MATERIALS ANALYSIS IN ARCHAEOMETRICAL STUDIES AT BUCHAREST PARTICLE ACCELERATORS

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Abstract

The analysis of archaeological objects requires simultaneously, non-destructive, fast, versatile, sensitive and multielemental methods. Our purpose was to help Romanian archaeologists to identify objects provenance (workshops, technologies, mines) and to explain commercial, military and political aspects. Ancient Greek silver and Dacian gold coins were studied. For silver coins, two methods were used : in air 3 MeV protons PIXE (Particle Induced X-ray Emission) at U-120 classical Cyclotron and Am-241 source based XRF (X-Ray Fluorescence). We obtained the coins composition and, comparing the quantities of Ag, Cu, Sn, Pb and Au, we found which are original, which are copies and which are Barbarian imitations. For gold coins, the methods used were XRF and PAA (Proton Activation Analysis). For PAA, each coin was irradiated in vacuum for 5 hrs at an incident proton energy of 11 MeV provided by a HVEC Tandem accelerator. Three groups of coins with different composition were found, corresponding to simple, complex and no monogram pieces.

SILVER COINS

The great number of Greek silver coins from the first century BC found in the Balkan – Carpathian region have aroused a sharp interest among numismatic researchers [1]. The problem is to classify these coins - tetradrachmae of Thasos (Greek island near Thessaloniki) and drachmae of Apollonia and Dyrrachium (ancient Greek commercial cities, now in Albania) into originals, copies and imitations, in relation to their provenance. Well known are Celtic Thasos tetradrachmae copies (good quality coins, closest to the originals) [2], and also Barbarian imitations (absence or misspelling of the legend, disproportionate and simplified figures) [3]. The dies used for coining were bought or stolen from the Greeks, while some local engravers manufactured their own dies. Visual examination, the first step of a numismatist's work, is insufficient to classify the coins. This is the reason why elemental analysis is required 3 MeV protons external PIXE at the Bucharest U-120 Cyclotron and energy dispersive XRF, based on a 30 mCi Am-241 source [4]. In our case, PIXE analysis is faster and has a better sensitivity than XRF (3-5 ppm for Ti-Fe-Ni region), but implies a higher cost per analysis. The external beam technique also makes it possible to examine objects of any size and shape without sampling. External 3 MeV protons PIXE was employed to determine elements with $20 \le Z \le 40$ and Au, Hg, Pb, Bi (using L rays) because of their high ionization cross section. For elements with $41 \le Z \le 60$ (Ag, Cd, In, Sn, Sb especially), XRF was used as a complementary technique, because of the higher sensitivity for higher Z elements. The method is simpler and cheaper than PIXE, even if longer times of acquisition are required. The sensitivity in our case is 20-30 ppm (for Ag region). A drawback of the XRF method using Am-241 source is the complicated spectrum of the source.

For external PIXE we used an approx. 3 MeV proton beam obtained from the 6.5 MeV Cyclotron nominal regime protons extracted through a 60 μm aluminum foil into air (gamma background from the Al foil can be neglected). The beam passed through a couple of aluminum collimators in order to obtain a well-delimited spot on the target ($1 cm^2$). The distance between extraction foil and sample was 25 cm. The current intensity of the beam was 1-2 nA (it was maintained low, to minimize the counting rate). Special holders were constructed for handling the samples. All excitations were made in flat external and bright regions, to avoid the irradiation of possible inclusions or deposits. X-rays were detected through reflection (90°), using a horizontal HPGe detector (5 mm thickness, 10 mm diameter), placed at 8.5 cm distance from the target. The detector resolution was 280 eV at Mn K_α line (5.9 keV). A conventional electronic chain (preamplifier and amplifier) and an MCA (Multichannel Analyzer) were used to accumulate the spectra. To monitor the beam we used an air ionization chamber, consisting of a pair of insulated metallic plates, at 1 kV potential, which integrates the beam. XRF measurements were performed with a spectrometer consisting of a 30 mCi Am-241 annular gamma-source attached to a support that defines the angle of the incident photons and collimates the fluorescent X-rays on their path to a vertical Si(Li) detector (resolution: 260 eV at 5.9 keV).

Pure thick metal foils and alloys (Goodfellow) of known composition were used as reference materials. These standards were irradiated (PIXE) or excited (XRF) under the same conditions as the samples to be analyzed. This approach has some drawbacks: because the standard and the sample are not identical, but only similar, enhancement and absorption effects in the real sample introduce some errors. Computer software designed in our laboratory was employed to determine the quantitative results.

The overall uncertainty for PIXE method was: 2% for major elements, 3-10% for minor elements and 15% for trace elements. (Major element means more than 10% from overall composition, minor element 0.1-10% and trace element less than 0.1%, down to sensitivity limits – see above) The errors are not only statistical. They also originate from the roughness of coin surface and from the chemical corrosion and/or wearing of the objects, altering the accuracy of the results.

In silver matrix case, for the archaeologist, the concentration values of trace elements are not relevant.

181 pieces silver coins (36 Thasos tetradrachmae and 145 Apollonia and Dyrrachium drachmae), struck between 60 and 48 BC, a very intense period of civil Roman wars, were analyzed. These pieces were found in various places on the Romanian territory, concentrated in the North-West of Transylvania and South-East of Muntenia regions. After completion of analyses, the coins can be grouped into several categories, taking into account their chemical composition. Regarding the first group of Thasian tetradrachmae, they are similar in composition to the so-called Celtic imitations, e.g. the pieces found in Slovenia and Austria. They are good quality minted coins. The coins from the second group were deliberately alloyed with copper (0.7 --5 %). The low concentration of copper may show that the alloying was made for hardening and not for debasement reasons. Hg traces presence could indicate an amalgamation procedure for silver metallurgy, but additional arguments are necessary. The “fingerprint” of the third group of Thasian tetradrachmae is the bromine [5]. Taking into account the presence of bromine in silver ore from some Transylvania mines Rodna (embolite – Ag(Cl Br) and bromargirite - AgBr) and supposing an imperfect procedure of refinement (see also Cu and Pb high content), these coins could be attributed to local Barbarian (Dacian) workshops.

As for the Apollonia and Dyrrachium drachmae, a similar situation can be retraced. Because of the high silver content and refined aspect of the coins belonging to the first group, one can assume that these drachmae are the original ones, minted of Macedonian silver. The percentage of copper in the second group of coins is higher than in the previous case. The conclusion is that copper was deliberately added to the alloy, reflecting a difficult economic situation during the civil wars. These drachmae were struck in Apollonia, using Dyrrachium dies belonging to MENISKOS magistrate. The third group of drachmae is similar in composition to a category of the tetradrachmae table (the third one): again a relatively high content of bromine (local silver?). Another important group is bronze Dyrrachium drachmae, found in South-East of Romania. Some of these coins were covered with a thin (submicronic) layer of tin, which can be partly noticed by visual examination. The tin layer was strongly corroded. The Cu-Sn proportion is unbalanced, triggering a frailty process because of the high content of Sn. Moreover, the absence of Zn brings about a certain degree of porosity that can be noticed in some coins. The result of this alloying is a compound named “white bronze”, which can easily be mistaken for silver. This was in fact, the intention of the manufacturer. This artifice was used in extreme situations, when silver resources were completely exhausted. Only one sample differs in composition from the above one. One could assume this Dyrrachium drachma bearing the inscription XENON was minted using Illyrian tin. A special case was the plated drachmae. The crust (0.3-0.5 mm thick) was made of high purity silver (95-97%). This crust was broken in some areas, baring an inside core (0.2-0.3 mm), made of bronze (90-97% Cu, 3-10% Sn).

As a possible economic and political explanation for these last categories of coins, one can assume that during the Roman civil wars (1st century BC), the connection with Macedonian silver mines was often interrupted. Therefore, the local administration started to mint coins just with a silver skin. After ingot exhaustion, the coins were only made of bronze, and the silver was reduced to a thin covering, sometimes even this covering was replaced with tin. These coins have a very elaborate aspect; one can conclude that they are struck using the original dies.

GOLD COINS

Many isolated pieces or large treasures of ancient gold coins (staters, mainly "kosons" and "pseudo-Lisimachs") were discovered in Romania, especially around Sarmizegetuza - the capital of Dacia. The koson-type is considered the only kind of gold coins issues by the Dacians. The strangeness consists in its Roman iconography (inspired by two different silver denarii) coexisting with a Greek legend and a Persian weight system.We analyzed a set of 21 kosons, together with 20 other different gold coins having circulated in Romanian territory (pseudo-Lysimachs, Roman republican and imperial aureii, celtic and medieval Transylvanian coins), using X-ray fluorescence (XRF) and proton activation analysis (PAA).

For XRF, three annular excitation sources - Pu-238 (30 mCi), Am-241 (30 mCi) and Am-241 (10 mCi, with nickel window for absorption of soft X-rays) and two X-ray (a Si(Li) and an HPGe) detectors with beryllium windows were used. The plutonium source is more suitable for Cu, Fe, and Pb detection, and the americium source for Ag, Sn, Au and, possibly, other elements with Z around 50.

For PAA, each coins was irradiated in vacuum for 5 hrs at an incident proton energy of 11 MeV provided by the Bucharest HVEC - Tandem accelerator at a current of ca. 50 nA [6]. Since a focalized proton beam was used, the inhomogeneity of the alloy may yield different concentrations by PAA in comparison with XRF results. After a cooling time varying between 22 hrs and 16 days the coins were counted at least three times each using a properly protected Ge(Li) gamma spectrometer (resolution 2.1 keV for 1.332 MeV gamma-line of Co-60). In order to prevent the pile-up effect of the soft lines of Hg-197, a 0.6 mm cadmium filter was interposed between detector and coin. The concentration of an element was only determined relatively to the gold (matrix) concentration. In this way the integrated charge of protons becomes unimportant. Lisimachs Greek coins, issued from different cities at the Black Sea coast in actual Eventually, the element concentration was obtained considering the sum rule (all concentration must give 100%). Two modern gold coins with known ("catalogue") composition values and the gamma yields for the (p,n) reaction taken from Refs. 7 and 8 were used. Except for Ti, Fe, Cu, Pd, Ag, Sn, Sb, Pt and Pb, no other element was seen in the activation gamma-ray spectra.

From the Cu/Ag plot using obtained composition values, it shall be noticed that the three types of analyzed kosons (without monogram, with simple monogram and with complex monogram) are evidently clustered (Ag 10% and Cu 0.8% ; Ag 2-3.5% and Cu 0.1-0.25% ; respectively Ag 4.2-5.1% and Cu 0.13-0.28%), denoting three different emissions (workshops, periods or, more probably, gold sources). The kosons compositions are clearly different from Roman aureii and celtic coins Compared to Transylvania's natural gold composition (as reflected in Transylvanian medieval coins) - silver from 8 to 15%, copper less than 0.05% -, it is evident none of kosons type are made from such natural gold. The most close to kosons' compositions are the pseudo-Dobroudja : Histria, Callatis, Tomis. This means the probability the workshops for kosons were situated in these cities or, at least the "specialsts" were "imported" by the Dacians from there is quite large. To a better understanding of kosons' provenance, we intend to study the Platinum-elements (Pt, Ir, Os, Pd, Ru) inclusions, which are a real fingerprint of each gold mine, using microPIXE.

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