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The Fortios disks revisited

Una revisión de los discos de Fortios

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ABSTRACT

We have used EDXRF, Micro-PIXE and optical microscopy (metallographic analysis), complemented with SEM-EDS, to first determine the elemental content, and second, to identify the process used to join the components (disk, peripheral rod and tab) of several Iron Age gold buttons. These have a very similar typology and were found at three archaeological sites in the South-Western part of the Iberian Peninsula. A set of 35 buttons from Castro dos Ratinhos (7), Outeiro da Cabeça (23) and Fortios (5) were analyzed and the results published in *Trabajos de Prehistoria* (Soares *et al*. 2010). Recently Perea *et al.* (2016) have published analyses of other 4 gold buttons from Fortios with the same purpose, but only using one technique, SEM-EDS. As they only analysed the rough surface layer, the results are neither effective nor reliable, taking into account the constraints associated with the technique, namely the small depth reached (< 2 μm) by the incident beam and, consequently, its sensitivity to the topography of the analyzed surface. Despite these constraints, they have accepted uncritically their results and, at the same time, question our own analyses and results and the interpretation we have made. Here we discuss the approach of Perea *et al*. in order to determine not only the elemental content of the Fortios gold buttons, but also to identify the joining process used in their manufacture.

RESUMEN

Hemos empleado fluorescencia de rayos X por energía dispersiva (EDXRF), *emisión de rayos X inducida por partículas* (Micro-PIXE) y *microscopía (análisis metalográfico), complementada con microscopia electrónica de barrido y espectroscopia de rayos X en energía dispersiva* (SEM-EDS*), primero para determinar el contenido elemental y segundo para identificar el proceso empleado para unir los componentes (disco, anillo periférico y presilla) de varios de los discos de oro de la Edad del Hierro. Su tipología es muy similar y fueron encontrados en tres yacimientos arqueológicos de la zona suroccidental de la Península Ibérica. Una serie de 35 discos del Castro dos Ratinhos (7), Outeiro da Cabeça (23) y Fortios (5) fueron analizados y sus resultados publicados en* Trabajos de Prehistoria *(Soares* et al. *2010). Recientemente Perea* et al. *(2016) han publicado análisis de otros 4 discos de oro de Fortios con el mismo propósito pero usando solo* SEM-EDS. *Al haber analizado solo la capa superficial irregular, los resultados no son reales, ni fiables, considerando las limitaciones asociadas con la técnica, especialmente la escasa profundidad alcanzada (< 2 μm) por el haz incidente y, consecuentemente, su sensibilidad a la topografía de la superficie analizada. A pesar de esas limitaciones, han aceptado acríticamente sus resultados y, a la vez, han puesto en cuestión nuestros análisis y resultados y las interpretaciones que hemos hecho. Aquí discutimos el enfoque de Perea* et al. *para determinar no solo el contenido elemental de los discos de oro de Fortios, sino también para identificar el proceso de unión empleado en su manufactura.*

Key words: Gold buttons; Iron Age; Fortios; Analytical techniques; Joining processes.

Palabras clave: *Discos de oro; Edad del Hierro; Técnicas analíticas; Procesos de unión.*

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"Starting from the topographic study and the elemental analysis of four gold" disks, Alicia Perea and others (2016: 352) define "a little known type of gold objects and survey all examples known to date". They also state, and we agree, that "it is important to select the appropriate analytical technique depending on the problem to be solved and in order to obtain reliable results" (Perea *et al.* 2016: 352). The only analytical technique these authors used to determine the elemental composition and to identify the technique used to join the components of the so-called gold disks was SEM-EDS. In our work (Soares *et al.* 2010), we analyzed not only 5 gold disks (or gold buttons, as we called them) from Fortios, but also 23 from Outeiro da Cabeça and 7 from Castro dos Ratinhos, using several analytical techniques, namely EDXRF, Micro-PIXE, Optical Microscopy (metallographic analysis) and also SEM-EDS.

EDXRF, Micro-PIXE, and SEM-EDS are well-established non-invasive and multielemental analytical techniques. They have been used for many decades in the study of ancient gold alloys. However, only the superficial layer is analyzed and the thickness of the analyzed layer depends on the nature of the incident beam. EDXRF uses X-rays, while a proton beam generated by a Van de Graaff accelerator is used by Micro-PIXE and an incident electron beam by SEM-EDS. However, it is well known that gold alloys that have been buried for a long time normally have a superficial layer enriched in gold and depleted in silver and copper. As the X-ray incident beam could reach energies up to 40 keV, penetrating more deeply than the proton beam of the used Micro-PIXE set-up (typical proton beam energies up to 2.3 MeV), the elemental composition determined by the first technique should give better results concerning the bulk metal (see, for instance, a previously published work by some of us: Araújo *et al.* 1993). In contrast, the electron beam of SEM-EDS penetrates less than 2 μm (see, for instance, Troalen *et al.* 2014) and, consequently, results obtained by this technique will be away from the true content values of the bulk metal. In addition, SEM-EDS is very sensitive to variations in relief (experimental geometry), as well as to variations in chemical or physical degradation, regardless of how small these may be on the analyzed surface. Besides, the effective probe depth of analysis in any of the used X-ray spectroscopy techniques is not only dependent on the energy of the exciting source (electrons, X-rays or protons) but especially on the energy of the characteristic X-rays (transition) emitted by the sample elemental constituents. Therefore, due to the energy differences of the emitted X-rays, the Au-M lines or Ag-L lines provide information from a much shallower surface sample layer than the Au-L and Ag-K lines (Valério *et al.* 2017). Our results, both for EDXRF and Micro-PIXE, were obtained considering the measured Au-L and Ag-K lines intensity. As we noted in our previous paper (Soares *et al*. 2010) our SEM-EDS analysis were performed with a Zeiss DSM 962 with an Oxford Instruments INCAx-sight EDS spectrometer, and the mounted cross section of the gold button sample was highly polished before analysis. Although not listed in our previous paper, the experimental conditions used for SEM-EDS data acquisition were: accelerating voltage 20 kV, working distance 25 mm, EDS take-off angle 30 degrees, emission current adjusted to 70 μA, dead time adjusted to 30%, live time 120 s (process time 3); standardless quantitative analysis (semi-quantification by ZAF correction), with a EDS resolution of 133 eV at 5.9 keV; energy calibration with a cobalt sample.

Taking into account all the characteristics of the mentioned techniques, we started to analyze the gold buttons using EDXRF. "The obverse and reverse faces of each button were analyzed in order to identify compositional deviations due to the different artefact geometries (e.g. convex and concave surfaces), different components (e.g. button main body and tab) and/or joining areas (e.g. junction between button main body and tab in reverse face). However, since each EDXRF analysis corresponds to the entire face of each button, compositional deviations were investigated in detail by micro analyses", using the Micro-PIXE technique (Valério *et al*. 2007: 371). EDXRF analyses of the gold buttons from each site present analogous gold, silver and copper contents indicating that the different components of each button are very probably made from the same gold alloy. Besides the elemental composition of these jewels is similar whatever their origin, Fortios, Outeiro da Cabeça or Castro dos Ratinhos (Soares *et al*. 2010: table 1). Two gold ingots recovered at Outeiro da Cabeça together with the gold buttons were also analyzed using EDXRF. The results show an elemental content very similar to that one of the buttons (Soares *et al.* 2010: table 2), which strengthens the inference that the buttons of these three sites would probably came from the same gold metallurgical workshop.

Micro-PIXE analyses of the gold buttons from Castro dos Ratinhos involved the quantification of several points from different components (disk, tab, and rod) of each button. Results show similar compositions regardless of which component was analyzed. It should be noted that tabs were made from flattened fragments of the rods: i.e., we can say that disks and rods were made with the same or very similar alloys (Soares *et al.* 2010: table 3). Obverse and reverse faces of the buttons were also scanned using Micro-PIXE over several selected areas to obtain elemental distribution maps (Valério *et al.* 2007: figs. 4 and 5). Particular attention was paid on the reverse face since there it would be possible to investigate compositional differences between the button components in the joining areas (Valério *et al.* 2007: fig. 7). These analyses did not identify any compositional differences among components or the presence of a solder alloy. And, as we wrote, "beam currents of 100 pA were used for all spectra and the beam spatial resolution was kept at 2-3 μm" (Soares *et al*. 2010: 504-505). Taking into account the methods we used, it is difficult to understand why the authors of the paper that we are commenting upon wrote: *En nuestra opinión, los mapas de distribución elemental en el modo y a la escala elegidos son inadecuados para detectar muy pequeñas diferencias de composición, máxime cuando esas diferencias sólo se pueden encontrar en zonas de difícil acceso para el detector, y sólo hubiera sido posible tomando espectros puntuales en áreas micrométricas para obtener un patrón estadístico de composición más preciso* (Perea *et al.* 2016: 356).

The text of these authors continues as follows: *Hay que tener en cuenta, además, que la zona de soldadura se sitúa por debajo de la propia presilla, que se abre en abanico a ambos lados, precisamente para aumentar la zona de contacto y facilitar la unión*. If a soldering area exists and is below the tab, why would Perea and her collaborators use a technique which incident beam penetrates much less than the incident beams of Micro-PIXE or Micro-EDXRF? Besides, and as mentioned above, the incident beam of SEM-EDS penetrates less than 2 μm in the surface layer and, consequently, it is very sensitive to variations in topography of the surface, as well as to very small variations in chemical or physical degradation of the metal. As Newbury and Ritchie (2015: 497) have noted, "specimen geometry effects such as shape and local surface inclination to the beam can have a profound impact on electron scattering and even more importantly, on the path length along which X-rays must travel to the detector and along which they suffer absorption. These "geometric effects" modify the measured relative elemental intensities in ways that have nothing to do with the composition of the specimen". The surfaces that were analyzed by Perea and collaborators (2016: fig. B - Fortios 14, for instance) are not highly polished areas but rough ones, that had been subjected to heat treatments and degradation processes during manufacture and use.

Our approach to the problem, i.e., to determine if a solder material was or was not used for joining the button components, seems more effective and reliable. As one of the buttons from Outeiro da Cabeça was broken (see Soares *et al*. 2010: fig. 6), "a small representative fragment from a joining area (disk/rod) was sampled" and "the optical microscopy images of this [polished] cross section clearly identify both button components due to their distinct microstructural characteristics, i.e., different grain size (Fig. 7)" (Soares *et al*. 2010: 505-506). SEM-EDS and Micro-PIXE analyses clearly show that no solder material is present between the two components (Soares *et al*. 2010: figs. 8 and 9). Scans of two areas of the mounted polished cross section establish "that the gold, silver and copper contents remain almost constant throughout the analyzed profiles (observed deviations along line scans are due to topographic differences, e.g. scratches or pores)" (Soares *et al*. 2010: 506), but Perea and collaborators (2016: 357) appear to give some importance to the word *almost*, perhaps because they did not see in brackets the explanation for that word and accept without any criticism the results that they obtain in rough superficial layers.

Perea *et al.*'s use of SEM-EDS does not take sufficient account of the potentials and constraints of the technique. They themselves claim that *los análisis MEB-EDX son semicuantitativos y, en segundo lugar, que cualquier objeto enterrado en la tierra sufre un enriquecimiento* *superficial en oro* (p. 359). We think that the enrichment in silver and copper of the joining regions of gold buttons from Fortios determined by Perea and collaborators are most probably due to geometric effects and so are unreliable. If we look closely to their Table 1, how can one explain, for button 9 for instance, values between 6.3 wt% Ag and 11.8 wt% Ag (values that are considerably distant from their claimed "small variations") determined for non-joining areas of button components, when joining regions present Ag values between 11.8 wt% and 12.7 wt%? What is the precision and accuracy of the technique they used? The mean content value of c. 10 wt% Ag for the buttons from Fortios obtained by Perea and collaborators demonstrates well the depletion in silver of the surface layer, since we have obtained a mean content of 13.3 wt% Ag for bulk metal of 5 buttons with the same provenance using EDXRF.

We conclude that the results presented by Perea, Vilaça and Armbruster (2016, fig. 4, table 1) are unreliable because their use of SEM-EDS is incorrect: the rough surfaces analyzed induce geometric effects that "modify the measured relative elemental intensities in ways that have nothing to do with the composition of the specimen". Moreover, they fail to explain why the "most adequate methodology" (*creemos que la metodología MEB-EDX es la adecuada para resolver un problema de interpretación que estaba planteado en la literatura científica desde hacía tiempo*, Perea *et al.* 2016: 361) is capable of determining a compositional variation tendency in rough surface sample areas but unable to establish composition variations (and then the presence of a solder alloy) in a flat and polished surface as performed in our work. Finally, micro analyses made by our team show that the button components (disk, tab/peripheral decorated rod) are made from similar gold alloys that had been mechanically and thermally worked (forging and annealing). No solder alloy was identified in the joining regions. Instead a partial melting/solid state diffusion process was used for the joining of button components. A similar joining process is mentioned by Perea (1990: 137, 138) in the manufacture of a gold pendant from Tutugi (Galera) and probably of an earring from Villaricos necropolis. Both jewels are chronologically later (5^{th}-3^{rd} century BC) than the analyzed buttons (8^{th} century BC), which means that this process started earlier than thought or is commonly accepted.

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