Towards a More Objective Approach in Numismatics Research Using Compositional Analyses Based on Nuclear Methods

The scientific analysis of archaeological objects ideally requires the availability of methods simultaneously non-destructive, fast, universal, sensitive and multielemental. For coins, chemical differences that occur during preparation of alloys affect the elemental composition and can be used for the identification of technologies and mints and also to distinguish between originals and counterfeits.

X-ray Fluorescence (XRF) method, most frequently used by us in numismatics studies, is a fast, cheap and reliable analytical tool. It does not require sampling or complicated sample preparation, the equipment is relatively simply to operate and presents the advantage to be easily transported or designed in a portable form, to allow in-situ measurements.

In this paper, we intend to explain what should be expected from XRF archaeometrical analyses and some applications using this technique will be given. The elemental composition provided by XRF can be used for the following purposes:

- Originality testing – e.g. it is known that modern silver obtained through electrolysis contains no gold traces; as a consequence, the counterfeits of ancient silver coins do not contain gold at trace level; Greek – Roman bronze (Cu – Sn) objects, which always contains lead in variable amounts, can be faked by using modern brass alloy (Cu - Zn);

- Provenance - minor and trace elements determined through elemental analysis can be used for ore and/or workshop identification;

- Conservation - protective measures can be decided on compositional basis; e.g. anticorrosion treatments for less noble metal objects;

- Restoration - it is better to have the elemental composition of a deteriorated object, in order the use similar or compatible materials to accomplish a good restoration;

- Historical studies - based on the elemental composition determined through XRF, conclusions regarding manufacturing technologies, commercial, military and political relationships between ancient populations and/or trade routes can be revealed; e.g. selection of the high-purity silver coins from adulterated silver plated (using edge measurements) and /or silvered items belonging to similar official emissions is possible.

In special cases we also used PIXE (Proton Induced X-ray Emission) or activation techniques, such as PAA (Proton Activation Analysis) and/or NAA (Neutron Activation Analysis). These methods are more sensitive than XRF, but the cost of analysis is much higher, a particle accelerator – for protons - and/or a nuclear reactor – for neutrons - being necessary to perform these measurements. However, PIXE, PAA and NAA are invaluable tools when the question of trace elements is of crucial importance in archaeometrical research (e.g. provenance studies).

Some illustrative examples of nuclear methods application for numismatics studies are given.

The Geto-Dacian coins of Inoteşti-Răcoasa type belong to the large imitation class of the Philip II Macedonian coins. It was made the hypothesis that they have been issued by a tribal unions living in the half East of Walachia and in the South of Moldavia. In a recent numismatic essay of Gramatopol it was stated without no compositional analysis that “so called Inoteşti-Răcoasa type is ending by being only coins of bronze so gentle silvered, that silver disappeared completely”. It was interesting to verify these hypotheses about the Inoteşti-Răcoasa

coins, i.e. to see if they are made of copper/bronze. In order to analyze these coins XRF, PAA (Proton Activation Analysis) and GT (Gamma Transmission) analytical methods were used. The results turned out that all the analyzed coins, but one, exhibited silver in different proportions – varying from 15% to 70%. The conclusion of this study was the Inoteşti-Răcoasa coins were not made of copper or bronze as it was supposed based only on visual examination, but all of them were made from a silver alloy more or less debased (billon).The dispersion of the silver concentrations values led to the conclusion that a gradual debasement took place. These above facts support the hypothesis that Geto-Dacians never coined copper/bronze coins, but only coins made of a silver alloy, more or less debased.

21 gold coins of Koson type, considered the only kind of gold coins issued by the Dacians, were analysed using XRF and PAA (Proton Activation Analysis) methods at Bucharest National Institute of Nuclear Physics and Engineering "Horia Hulubei" facilities. For XRF, three annular excitation sources – ^{238}Pu (30 mCi), ^{241}Am (50 mCi) and ^{241}Am (10 mCi, with nickel window for absorption of soft X-rays) and two X-ray detectors with Be window – a Si(Li) and an HPGe were used. For PAA, each coin was irradiated in vacuum for 5 hours at an incident proton energy of 11 MeV at a current of ca. 50 nA at the 8 MV FN High Voltage Bucharest TANDEM and measured using a properly protected Ge(Li) gamma spectrometer. Three groups of coins of different composition were found, corresponding to the shape of the monogram: simple, complex or no monogram at all. The gold of the Koson coins is not a natural one (electrum) from present Romania's territory, but is similar to the gold of pseudo-Lysimachus type staters. Some possible historical conclusions are discussed.

We also analyzed approx. 300 Greek silver drachms, emitted by Apollonia and Dyrrachium cities during the first Roman Civil War between Julius Caesar and Pompeius. Five main categories were found: - original coins (similar to drachms emitted before the Civil War) with 97-99% silver, low (1-2%) copper content, -debased coins with silver content down to 70% and copper content from 5 to 25%, probably emitted due to inflation problem, a normal phenomenon for an economy during wars, - official (original dies) counterfeits from bronze (70% copper and 30% tin) covered by a very thin layer of argentarium (tin-lead alloy imitating the silver), -official counterfeits from tin (actual Yugoslavia territory is very rich in tin mines), - plated coins consisting in a bronze core covered by 0.2-0.5 mm silver plates, using argentarium or lead as intermediate layer between bronze and silver. For 'quality control', many coins present attempts made on their edge to verify the real silver content in the bulk using a knife. Some historical and economical considerations about the adulterations during silver coining process are presented.

Another studied case was the one of *brakteaten pfennige* (one side thin foil coins), minted by the medieval German princes and bishops (10^{th}-12^{th} centuries). The National Museum of Romania's History has some hundreds of such coins in its collections, and a quick sorting of them was necessary. A way of solving this problem was to use in-situ ED-XRF measurements. Very few coins were high fineness silver coins, for which the following composition: Ag=96%, Au=0.75%, Pb=0.65%, Cu=2.05% was determined. However, most of the coins were silvered coins, with either copper or bronze or leaded bronze (Pb=65%, Cu=22%, Sn=12%, Sb=0.4%) core, being covered with a very thin silver layer. This thin silver layer contains a lot of mercury, which remained from the silvering (plating) procedure using Ag-Hg amalgam. A possible explanation for these numerous silvered coins can be the fact that the old German silver mines were probably exhausted during 11^{th} century, only in the 14^{th} century being discovered new mines in Saxony (e.g. Freiberg and Schneeberg). However, during this period (10^{th}-12^{th} centuries) the construction of the great cathedrals had started, and there was a high need for money; therefore, a strong debasement of these silver coins took place. A similar amalgamation silvering procedure was revealed for some Moldavian Stefaniță "silver" coins dating from the first half of the 16^{th} century.