructure.

Figure 5 : Image MEB d'un couteau en or. La surface du métal est lisse avec des traits irréguliers et nombreux petits trous. Une microstructure arrondie peut aussi être observée.

cesses affecting gold alloys (Ontalba Salamanca *et al.*, 1998; Ott and Schindler, 2001; Gusmano *et al.*, 2004; Craddock, 2009). Thus, the results obtained from the combined methodological approach are in good agreement with the presumed period of the object.

Example 3

The SEM examination of an East Central Asian gold belt presumed to date from the 6th-3rd centuries BC indicates that superficial deposits are composed of a mix of silicated mineral phases, such as clay, and calcium carbonate. They also contain numerous microparticles of silver salts, which should result from the natural weathering of the gold alloy. The object has a smooth surface with irregular features, a rounded microstructure and a superficial micro-porosity. We also did not detect any modern tool marks or indications of a chemical treatment. The solders are composed of a gold-silver-copper alloy, which is consistent with ancient techniques, and we did not detect the presence of any modern element, such as zinc or cadmium. We detected iron and calcium as trace elements, but they most likely correspond to the contribution of superficial deposits.

Furthermore, the alloy also contains significant concentrations of tin, antimony and nickel as trace elements (Table 1). Their presence is in good agreement with ancient extraction techniques that were not able to remove these elements. Thus, once again, the combined study of both the surface microstructure and the composition of the alloy and the solders indicate that the object corresponds to ancient and traditional goldwork practices.

4. DISCUSSION AND CONCLUSION

This paper emphasizes that the authentication of gold objects requires the use of complementary approaches. A combination of SEM and PIXE analyses is very powerful for this purpose. The use of a single method only provides partial information regarding the antiquity of the object.

SEM investigates the surface of the object, and is able to identify fashioning and polishing tool marks, weathering features, traces of acid attacks, and the composition of the burial deposits. These investigations are limited to a surface study. Thus, in most cases, the observations of the microstructure of the gold are insufficient for obtaining formal evidence about the authenticity of an object, except for the cases of obvious fakes.

PIXE determines the composition of the alloy and characterises the concentration of trace elements, providing information about gold working techniques. This method is non-intrusive and offers powerful results, which allow estimating the chronological compatibility of the objects with their presumed antiquity. However, using this method exclusively does not allow us to discriminate forgeries made with ancient gold shreds.

As a matter of fact, the forgers take advantage of the new scientific knowledge available. If we want to be ahead of them, we have to combine several methods in order to investigate different characteristics of the objects and to improve our results in different ways. Thus, X-ray radiography or CT scanning can contribute complementary information about the homogeneity of the objects and the manufacturing techniques used. When sampling is possible, other types of analytical methods, such as ICP-MS (Guerra and Calligaro, 2004) can be useful to improve the limits of detection of lead and platinum, for example, and to neutralize the effect of specific treatments, such as superficial enrichment of gold by burnishing or *la mise en couleur de l'or* (Grimwade, 1999; Jacobson, 2000; Bachmann *et al.*, 1999).

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