Revista de Investigación de Física **17**, 141701102 (2014)

Composition and thickness of gold and silver nose decorations from the tomb of the Lady of Cao determined by combining EDXRF-analysis and X-ray transmission measurements

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Received May 20, 2014 – Accepted July 10, 2014

Thirty four nose decorations from the tomb of the Lady of Cao has been analyzed by EDXRF-analysis and transmission measurements. These nose decorations are made partially on gold, and partially on silver. EDXRF-analysis showed that, while gold areas all show a similar composition, silver areas exhibit an erratic composition, and also an unusual high percentage of gold, up to 35 %. To verify that this erratic composition is not depending on surface enrichment processes, X-ray transmission measurements were carried out, which gives the bulk composition of the samples. These last measurements completely confirm EDXRF-results. Therefore the conclusion could be that a high quantity of gold was added intentionally to the silver alloys, for not clear reasons, may be to avoid the oxidation process typical of high concentration silver in silver alloys.

Keywords: Energy-dispersive X-ray fluorescence, Au-Ag-Cu alloy, Moche pre-hispanic culture.

Composición y espesor de las decoraciones nasales de oro y plata provenientes de la tumba de la Dama de Cao determinados por la combinación del análisis EDXRF y las medidas de transmisión de rayos X

Treinta y cuatro adornos de nariz de la tumba de la Señora de Cao han sido analizados por análisis de EDXRF y medidas de transmisión. Estas decoraciones de nariz están hechas en parte en oro, y en parte en plata. Análisis EDXRF mostró que, mientras que las áreas de oro todas muestran una composición similar, las áreas de plata exhiben una composición irregular, y también un alto porcentaje inusual de oro, de hasta 35 %. Para verificar que esta composición errática no depende de los procesos de enriquecimiento en la superficie, se llevaron a cabo medidas de transmisión de rayos-X, lo que da la composición en el bulk de las muestras. Estas últimas mediciones confirman completamente los resultados de EDXRF. Por lo tanto, la conclusión podría ser que una gran cantidad de oro fue añadida intencionalmente a las aleaciones de plata, por razones no claras, se puede evitar los procesos de oxidación típica de alta concentración de plata en aleaciones de plata.

Palabras claves: Fluorescencia de energía dispersiva de rayos X, aleacionesde Au-Ag-Cu, cultura pre hispánica Moche.

Energy-dispersive X-ray fluorescence, EDXRF-analysis, is a technique which, in the case of metals, analyzes thin surface layers. For example, when gold and silver-alloys are analyzed, it typically interests a depth of microns up to a maximum of tens of microns. Therefore it can give wrong results or be affected by a large indetermination when the sample composition is altered because of surface slide *patina*, as often happens in the case of oxidation of silver alloys, and sometimes in the case of gold-alloys rich on copper or silver.

A complementary technique was therefore developed, of bulk analysis, which use the same equipment employed for EDXRF-analysis; the X-ray beam from the X-ray tube is monochromatized by means of a tin secondary target,

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which K-lines bracket the silver-K discontinuity. The sample to be analyzed is positioned between the secondary target and the detector. This technique is able to determine, by measuring the attenuation of tin-K rays, thickness and/or composition of gold and silver alloys having a thickness of less than about 120 μm for gold and about 0.7 mm for silver. The method was tested with proper Au-Ag-Cu alloys with known composition and thickness, and then applied to gold and silver artifacts from the tomb of the Lady of Cao, belonging to the Moche pre-hispanic culture from the North of Peru, dating about 300 AD.

Theoretical background

The attenuation coefficient of all elements versus energy, in the range of X-rays, is characterized by a K-discontinuity (K$_{ab}$) and by three L-discontinuities (LI, LII and LIII). The relative minimum and maximum of the attenuation coefficient are just below and above the energy K$_{ab}$ of the discontinuity [1].

This fact can be usefully employed to measure in an accurate manner the thickness of a metal sheet, but also, for example, to selectively visualize single elements in radiography and tomography by *differential attenuation* [2]. To determine the thickness of a thin sheet of element a -alone or in the form of an alloy-, a second element, b, can be therefore employed, which X-rays (K$_\alpha$ and K$_\beta$) bracket the photoelectric discontinuity K, see Figure 1. The intensity ratio of K$_\alpha$/K$_\beta$ (or in a similar manner L$_\alpha$/L$_\beta$) versus thickness of element a is then given by

$$\left(\frac{\mathrm{K}_\alpha}{\mathrm{K}_\beta}\right)_a = \left(\frac{\mathrm{K}_\alpha}{\mathrm{K}_\beta}\right)_{b0} \exp[\Delta\mu d(a)] \ , \tag{1}$$

where $(\mathrm{K}_\alpha/\mathrm{K}_\beta)_{b0}$ is the ratio $(\mathrm{K}_\alpha/\mathrm{K}_\beta)_b$ in absence of element a; $\Delta\mu = \mu_{a\beta} - \mu_{a\alpha}$ is the difference of linear attenuation coefficients of element a between energy of $\mathrm{K}\alpha(\mathrm{L}_\alpha)$-rays and $\mathrm{K}_\beta(\mathrm{L}_\beta)$ and $d(a)$ is the thickness of element a in cm.

For example, to measure the thickness of a silver sheet, which K-discontinuity has an energy of 25.52 keV, a sheet of tin can be employed, having K X-rays at 25.2 and 28.5 keV respectively (Figure 2). In this case Eq.(1) may be written as

$$\mathrm{Sn}\left(\frac{\mathrm{K}_\alpha}{\mathrm{K}_\beta}\right) = 5.8\exp[335.0d(\mathrm{Ag})] \tag{2}$$

where $5.8 = Sn(\mathrm{K}_\alpha/\mathrm{K}_\beta)$-ratio in absence of Ag-absorbers, this value was not corrected for the detector efficiency, and, therefore, depends on the X-ray detector.

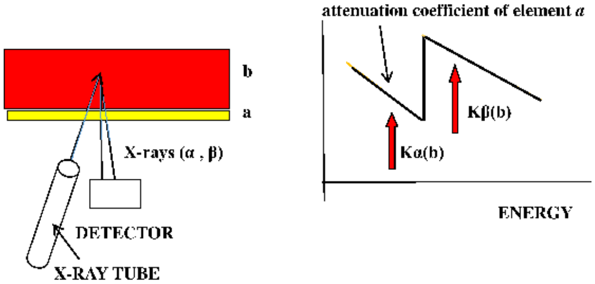

Figure 1: Attenuation and differential attenuation to determine the thickness of an element a or approximate composition of an alloy of element a. A second element b may be employed, emitting K$_\alpha$ and K$_\beta$ X-rays which bracket the photoelectric discontinuity of element a (image at the right). When crossing a sheet of element a (or alloy of element a) these K-X rays are selectively absorbed according to their thickness.

The attenuation of K$_\alpha$ and K$_\beta$-lines separately (or L$_\alpha$ and L$_\beta$-lines) emitted by element b can be employed to determine the thickness of sheet a. This attenuation is given by

$$\frac{[\mathrm{K}_\alpha]}{[\mathrm{K}_\alpha]_0} = \exp[-\mu_{a\alpha}d_a]$$
$$\frac{[\mathrm{K}_\beta]}{[\mathrm{K}_\beta]_0} = \exp[-\mu_{\alpha\beta}d_a] \tag{3}$$

In Eqs.(3), [K$_\alpha$]$_0$ and [K$_\beta$]$_0$ indicate K$_\alpha$ and K$_\beta$ values of element b, in absence of element a.

When sheet a is not a single element, for example Ag or Au, but an Ag or Au-alloy, which are typically composed by three elements, Ag-Cu-Au and Au-Ag-Cu, then Eqs.(1) and (3) may be written as

$$\frac{\left(\frac{\mathrm{K}_\alpha}{\mathrm{K}_\beta}\right)_b}{\left(\frac{\mathrm{K}_\alpha}{\mathrm{K}_\beta}\right)_{b0}} = \exp\left[-[\Delta\mu c_a + \Delta\mu' c_{a'} + \Delta\mu'' c_{a''}]\rho_{\mathsf{alloy}} d\right] \tag{4}$$

$$\frac{[\mathrm{K}_\alpha]}{[\mathrm{K}_\alpha]_0} = \exp\left[-(\mu_{a\alpha}c_a + \mu_{a'\alpha}c_{a'} + \mu_{a''\alpha}c_{a''})\rho_{\mathsf{alloy}} d\right] \tag{5}$$

$$\frac{[\mathrm{K}_\beta]}{[\mathrm{K}_\beta]_0} = \exp\left[-(\mu_{\alpha\beta}c_a + \mu_{\alpha'\beta}c_{a'} + \mu_{\alpha''\beta}c_{a''})\rho_{\mathsf{alloy}} d\right] \tag{6}$$

$\Delta\mu$, $\Delta\mu'$ and $\Delta\mu''$ indicates the attenuation coefficient difference, at energies of K$_\alpha$ and K$_\beta$-rays of element b of the three elements of the alloy respectively; c_a , $c_{a'}$ and $c_{a''}$ are the concentration values (in % of weight) of the three elements in the alloy; ρ_{alloy} in g/cm^3 is the density of the alloy and d its thickness. [K$_\alpha$]$_0$ and [K$_\beta$]$_0$ indicate K$_\alpha$ and K$_\beta$ values of element b, with no element a. μ_a,

$\mu_{a'}$, $\mu_{a''}$ indicate the attenuation coefficient of the three elements in the alloy, for example Au, Ag, Cu in a Au-alloy.

The density ρ_{alloy} of the alloy in g/cm^3 is given by

$$\frac{1}{\rho_{\text{alloy}}} = \frac{c_{\text{Ag}}}{\rho_{\text{Ag}}} + \frac{c_{\text{Cu}}}{\rho_{\text{Cu}}} + \frac{c_{\text{Au}}}{\rho_{\text{Au}}} \,. \tag{7}$$

For a Ag-Cu-Au alloy, Eqs.(4),(5) and (6) may be written as

$$\frac{\text{Sn}\left(\frac{\text{K}_\alpha}{\text{K}_\beta}\right)}{\left[\text{Sn}\left(\frac{\text{K}_\alpha}{\text{K}_\beta}\right)\right]_0} = \exp\left[\left(31.5c_{\text{Ag}} - 5c_{\text{Cu}} - 11.5c_{\text{Au}}\right)\rho_{\text{alloy}}d\right] \tag{8}$$

$$\frac{(\text{SnK}_\alpha)}{(\text{SnK}_\alpha)_0} = \exp\left[-\left(9.0c_{\text{Ag}} + 17.5c_{\text{Cu}} + 41.5c_{\text{Au}}\right)\rho_{\text{alloy}}d\right] \tag{9}$$

$$\frac{(\text{SnK}_\beta)}{(\text{SnK}_\beta)_0} = \exp\left[-\left(40.5c_{\text{Ag}} + 12.4c_{\text{Cu}} + 30.0c_{\text{Au}}\right)\rho_{\text{alloy}}d\right] \tag{10}$$

Each of the Eqs.(8), (9) and (10) can be employed to determine the thickness of the alloy. The values of mass attenuation coefficients were taken from the program XCOM [3], Figure 2.

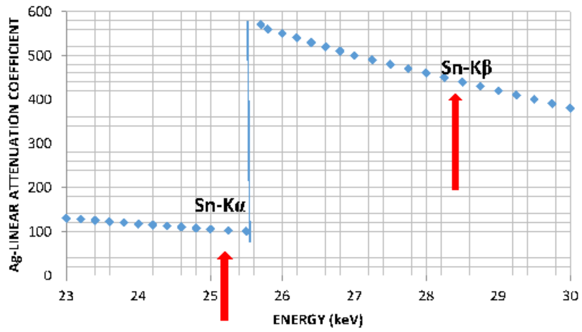

Figure 2: Linear attenuation coefficient of silver, showing its photoelectric discontinuity and the position of the Sn K-lines. Sn-K$_\beta$ lines are more attenuated than Sn-K$_\alpha$ lines, and the ratio Sn-K$_\alpha$/Sn-K$_\beta$ increases versus Au-thickness.

Alternatively, when the thickness of the alloy is known or can be measured, and has a value approximately less than 0.7 mm for silver alloys, and less than 120 μm for gold-alloys, then Eqs.(7) can be employed to determine, with some approximation, the alloy composition, or, at least, to confirm measurements carried out using EDXRF-analysis. That gives the possibility to check, with a simple volume analysis based on transmission of monoenergetic X-rays, analytical results from EDXRF-analysis, which are related to a thin surface layer and can be affected by surface processes which alter the surface composition and the reliability of EDXRF-analysis [4].

Experimental setup

The experimental set-up is shown in Figure 3. It includes a Ag-anode X-ray tube working at 40 kV and 200 μA maximum voltage and current, respectively [5], a Si-drift X-ray detector [5] and a Sn-target, which monochromatize the X-ray tube output allowing a bulk analysis of thin sheets of Ag or Au-alloys. The photons emitted by the X-ray tube, filtered and collimated, irradiate the Sn-target, producing by photoelectric effect Sn-K X-rays at 25.2 and 28.5 keV respectively. The Ag or Au-sheets to be measured are inserted between the Sn-target and the detector entrance. The Si-drift detector entrance is collimated, in order to approximate the *good geometry* conditions [6].

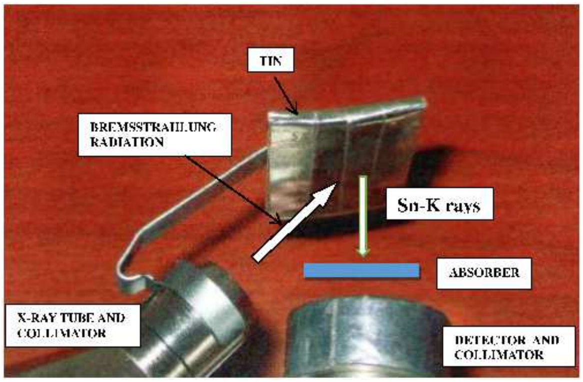

Figure 3: Experimental set-up for the transmission-measurements on Ag or Au thin sheets. The X-ray tube emits Bremsstrahlung radiation which is filtered and collimated. This radiation induces photo-electric effect in a Sn-target, with emission of Sn-K rays, of 25.2 and 28.5 keV. The Ag or Au-sheet of unknown thickness or composition is put between the Sn-target and the detector and selectively absorbs the Sn-K rays according to ist thickness and composition.

Results ans discussion

The Figure 4 shows, as an example, the application of the theoretical background described in previous section to the analysis of 33 nose decorations on gold and silver-alloys from the tomb of the *Lady of Cao* a Mochica queen and religeous figure from the 300 A.D. approximately (an example of these beautiful nose decorations in shown in Figure 5).

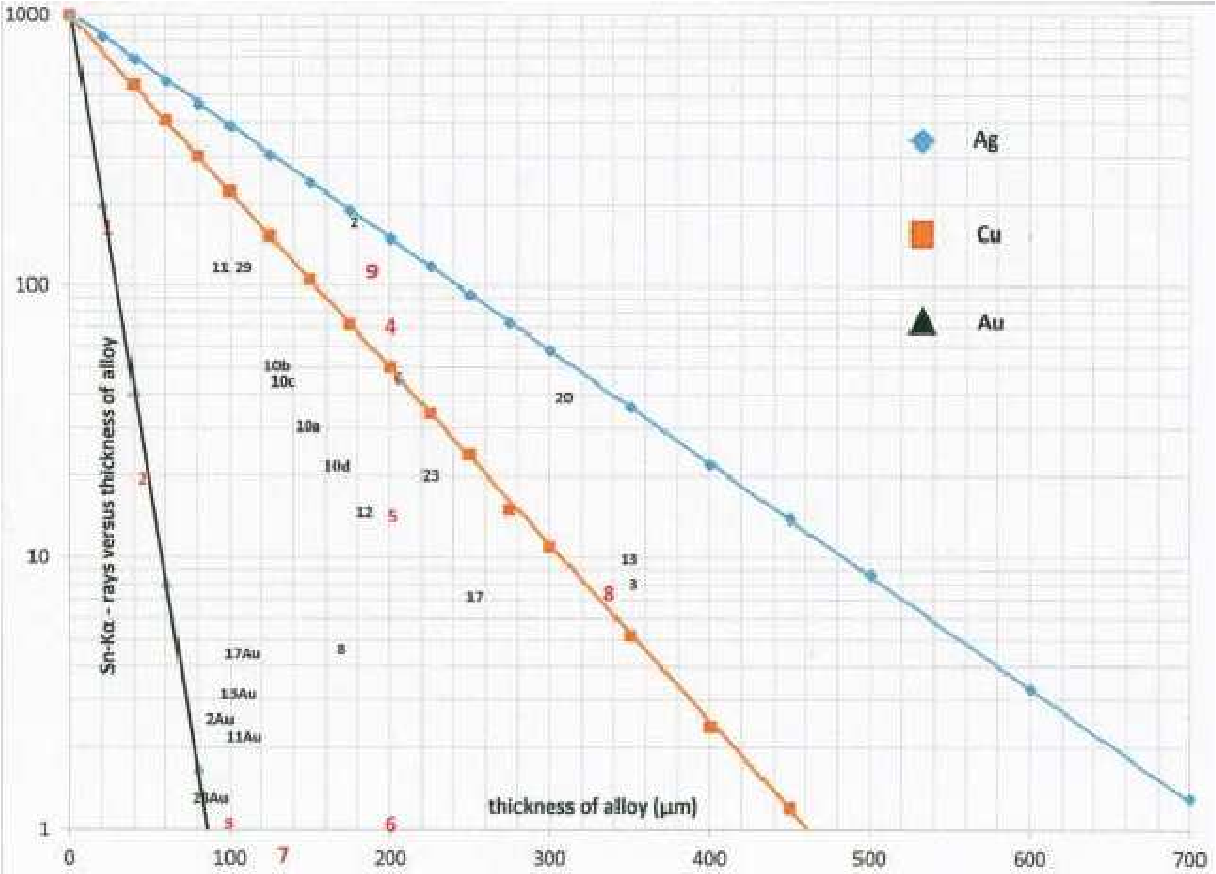

Figure 4: Attenuation of Sn-K$_\alpha$ line versus thickness of Ag, Au and Cu layers. Results on following standard samples are reported (red colour): 1) d(Au)=23 μm (Sn-Kα/ Sn-K$_{\alpha^0}$= 0.147); 2) d(Au)=46 μm (Sn-Kα/ Sn-K$_\alpha^0$=0.019); 3) Au=90 %, Ag=10 % , d=100 μm (Sn-Kα/ Sn-K$_{\alpha^0}$=0.001); 4) Ag=90 %, Au=10 % , d=200 μm (Sn-Kα/ Sn-K$_{\alpha^0}$= 0.07); 5) Ag=80 %, Au=20 % , d=200 μm (Sn-Kα/ Sn-K$_{\alpha^0}$= 0.013); 6) Au=50 %, Ag=50 %, d=196 μm (Sn-Kα/ Sn-K$_{\alpha^0}$= 0.001); 7) Ag=40 %, Au=40 %, Cu=20 %, d=130 μm (Sn-Kα/Sn-K$_{\alpha^0}$= 0.0008); 8) Cu=100 %, d=335 μm (Sn-Kα/ Sn-K$_{\alpha^0}$= 0.0075); 9) Ag=90 %, Au=10 %, d=180 μm (Sn-Kα/Sn-K$_{\alpha^0}$= 0.105). Also typical results on nose decorations from the *Lady of Cao* are reported (black numbers). Details on the nose decorations are reported in Table 1 and 2.

PACEB-F4 Gold areas	**EDXRF measurements**			**X-ray transmission**
Numbers	**Au(%)**	**Ag(%)**	**Cu(%)**	
2	74.5	19.5	5.5	Au$\sim 80\,\%$, Ag+Cu$\sim 20\,\%$, d=90 μm
11	81.0	13.5	5.5	Au$\sim 80\,\%$, Ag+Cu$\sim 20\,\%$, d=105 μm
13	78.0	19.0	3.0	Au$\sim 80\,\%$, Ag+Cu$\sim 20\,\%$, d=100 μm
17	78.5	16.5	5.0	Au$\sim 75\,\%$, Ag+Cu$\sim 25\,\%$, d=105 μm
23	82.0	14.5	3.5	Au$\sim 85\,\%$, Ag+Cu$\sim 15\,\%$, d=90 μm

Table 1: EDXRF and X-ray transmission results on gold areas of nose decorations from the tomb of the Lady of Cao.

PACEB-F4	EDXRF measurements			X-ray transmission
Numbers	Au(%)	Ag(%)	Cu(%)	
2	99.2	0.02	0.8	Ag$\sim 99\,\%$, Au+Cu$\sim 1\,\%$, d=180 μm
3	83.0	7.50	9.5	Ag$\sim 85\,\%$; Au+Cu$\sim 15\,\%$, d=350 μm
6	91.5	4.00	4.5	Ag$\sim 88\,\%$; Au+Cu$\sim 12\,\%$, d=210 μm
8	41.0	25.00	34.0	Ag$\sim 40\,\%$, Au+Cu$\sim 60\,\%$, d=170 μm
10	52.0	21.00	27.0	Ag$\sim 50\,\%$, Au+Cu$\sim 50\,\%$, d=150 μm
11	64.0	21.00	15.0	Ag$\sim 60\,\%$, Au+Cu$\sim 40\,\%$, d=95 μm
12	45.5	35.5	19.0	Ag$\sim 50\,\%$, Au+Cu$\sim 50\,\%$, d=190 μm
13	85.5	10.5	4.0	Ag$\sim 85\,\%$, Au+Cu$\sim 15\,\%$, d=350 μm
17	64.0	16.0	20.0	Ag$\sim 60\,\%$, Au+Cu$\sim 40\,\%$, d=250 μm
23	76.0	11.5	12.5	Ag$\sim 75\,\%$, Au+Cu$\sim 25\,\%$, d=230 μm
29	57.5	25.5	17.0	Ag$\sim 60\,\%$, Au+Cu$\sim 40\,\%$, d=110 μm

Table 2: EDXRF and X-ray transmission results on silver areas of nose decorations from the tomb of the Lady of Cao.

Figure 5: Nose decoration N.10, on gold and on silver-alloys. Following concentrations were determined by EDXRF-analysis, **gold**: Au=78 %, Ag=18.5 %, Cu=3.5 %; **silver**: Ag=52 % , Au=27 %, Cu=21 %. Transmission measurements on the four iguanas confirm these results, giving also $d_{\text{Ag}} = 150$ μm.

Energy-dispersive X-ray fluorescence analysis carried out in 2013 gave following results. The gold composition is approximately the same for all golden areas, i.e., Au=78 %, Ag=17.5 %, Cu=4.5 %; also the thickness of the gold-leaf seems to be the same, i.e. about 100 μm; the silver composition is completely erratic, Ag=(45-99) %, Au=(1-34) %, Cu=(0-33) %; also the thickness of the silver sheets is erratic, ranging from about 100 μm to about 400 μm.

To test these results, and especially those concerning the Ag-sheets, the method of X-ray transmission using a Sn-secondary target was developed. This method is able to determine the approximate composition of the three components of gold or silver-sheets (Ag-Au-Cu) when their thickness is known, or the determine the thickness of these sheets when the composition is known, or, finally, to check the approximate composition and thickness of the sheets.

Conclusions

From the analysis of the 33 nose decorations from the tomb of the *Lady of Cao* by using both EDXRF-analysis and X-ray transmission measurements, following may be concluded. Transmission measurements using the monoenergetic X-lines emitted by a Sn- secondary target confirm the previous measurements carried out by using energy-dispersive X-ray fluorescence analysis; it is therefore confirmed that the areas on silver have a very erratic composition and thickness; these areas also contain a high concentration of gold (up to 34 %).

The areas on gold have, at the contrary, a very similar composition and thickness, i.e., Au=78 %, Ag=17.5 %, Cu=4.5 %.

Additional measurements would be required to better understand the strange composition of silver areas and to specifically analyze the soldering areas between gold and silver areas.

Finally, transmission of monoenergetic X-rays could be an useful method to complement energy dispersive X-ray fluorescence analysis, especially in all cases where this last method is affected by large uncertainties due to surface enrichment processes.

Acknowlegdements

This work was carried out with the support of CONCYTEC of Perú and CNR of Italy.

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