Characterization of Dyrrhachium Silver Coins by Micro-PIXE Method

I. Uzonyi[a], R. Bugoi [b], A. Sasianu [c], Á. Z. Kiss [a], B. Constantinescu [b], M. Torbágyi [d]

[a] *Institute of Nuclear Research of the Hungarian Academy of Sciences (ATOMKI), Department of Electrostatic Accelerators, Debrecen, Hungary*

[b] *Institute of Atomic Physics, Cyclotron Laboratory, Bucharest, Romania*

[c] *Cris County Museum, Department of Numismatics, Oradea, Romania*

[d] *Hungarian National Museum, Department of Numismatics, Budapest, Hungary*

Abstract

Ancient silver coins (drachms) issued by the Greek city Dyrrhachium 68-43 years BC were analysed non-destructively by micro-PIXE method. The selected 27 drachms, including four imitations, belong to the numismatic collection of the Hungarian National Museum (HNM). Nine elements (Fe, Cu, Zn, Br, Ag, Sn, Au, Pb and Bi) were determined quantitatively. Samples are characterised with a uniformly low ~92% Ag concentration. Debasement is supposed.

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Corresponding author: Imre UZONYI

Postal address: Institute of Nuclear Research of the Hungarian Academy of Sciences, P.O. Box 51, H-4001 Debrecen, Bem tér 18/c, Hungary.
Telephone: +36-52-417266
Fax: +36-52-416181
E-mail: uzonyi@atomki.hu

1. Introduction

Ag drachms issued by the two Greek cities of Illyria, Apollonia and Dyrrhachium, in the second and first centuries BC have been frequently found in the Carpathian Basin and in the Balkan region. From the archaeological point of view, the main problem is to classify them in order to explain related economical and political aspects such as the impetuous increasing of their amount in the first century BC, especially before and during the Roman civil war between Pompeius and Caesar [1-3].

The first modern classification of Apollonia and Dyrrhachium coins discovered in Albania was accomplished by Ceka [4] who found a connection between elemental composition and the minting period. Four years ago, the Romanian co-authors of the present paper also started a comprehensive and systematic study of the coin-hoards discovered in Romania the results of which will be published elsewhere [5]. The existence of similar artefacts at the Hungarian National Museum (HNM) led to this collaboration in order to reveal connections between drachms found in the neighbouring countries.

2. The archaeological samples

Out of a 153 pieces Dyrrhachium drachma collection of the Coin Cabinet of HNM [3] 27 were selected for analysis including four ancient imitations (see Fig. 1 and Table 1.). Imitations are characterised by misspelled legends and the lack of refinement of decorations, while the original drachms have readable inscriptions. All analysed coins were minted during the 68-43 years BC. The exact finding spot of this hoard is still unknown but, supposedly, it should have been found in southern or south-eastern part of Hungary.

3. Experimental

The analysis of drachms was performed at the Debrecen scanning nuclear microprobe [6]. The experimental conditions were as follows: proton energy of 2.0 MeV energy, beam current of ~ 200 pA, total collected charge of ~ 0.2 μC and a beam spot size was ~3 × 3 μm^2. For the selective filtering of the most intense Ag L_α line, a 10 mg/cm^2 Al foil was placed between sample and the Si(Li) detector. In all cases three different areas were scanned in flat and bright regions of the coins where the surface is more likely free from patina due to continuous rubbing and cleaning effect of use. Spectrum fitting and calculation of elemental composition was carried out by using the PIXYKLM programme package [7]. In the spectra of coins, altogether, the characteristic lines of nine elements such as Fe, Cu, Zn, Br, Ag, Sn, Au, Pb and Bi could be detected.

4. Results and discussion

In this study, X-ray intensity maps were generated in all measurements for all analysed elements. The scan size was 1 x 1 mm^2. This way it was possible to exclude deposited or heavily corroded areas as well as inclusions from the evaluation. For example, Fig. 2 shows Cu enrichment on the surface of a silver coin. The unaffected area is characterised by 94% Ag and 5% Cu concentrations, while the corresponding values at the Cu-rich spot (diameter ~1 mm!) are completely different: 74% Ag and 25% Cu.

X-ray lines of Fe have been often observed in the spectra of silver coins [8]. Here again, the excellent lateral resolution of the microprobe helps to interpret their origin. As it can be seen from Fig. 3, Fe-K_α counts are concentrated in a few extremely protruding peaks with a diameter of <20 μm. A possible explanation for this fact is that Fe-peaks originate mainly from either surface contamination or inclusions present in the sample.

Depth profiling was carried out on an "average quality" area by using 2.0, 2.5, 3.0 and

3.5 MeV beam energies. As Ag-K_α radiation may emerge from five times deeper layer (~40 μm) of the surface than Cu-K_α (~8 μm), inhomogeneities in depth distributions of Cu or Ag should be reflected in changes of calculated concentrations when energy increases (similar statement can be made for minor elements such as Au or Pb). At the above energies, the determined concentrations varied less than 0.5% (absolute) for the major elements Cu and Ag. The measure of this effect is comparable with the accuracy of the used fundamental parameter method, therefore, within these limits, the homogeneity hypothesis was accepted.

Table 2 summarises the micro-PIXE results for the Hungarian drachms. Following the archaeological classification, coins were divided into four groups and analytical data were subjected to statistical evaluation. Each coin was represented by averaged concentrations from three independent measurements. From the individual values group averages as well as standard deviations were calculated, which can be seen in Table 2. Compositional data for series of similar type Dyrrhachium coins from Romanian Viisoara's hoard are also presented for comparison. They were measured by 3 MeV external PIXE and XRF methods in the Cyclotron Laboratory of the Institute of Atomic Physics, Bucharest, Romania [5].

As a first step, one way ANOVA analysis was carried out to test the hypotheses of equality of group averages. In statistical sense, at a probability level of $P<0.05$, there are no significant differences between the elemental compositions of the Hungarian groups. In contrary, the Romanian results were statistically different from the Hungarian ones in some cases (see Table 2). It is worth mentioning that, except Cu and Ag, the differences are not serious. They may arose from either biases in the analytical techniques used (e.g. in case of Au) or the varying degree of surface contamination (Fe, Br). Namely, bromine can be associated to air pollution of the coin as it was pointed out by Brissaud et al. [9]. In case of Cu and Ag, the large variances of Romanian results are remarkable. It is worthwhile to mention that the Au concentration is practically constant (=0.35%) for all analysed coins. This metal

may be a fingerprint of the silver ore. Pb was supposedly used to lower the melting point of the alloy. It is also interesting to note, that there are strong correlations between Cu(Ag)-Zn (r=0.86) and Cu-Ag (r= -0.99) (see Fig. 5) and practically no other significant correlations. The high negative correlation between Cu and Ag means the substitution (probably intentional) of silver by copper. Measurements have shown that the quality of silver drachms degraded from an initial ~98% Ag value down to 70-90% until the middle of the first century BC [5]. This degradation may explain the significant differences in Cu and Ag concentration between the Hungarian and Romanian coins.

A characteristic element for imitation is Sn, which was found only in three of the suspected samples. With the permission of HNM one of these coins (no. 150) was finely scratched at its edge in order to study its structure with the microprobe. PIXE analysis revealed a low quality silver core (Cu=46%, Zn=0.3%, Ag=50.5%, Sn=2.5%, Au=0.2%, Pb=0.4%, Bi=0.06%) below the surface. This way, the supposition that these samples are coated counterfeits was proven. The fourth coin (no. 151) doesn't differ in composition from the normal ones, which suggests a misidentification of this coin.

5. Conclusion

The investigation gives contributions to the extensive Romanian studies and helps to establish an exact chronological classification of Dyrrhachium Ag coins. The results of both laboratories present the same phenomenon of degradation of the fineness of Ag by introducing increasing quantity of copper (~ 8-10%) as compared to the coins minted in the second century BC.

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Figure 1. Photo of some analysed silver drachms (front and reverse sides). Catalogue numbers are: 52, 82, 128.

Figure 2. Elemental maps showing Ag-K_α and Cu-K_α intensity distributions on a corroded layer of a Ag coin. Scan size: 2500 x 2500 μm^2.

Figure 3. A typical Fe K_α intensity map. Scan size: 1000 x 1000 μm^2.

Tables

Table 1. Identification of the analysed Dyrrhachium coins (minted 68-43 years B.C.).

Table 2. Elemental composition of Dyrrhachium silver coins. For comparison, analytical results characterising the Viisoara's (Romania) coin-hoards are involved [5]. Equality of group averages was tested by using one way ANOVA analysis at a probability level of $p<0.05$. The four Hungarian groups were statistically not distinguishable. In the case of some elements, the Hungarian and Romanian average values differed significantly (denoted by *). Abbreviations and remarks: R: Romanian results; n.d.: not detectable; **: one of the imitations (No. 151) doesn't contain Sn.

Figure 1

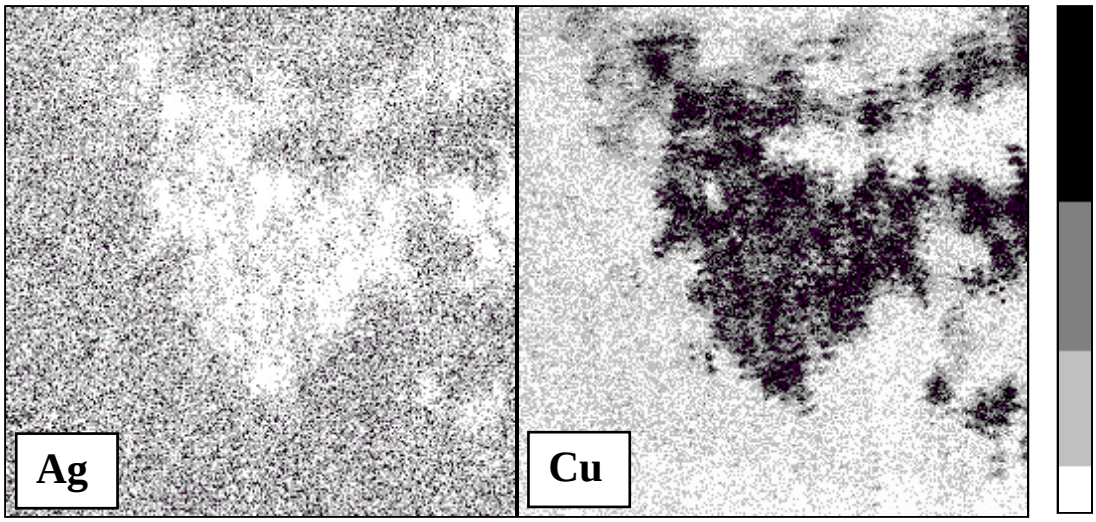

Figure 2

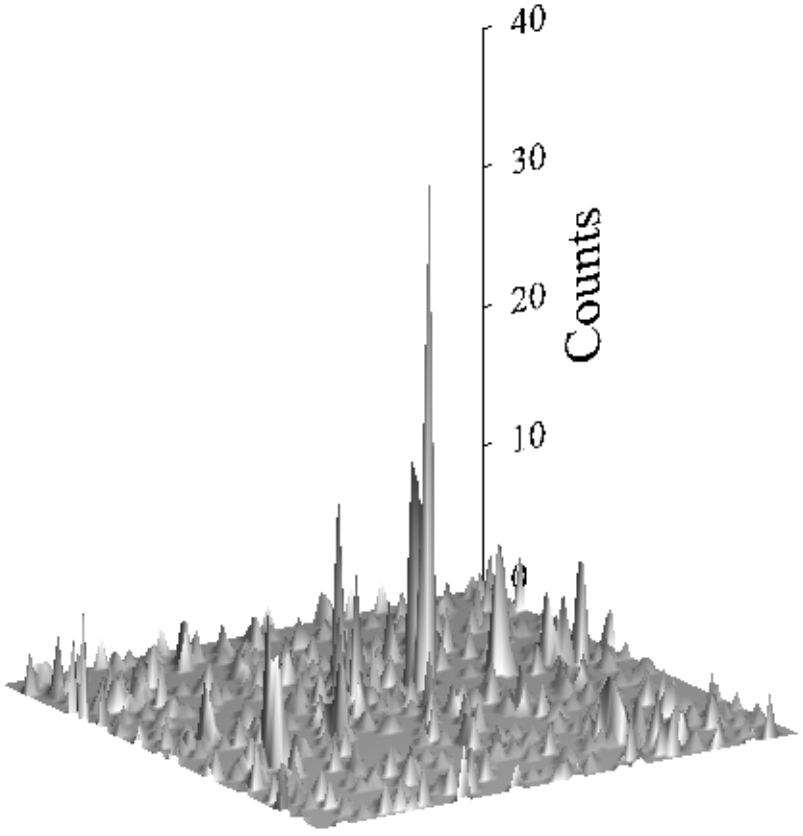

Figure 3

Table 1.

Group	Catalogue number	Type
I (n=15)	24, 26, 27, 28, 31, 33, 34, 36, 40, 42, 43, 52, 53, 59, 61	ΜΕΝΙΣΚΟΣ-ΔΙΟ-ΝΥ-ΣΙΟΥ, Ceka 320 [4]
II (n=4)	79, 82, 89, 106,	ΜΕΝΙΣΚΟΣ-ΛΥ-ΚΙΣ-ΚΟΥ Ceka 325
III (n=4)	127,128, 129, 130,	ΞΕΝΩΝ-ΔΑ-ΜΗ-ΝΟΣ Ceka 357
IV (n=4)	150, 151, 152, 153	imitations

Table 2.

Group	Fe [ppm]	Cu [%]	Zn [ppm]	Br [ppm]	Ag [%]	Sn [ppm]	Au [%]	Pb [%]	Bi [%]	Mass [mg]
I (n=15)	**830 ±50**	**8.24 ±2.2**	**670 ±210**	**70 ±20**	**90.4 ±2.1**	**n.d.**	**0.35 ±0.03**	**0.77 ±0.5**	**0.12 ±0.06**	**3.23 ±0.2**
I(R) (n=16)	**2200 ±1800***	**13.1 ±7.3***	**n.d.**	**400 ±270***	**85.3 ±7.1***	**180 ±80**	**0.45 ±0.08***	**0.83 ±0.4**	**0.10 ±0.09**	**3.08 ±0.2**
II (n=4)	**580 ±200**	**6.74 ±1.1**	**560 ±180**	**70 ±30**	**91.8 ±1.4**	**n.d.**	**0.36 ±0.05**	**0.87 ±0.3**	**0.09 ±0.06**	**3.21 ±0.2**
II (R) (n=11)	**1000 ±800**	**11.3 ±6.6**	**n.d.**	**450 ±220***	**86.8 ±6.4**	**230 ±210**	**0.40 ±0.15**	**1.02 ±0.8**	**0.03 ±0**	**3.03 ±0.3**
III (n=4)	**740 ±100**	**6.26 ±1.4**	**460 ±120**	**50 ±10**	**92.6 ±1.7**	**n.d.**	**0.33 ±0.16**	**0.58 ±0.2**	**0.13 ±0.07**	**3.28 ±0.1**
IV (n=4)	**1200 ±600**	**8.21 ±4.8**	**780 ±520**	**130 ±130**	**90.1 ±5.4**	**7700** ** **±5800**	**0.43 ±0.06**	**0.42 ±0.2**	**0.14 ±0.02**	**2.98 ±0.2**