

GOLD AND SILVER COATING CHARACTERIZATION USING AN X-RAY FLUORESCENCE BASED METHOD – THE CASE OF ARCHAEOLOGICAL ARTIFACTS

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Abstract. To elucidate some aspects of the manufacturing procedures - from simple mechanical application of a thin malleable gold foil to amalgamation, used in ancient times for coating copper, bronze or silver objects with thin layers of gold or silver, thin layers of coatings were studied using an X-Ray Fluorescence-based method. We present results for some gilded and silvered objects from different historical periods and different geographical areas.

Key words: XRF, gilding, silvering, thin layer, thickness.

1. INTRODUCTION

Gold plating of ancient silver and copper-alloy jewellery, statues, figurines, coins and other metal items served a variety of purposes [1]. In addition to its decorative effect, appearing in combination with *e.g.* inlay or relief decoration, gold plating improved corrosion resistance and created the deliberate impression of a gold object. These techniques were applied from Early Bronze Age. The earliest gilded-metal objects (dated 3rd millennium B.C.) were produced by covering the artifact with mechanically attached gold foils, *e.g.* by folding the foil around the object by riveting, or, later, hammering the gold foil edges into grooves cut into the substrate. Subsequently, gold leaf was used - produced by hammering the gold to a thin gage and then attaching it with an adhesive (usually a resin or a drying oil). Amalgamation was another gilding technique used in antiquity: it started by grinding a gold leaf in mercury to create a paste of amalgam, applied then to a copper-alloy or a silver object which was subsequently heated to produce a firmly bonded yet porous gilding layer. This layer was burnished to give a smooth and reflective surface. A possible variation of this technique was the application of gold foil on a surface coated with mercury and the formation of the gold amalgam in-situ with subsequent heating and burnishing. Fire gilding on silver or copper

retained approximately 10% of the mercury in gold, a substantial amount that can usually be identified by straightforward and non-destructive X-ray fluorescence analysis (XRF).

The determination of gold/silver layer thickness is based on the variation of characteristic X-rays intensity for a constitutive core element – j – with the respective layer properties (atomic number, thickness). Of course, this X-ray producing element must not be present in the coating layer. The composition (main elements) of the bulk and of the coating layer must be known [2]. To apply this method it is necessary that both layer and core be homogeneous in composition and thickness.

Our method uses differential X-ray attenuation: when an X-ray beam passes through a homogeneous layer, it is absorbed along its path depending on its energy. The transmission fraction (T) for single coating layer is given by:

$$T = \frac{I_{fc}^j - I_{\infty}^j}{I_{so}^j - I_{\infty}^j} = e^{-(\mu_e^c + \mu_{fc}^j)m}, \quad (1)$$

where: I_{∞}^j is the saturation intensity of the X-rays emitted by element j for infinite coating thickness; I_{so}^j the intensity measured when the coating thickness is equal to zero; μ_{fc}^j [$\text{cm}^2 \text{g}^{-1}$] the coating mass absorption coefficient for fluorescent X-rays emitted by element j ; μ_e^c [$\text{cm}^2 \text{g}^{-1}$] the coating mass absorption coefficient for the energy of the exciting radiation and m [$\text{cm}^2 \text{g}^{-1}$] is the mass per unit area of the coating: $m = d \cdot x$, with d the specific density [g cm^{-3}] of the coating and x its thickness [cm].

We can estimate the range of a measurable coating thickness using the criteria for maximum and minimum measurable thickness m_{\max} and m_{\min} [2]:

$$m_{\max} = \frac{\ln(20)}{(\mu_e^c + \mu_{fc}^c)} = \frac{3}{(\mu_e^c + \mu_{fc}^j)} \quad [\text{g} \cdot \text{cm}^{-2}], \quad (2)$$

$$m_{\min} = \frac{\ln(1.05)}{(\mu_e^c + \mu_{fc}^c)} = \frac{0.05}{(\mu_e^c + \mu_{fc}^j)} \quad [\text{g} \cdot \text{cm}^{-2}]. \quad (3)$$

For most metallic coatings, thickness from tens of nanometers to a few micrometers can be measured, while for less dense non-metallic coatings the limits are at least one order of magnitude higher.

Based on this theory we extract the intensity values for the elements of interest using a peak deconvolution method based on Least-Squares Fitting with Gaussian peak models integrated in the AXIL software[3], developed for analysis

using the X-MET 3000 TX+ spectrometer. For the determination of the attenuation of a single element or a mixture of more elements representative for archaeological objects alloys composition we develop a module in Mathematica [4].

2. EXPERIMENTAL

We selected two artifacts for this study:

- a Geto-Dacian “silver coin” of the Ocnita-Targu Carbunesti type [5], 5 samples, representing one of the first Geto-Dacian silver drachms monetary emissions (~ 250 - 150 BC).
- a gilded-silver Early Bronze Age (first half of the 3rd millennium BC) double spiral lock-ring found in a tomb Aricestii Rahtivani, Prahova County (Fig. 1) [6].



Fig. 1 – Gilded silver double spiral lock-ring from Aricestii Rahtivani.

In addition, we applied our method in electronics for the determination of the thickness of a thin gold layer deposited on an Al foil requested by Prof M. Fayez-Hassan from the Atomic Energy Authority, Cairo, Egypt (5 samples).

The acquisition of the X – Ray spectra was done with an Oxford Instruments portable spectrometer X-MET 3000TX+, equipped with a Rh-anode tube, operating at 40 KV, 6 μ A and a PIN silicon diode detector with Peltier cooling, with an energy resolution 270 eV for the 5.9 keV Mn K_{α} – line. The spectrometer is equipped with a Hewlett-Packard (HP) iPAQ personal data assistant (PDA) for software management and data storage. The analysed area is about 30 mm²; the sample–detector distance is 3 cm, the beam impact angle 50° and the detection

angle 57.9°. The error on the concentration values measured with X-MET 3000TX is within 10%.

For the evaluation of the intensity values of the characteristic lines for the elements of interest we used the IAEA standard program package AXIL [3].

3. RESULTS AND DISCUSSION

A significant variation in the elemental composition of the major elements on the surface on the both sides of the analysed sample can lead to the hypothesis that the respective object was obtained by gilding or silvering. The presence of mercury in the spectrum is a clear indicator of the use of the amalgamation technique.

3.1. THE OCNITA–TARGU CARBUNESTI DRACHMS

Table 1 presents the results of measurements on the 5 coins analysed. The data reveal a quaternary Ag/Sn/Cu/Pb alloy for all the coins, excepting no 4, which has 5.5% Hg in its composition, indicating the use of silver amalgamation. Another indicator of silvering is the variation of Ag/Hg/Cu/Sn ratio from 89.9/5.5/1.5/1.4 in the obverse side to 88.6/6.5/1.6/1.5 on the reverse side.

Table 1

Measured elemental composition for the Ocnita–Targu Carburnesti drachms

	Ag (%)	Sn (%)	Cu (%)	Pb (%)	Fe (%)	Au (%)	Hg(%)
1	74.4	13.6	7	2	1.4	0.7	-
2	71.5	17.7	6.7	1.5	2	0.5	-
3	74.1	14.5	8.3	1.4	1.3	-	-
4(av)	89.9	1.4	1.5	0.7	0.5	-	5.5
5	66.8	17.2	1.5	0.9	0.6	0.8	-

To estimate the thickness of the silver coating of coin no 4, we applied a model using measurement data of different bronze (Cu, Sn, Pb) ancient coins (see Table 2).

Table 2

Composition of the bronze coins used to simulate bronze bulk

Element	Cu	Sn	Pb	Fe
Coin 1	95.6	2.3	0.7	0.1
Coin 2	86.6	12.8	0.2	0.4
Coin 3	73.2	25.7	0.6	0.5

For the estimation of the thickness in the case of an object that is completely covered – the silvered coin – we have chosen the characteristics lines of the elements from the bulk with significantly different energies (Cu – 8.04 keV and Sn 25.2 keV). For a value of the composition for the coating layer chosen from amalgamation Ag/Hg common ratio (the density of this amalgam is slightly considering a few different percents of Hg), we calculate, using formula (1), the corresponding (Ag+Hg) alloy thickness for each bronze coin.

A second method – based on the extraction of the thickness from the attenuation curves of the two elements (Cu and Sn) – was used in order to verify that the composition of the bulk was correctly chosen and the thickness was correctly estimated.

Assuming the layer composition is 94.5% Ag+5.5% Hg, coin number 4 bulk values (after attenuation in the layer): 1.5% – Cu respectively 1.4% – Sn (Table 1) were reliably reproduced by a 16.1 μm thickness, for the Cu X-ray line, and by a 16.3 μm thickness, respectively for the Sn X-ray line. The assumed composition for the bulk was the one found for coin no.1.

Fig. 1 presents the K_{α} Cu line- and K_{β} Sn line-attenuation curves for the case of a layer of 94.5% Ag+5.5% Hg, calculated with Mathematica.

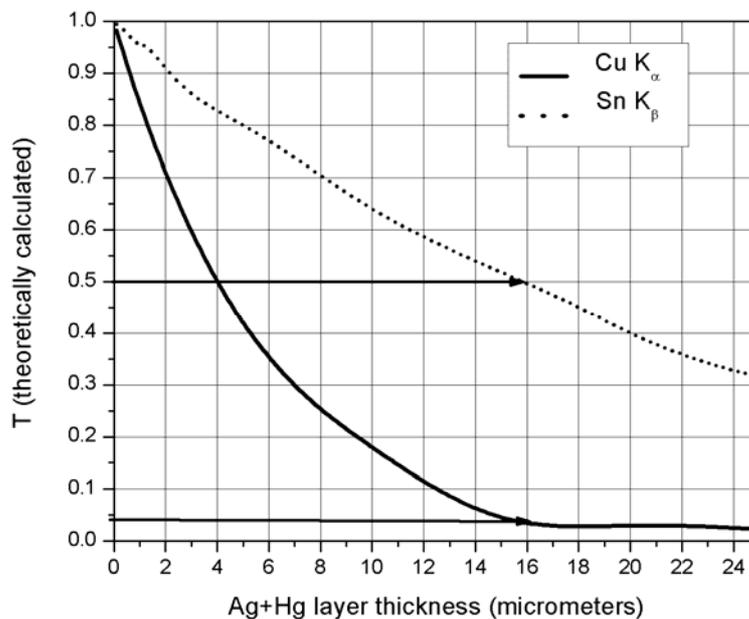


Fig. 2 – K_{α} Cu line- and K_{β} Sn line- attenuation curves through different values of layer thickness of the (94.5% Ag+5.5% Hg) alloy.

From this graph (Fig. 2) we obtain approximately 16 μm (Ag+Hg) layer thickness, which is in good agreement with the results obtained using the first method.

Due the assumptions made, it is difficult to estimate the overall uncertainty in the evaluation of the thickness. The copper and tin intensities were calculated with an uncertainty of 5–10%.

From the complete analysis of this group of coins, we conclude that coin number 4 is a modern fake, probably 19th–20th century, because no amalgamation cases are known for Geto-Dacian drachms.

3.2. THE ARICESTII RAHTIVANI LOCK-RING

In the case of the gilded silver hair ring, we could measure separately the composition of the bulk and of the gilded area; due to the irregular surface with apparent bulk spots and various coated areas (Fig. 1). The elemental compositions by the X-MET 3000TX+ of the two measured areas are given in Table 3.

Table 3

Measured elemental composition of the gilded silver double spiral lock-ring from Aricestii Rahtivani

Lock-ring	Ag(%)	Au(%)	Cu(%)	Fe(%)	Br(%)
Silver (bulk)	95.8	1.7	1.2	0.6	traces
Gilded area	61	36.3	0.7	2	-

From the variation of the Au content correlated with visual examination (Fig. 3), we concluded that this lock-ring was gilded in some areas. We cannot say if the coating is only gold or an Ag+Au alloy from the XRF analysis, because we evaluate only approximately 50 μm in depth of the object and it is not possible to separate gold contributions from bulk or coating (a few micrometers are used for gilding). A method allowing the measurement of such a thin layer is TXRF (Total Reflection X-Ray Fluorescence), which cannot be applied in our case due to the irregularities of the surface.

Knowing the composition of the bulk, we apply only the second method. To estimate the thickness of the coating layer in this case, we assumed an ideal model of “pure” gold coating. From the theoretically calculated Ag- K_{α} line attenuation curve (the experimental transmission fraction for the Ag- K_{α} line is (0.58 ± 0.02)) we obtained a value of 5 μm for the thickness of the gilding layer.

As a conclusion, the technique used in this case could be either the mechanical attachment of a relatively thin gold sheet obtained hammering a small gold nugget or the use of soldering agents as resins to attach the sheet.

3.3. THE AU DEPOSITION ON ALUMINUM SUBSTRATE

For the Au deposition on a thin Al backing layer for the electronic application, we applied a different procedure, because the gold layer deposition was made on Aluminum, which is below the detection limit of our spectrometer.

To estimate the thickness of the gold deposition we used a 63.8% Pb+36.2% Sn soldering sample as an additional metallic backing.

In order to estimate the absorption of Pb and Sn X-rays through the (Au + Al) sample, we performed measurements (spectra with a 60 s collection time) for the sample + backing package and only for the backing. The intensity (peak area in counts) of the Pb L_{α} line after attenuation through the (Au + Al) sample was $4\,364 \pm 130$. The same intensity in the absence of the (Au + Al) layer, only (Pb + Sn) backing was $4\,700 \pm 118$. With these values we calculated the transmission fraction of the Pb L_{α} line considering only attenuation through the Al layer with a thickness between 0.5 and 10 μm (Table 4). Using these new values, we calculated the total transmission fractions of Pb through the gold layer, for thickness values of 0.5, 0.4, 0.3 and 0.15 μm (Table 5).

Table 4

Pb- L_{α} line transmission fraction through different Al layer thickness values and Pb- L_{α} estimated intensity values considering the Al layer attenuation

Thickness Al layer (μm)	0.5	1	3	5	7	10
$T_{L_{\alpha}Pb}$	0.996	0.993	0.981	0.969	0.957	0.939
I_{estim}	4685 ± 117	4671 ± 117	4613 ± 115	4556 ± 114	4500 ± 112	4416 ± 110

Table 5

Pb- L_{α} line transmission fraction through different Au layer thickness-values and Pb- L_{α} estimated intensity values considering the Au layer attenuation, using the Al attenuation intensity-values

I_{estim} Thickness Al layer (μm)	I_{estim} Au 0.5 (μm) $T=0.902$	I_{estim} Au 0.4 (μm) $T=0.921$	I_{estim} Au 0.3 (μm) $T=0.969$	I_{estim} Au 0.15 (μm) $T=0.940$
0.5	4231	4318	4407	4544
1	4217	4304	4393	4530
3	4165	4251	4339	4474
5	4114	4199	4285	4419
7	4063	4147	4232	4364
10	3988	4070	4154	4283

The closest to the experimental value (4364.82 ± 130) is 4364.01, calculated for a 0.15 μm gold layer deposited on a 7 μm Al backing. These values were estimated with an uncertainty of 3 -5%.

To validate these results we calculated the intensity variation for K_{α} respectively K_{β} X-rays of Sn through Au (0.15 μm) respectively Al (7 μm) layers (see Table 6). The experimental intensity values for K_{α} and K_{β} X-rays of Sn are 374 and respectively 2 517.

Table 6

Sn K_{α} and K_{β} line transmission fractions through Al and respectively (Au + Al) layers and calculated intensity values, considering Au layer attenuation

	$T_{K_{\alpha}Sn}$	I_{estim}	$T_{K_{\beta}Sn}$	I_{estim}
Al (7 μm)	0.997	380	0.991	2534
(Au+Al) (7.15 μm)	0.990	377	0.987	2524

The results from Table 6 confirm our initial evaluation (see Tables 4 and 5): 0.15 μm gold layer deposited on a 7 μm Aluminum substrate.

4. CONCLUSIONS

XRF studies were performed for some ancient Au or Ag coated artifacts in order to evaluate the gilding/silvering layer thickness and to identify different techniques used during their manufacture – from simple mechanical application of a thin malleable gold foil to the use of (mercury) amalgamation. These results can be used for authentication of archaeological objects and for various historical studies for validation of various hypotheses on the habits, commercial and cultural exchanges of old populations.

XRF proved to be a useful tool for characterization of contemporaneous and modern monetary fakes, as well as for other coatings (nickel, copper, stainless steel) and thin layer structures (electronics, solid state physics) investigation.

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