ELSEVIER

Nuclear Instruments and Methods in Physics Research B 150 (1999) 640–644

NIM B
Beam Interactions with Materials & Atoms

PIXE, XRF and GRT for the global investigation of ancient gold artefacts

Guy Demortier *, Yvon Morciaux, Daphné Dozot

LARN, Facultés Universitaires Notre-Dame de la Paix, 61, Rue de Bruxelles, 5000 Namur, Belgium

Abstract

The study of ancient gold jewellery artefacts often requires surface and bulk characterisation using non-destructive methods. Curators of musea or owners of private collections do not allow any sampling (even at microscopic level) for the investigation of the bulk of massive gold objects, which often contain less noble metals. Neutron Activation Analysis of the whole sample is generally prohibited even if no danger may be feared from delayed radioactivity. Weight and density measurements are easy and convenient to assert the presence of a cavity or a core of lower density. A combination of PIXE (at various incident proton energies in a non-vacuum geometry) for the elemental distribution in the first 10 μm below the surface, XRF (induced by γ-rays of 59 keV and of higher energy from a source of ^{241}Am) to investigate the material up to several hundreds of microns, and GRT (Gamma Ray Transmission) of 662 keV photons (^{137}Cs) may give a more complete answer on the surface and bulk compositions of the artefacts. Examples are given for Hellenistic and Mesoamerican jewellery items.

1. Introduction

Amongst the metallic objects of ancient times, most gold jewellery artefacts are intact and are generally considered as homogeneous. Gold cannot indeed suffer from in-depth corrosion mechanisms, and a surface analysis can give results which may be extrapolated to the bulk. Large artefacts are generally made by the lost wax technique and some internal cavity may be empty or filled with remains of the casting procedure (clay or another silicate material). Other objects may be only apparently made with gold: another metal (copper or gold-copper alloys) could have been used to cast the bulk which was then covered by gold plating. Modern reproduction of jewellery items of ancient style are generally made in this way. In Amerindian civilisations (5th to 15th century) tumbaga (a man-made material containing a large copper content and therefore poor in gold) was widely used. In order to give the artefacts the appearance of gold, these ancient goldsmiths have used a depletion gilding procedure. The heating process of such samples (previously treated in a mixture of low acidity solutions from plants with salt) oxidises most of the surface copper and partially silver, in order to give a golden aspect to the final product. Depletion in thicknesses of the order 0.3 μm is sufficient to achieve the best golden aspect [1–3].

* Corresponding author. Tel.: ++32 (0)81 72 54 75; fax: ++32 (0)81 72 54 75; e-mail: guy.demortier@fundp.ac.be

0168-583X/99/$ – see front matter
PII: S0168-583X(98)00900-8

The study of gold jewellery items is not so easily approached by surface techniques alone, and analytical results obtained by PIXE would be reliable only if some depth profile of gold could be available. RBS with α-particles cannot be used for that purpose due to the low penetration of α-particles in heavy matrices. Furthermore, the kinematic factors to separate gold from silver and copper contributions are not sufficiently different when protons (whose range is about 10 times greater than that of α-particles) are used as incident particles. The combination of PIXE and RBS using various incident proton energies and various geometrical arrangements (tilting of the sample target but only if the material is sufficiently flat) has given pertinent answers to this problem [4,5].

We intend to briefly discuss here the complementarity of PIXE at various proton energies (we call this method differential PIXE), XRF induced by γ-rays of a ^{241}Am source and GRT of thick material to characterise the objects: thin surface layers (10 μm) by PIXE, deeper regions using XRF and qualitative bulk composition using GRT.

2. Experimental arrangements: special requirements and potentialities

2.1. PIXE

The Si(Li) detector is situated in the backward direction (∼165°): in that particular geometry the exit path of X-rays is very close to the entrance path of incident protons. This arrangement is compulsory because the surface of archaeological samples is not generally flat. Selective absorbers of zinc are inserted between the target and the detector in order to manage an equilibrated counting rate in all characteristic X-ray peaks. The measurement of Au is performed by using Lβ and Lγ lines, the other elements (Cu, Ag) by using their Kα and Kβ lines. Relative intensity ratios of lines of each elements may give valuable information on the homogeneity of the sample. Incident proton energies at the target site are varied from 2.2 to 3.2 MeV in order to check the variation of concentration versus depth [6].

2.2. XRF

Gamma-rays (59.54 keV) from an ^{241}Am source are collimated to give a narrow flux through a regular hole pierced in a 2 cm thick lead shield. The incident γ-ray beam is at 90° with respect to the detection of secondary X-rays. The surface of the sample is oriented in order to always observe the Compton peak at the same place, the sample surface is tilted at 45° with respect to both incident and outgoing directions. This arrangement is most convenient to irradiate narrow regions only and to avoid large shadowing effects if the surface is not flat. The relative intensity of K lines of gold (induced by the low intensity γ-rays of energy greater than 110 keV from the ^{241}Am source) to that of L lines is qualitatively used to recognise thin gold layers (20 μm or less) from samples containing gold in the bulk as well (100 μm or more).

L X-rays are indeed more absorbed than K ones, the K/L intensity ratio increases with the increasing of the gold layer thickness provided the geometry of the experiment is not modified.

2.3. GRT

For jewellery items of a thickness greater than 5 mm, the estimate of the core density (initially evaluated from weight and volume measurements) was locally checked by using collimated γ-ray beam (1 mm in diameter drilled in a 7 cm thick lead shield) from a ^{137}Cs source ($E_\gamma = 662$ keV). The scanning of transmitted γ-rays by moving the specimen in front of the collimator allows us to identify regions of high density. Other γ-rays sources giving lower energy γ-rays (like ^{226}Ra) or production of γ-rays by PIGE on materials producing a high flux of photons like Al (844 and 1013 keV), Na (439 keV), F (110, 197 keV) and Li (429 keV) could be an alternative to cover a larger region of attenuation coefficients in order to investigate materials of various thicknesses and compositions. The choice of μx factors of the order 0.3 to 3 in the attenuation law: $I_{\text{trans}} = I_0\ \mathrm{e}^{-\mu x}$ could give convenient intensity ratios with and without the specimen in front of the source. This procedure cannot be used to identify the elements in the core region (several mm below the surface)

of the specimen (no secondary fluorescence from the core may be detected due to a large absorption) but was only meant to qualitatively verify if the core is not empty.

3. Study of selected gold jewellery artefacts

A bracelet of Dacian origin (Hellenistic) (Fig. 1) was studied by using differential PIXE (E_p has been varied from 2.2 to 3.2 MeV), XRF and GRT. The weight and volume measurements give a mean density around 5.2 g/cm^3, only 35% of the density of the surface alloy whose composition was confirmed to be homogeneous down to a depth of minimum 10 μm by differential PIXE and at least down to 100 μm (by XRF), as far as the high gold content is concerned (Table 1). GRT indicates that the external surface of the toroïdal bracelet was of much higher density (as observed by a larger absorption of 662 keV γ-rays, in regions A and C of Fig. 2). The item is made with a sheet of a gold rich alloy surrounding a core of lower density. The transmission in region B indicates that the thickness of the gold sheet is of maximum 0.35 mm, an estimate which is qualitatively compatible with measurements at A and C (the γ-ray beam, 1 mm in diameter, is indeed too wide to give a precise estimate). The soldering of the heads of rams is probably of modern origin (repair?): the alloy in this region contains larger concentrations of Cu and Ag but also traces of Cd. The determination of the centre of gravity (Fig. 1) also indicates that the composition of the core of the item in the regions of both heads are not fundamentally different from that of the toroïdal region. Kα/Lα intensity ratio of gold lines observed by XRF is nearly twice the value observable for a flat thick gold sample. The high energy γ-ray of ^{241}Am have indeed the possibility to excite X lines of gold on both sides of the toroïdal structure, but only K lines induced in the second face may reach the detector due to the complete absorption of corresponding L lines.

A pectoral of Mesoamerican origin (Fig. 3) is made of a metal sheet not uniform in thickness (0.18 to 0.35 mm). PIXE analyses at one single proton energy (2.2 MeV) give copper, silver and gold values reported in Table 1, indicating that the material is quite homogeneous laterally. Several analyses at various proton energies, but at the same impact clearly indicate (Table 2) that the

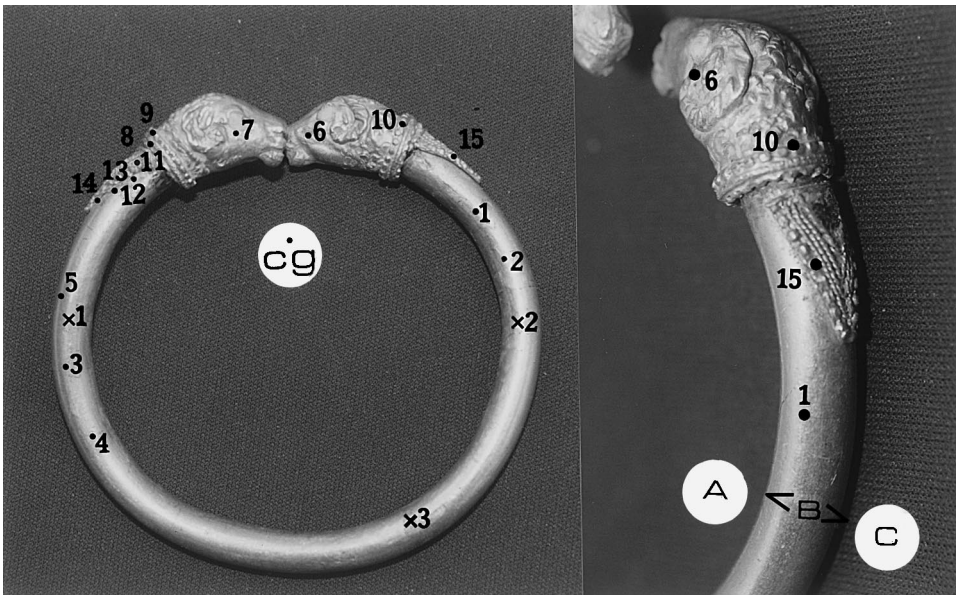

Fig. 1. Hellenistic bracelet (Dacia) (3rd century BC ?): Weight: 66.8 g; volume: 12.9 cm^3.

Table 1
PIXE and XRF analyses of the jewellery items

	Cu%	Ag %	Au %	Remark
Bracelet PIXE (2.8 MeV) see Fig. 1				
Impact				
1	0.5	<0.1	99.5	
2	2	0.1	97.9	
3	0.7	0.1	99.2	
4	0.2	0.2	99.6	
5	0.2	0.2	99.4	Possibly 0.2% Cd
6	0.2	0.1	99.7	
7	0.2	0.1	99.7	
8	2.0	0.1	97.5	0.4% Cd
9	2.2	0.1	97.3	0.4% Cd
10	0.9	0.1	99.0	
11	5.1	1.9	93.0	Granule
12	4.1	3.5	92.4	Granule
13	6.6	6.8	86.6	Soldering
14	3.0	1.8	95.2	Granule
15	4.5	4.8	90.7	Granule
Bracelet XRF				
x_1	$\leqslant 1.8^*$	0.05**	98.2	
x_2	$\leqslant 1.0$	0.02	98.9	
x_3	$\leqslant 1.1$	0.05	98.8	
Pectoral PIXE (2.2 MeV) see Fig. 3				
1	2.7	37.6	59.7	
2	2.6	40.1	57.3	
3	2.3	39.1	58.6	
4	2.1	39.9	58	
5***	1.8	41.4	56.8	
6	2.1	40.7	57.1	
7	2.2	40.3	57.5	
8	2.4	40	57.6	
9	2.5	40.2	57.3	
10	2.1	39.2	58.7	
Pectoral XRF				
x_1	2.4	38.9	58.7	
x_2	3.3	38.1	58.6	Grazing
x_3	2.3	38.9	58.8	
x_4	2.9	38.8	58.3	
x_5	2.4	38.9	58.7	

* bad sensitivity.
** high sensitivity.
*** region selected for in-depth scan by increasing proton energy (see Table 2).

copper content apparently increases when the proton energy is increased. These values, obtained by postulating a homogeneous composition, is a

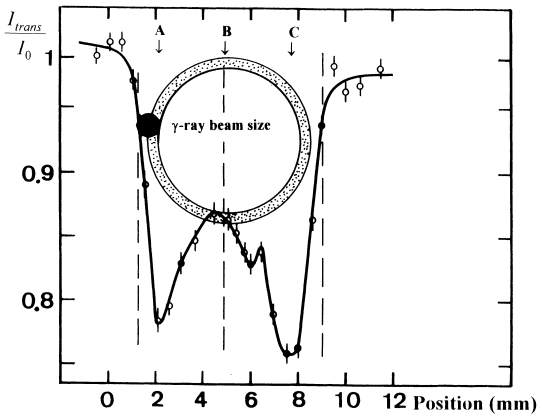

Fig. 2. Transmission of 662 keV γ-rays when a (1 mm^2 diameter) photon beam is scanned across regions A to C. The increase of absorption in regions A and C clearly indicates that the core is empty or contains a large quantity of low Z elements.

proof that the bulk contains more copper than the surface. Calculations using differential PIXE may be fitted with several depth profiles: in Table 3 we give two possible profiles. One is computed with no copper at the surface and then a maximum concentration in depth. The second refers to the profile which is compatible with the bulk content determined by XRF. Both profiles are calculated using the differential PIXE method [6].

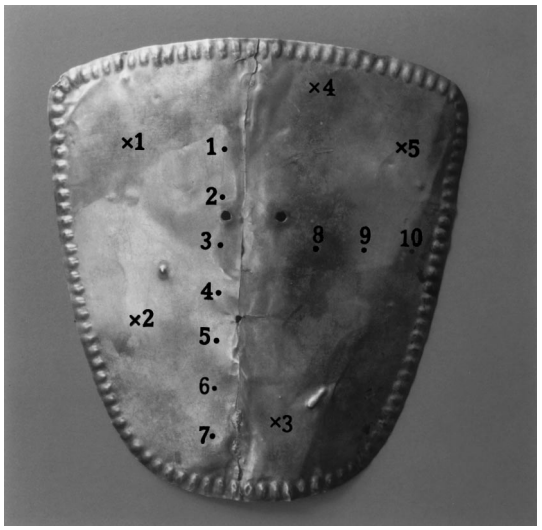

Fig. 3. Mesoamerican pectoral (Columbia) (500–1500 AD): Weight: 37.3 g; volume: 2.65 cm^3.

Table 2
Mesoamerican pectoral (impact 5). Apparent Cu concentration with increasing proton energy

E_p (MeV)	Cu PIXE value (%)
2.2	1.79
2.3	1.88
2.4	1.89
2.5	1.95
2.6	1.94
2.7	1.96
2.8	1.98
2.9	2.07
3.0	2.06
3.1	2.14
3.2	2.16

Table 3
Depth profiles compatible with data of Table 2

Profile 1		
Layer 1	2.75 μm	60% Au + 40% Ag
Bulk	∞	7.5% Cu + 52.5% Au + 40% Ag
Profile 2		
Layer 1	1.5 μm	1.5% Cu + 58.5% Au + 40% Ag
Layer 2	2.5 μm	2.5% Cu + 57.5% Au + 40% Ag
Bulk	∞	3.3% Cu + 56.7% Au + 40% Ag

If we suppose that the first layer is copper free, it should contain 60% Au and 40% Ag (profile 1) and have a thickness of 2.75 μm. In this hypothesis, the Cu content in the bulk must be 7.5%. This situation is unphysical and does not fit with the XRF measurements. If we take, from the bulk copper, the observed concentration values obtained by grazing XRF (minimum absorption of Cu Kα X-rays), the calculation of the Cu profile from the whole series of PIXE measurements from 2.2 to 3.2 MeV protons gives a Cu concentration increasing from 1.5% at the surface up to 3.3% at 4 μm in the depth. The density measurement is in agreement with these determinations by differential PIXE. The depletion of copper at the surface cannot be understood by a depletion gilding procedure used by ancient Amerindian goldsmiths: this last procedure was used in Antiquity for jewellery items containing a large concentration of copper. Besides, natural wearing leading to the selective elimination of Cu from the surface cannot be accepted for the explanation of the measured depth profile because the concerned thickness (up to several microns) is too large. The shape of the Cu profile could be due to modern cleaning using acidic agents. The PIXE results at various proton energies give a proof that the use of PIXE at one single proton energy to study complex matrices cannot be satisfactory [6].

4. Conclusions

PIXE measurements at various energies and the treatment of the data using a program able to manage depth profiling and complementary measurements using XRF and GRT were necessary to confirm or to implement the conclusions of classical PIXE for the analytical investigation of gold jewellery artefacts.

Acknowledgements

We thank the owners of the archaeological items for allowing us to keep the objects for a long time, and, therefore, providing young graduate students with the opportunity to be introduced to archaeometry.

References

[1] H. Letchmann, in: R. Maddin (Ed.), Traditions and Styles in Central Andean Metallurgy, MIT Press, Cambridge, 1988, p. 344.
[2] D.A. Scott, Archaeometry 28 (1) (1986) 33.
[3] H. Letchmann, Scientific American 250 (6) (1984) 38.
[4] J.L. Ruvalcaba-Sil, G. Demortier, Nucl. Instr. and Meth. B 130 (1997) 297.
[5] J.-L. Ruvalcaba-Sil, Ph.D. Thesis, FUNDP-Namur, 1997.
[6] G. Demortier, these Proceedings (PIXE-8), Nucl. Instr. and Meth. B 150 (1999) 520.