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Complex archaeometallurgical investigation of silver coins from the XVIth-XVIIIth century

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ABSTRACT

When dealing with cultural heritage artifacts, the use of non-invasive and non-destructive analyses techniques is *a must*. Determination of the surface corrosion layers and coin composition is important both for identifying compounds that form different alloys (which can be considered support material for important objects, such as numismatic artifacts), and also for their conservation. The selection of analytical techniques is of great importance, as it is a strict condition that the structure of the artifacts should not be affected.

The paper presents the archaeometallurgical study of seven silver coins, using several nuclear techniques (X-ray fluorescence – XRF, X-ray diffraction – XRD, Particle induced X-ray emission – PIXE) and optical microscopy. The study was performed using *bulk* methods and *micro-area* measurements in order to establish their composition, as well as the presence of corrosion products. This could, in turn, provide information in support of the categorization in genuine/possible forgery. From the analyzed set of samples, six can be surely categorized as genuine, while one raises some questions. A decisive conclusion cannot be drawn for one of the analyzed samples, but the scientific evidences suggest either a misstruck or a forgery approximately contemporary with the original issue of these coins.

1. Introduction

Discovering mineral processing and, later, the procedures for obtaining metal alloys constituted the engine of human development, being comparable in terms of the effects on human civilizations with the discovery of fire. All human pursuits (hunting, working the land, creating objects for beautification, housing construction, etc.) would not have been possible if men did not master the metalworking technologies. In most of the history of metallurgy, few metals were used, like silver, copper, gold or zinc. This is the case of numismatic artifacts, too. Coins are objects of great historical value and can provide information on manufacturing technology, authenticity and mint, the monetary history of a certain period or dynastic succession [1].

Silver was the most used material in coin production, its durability being enhanced by the addition of alloying elements, as copper [2]. Due to storage conditions and their age, the coins can present corrosion products, whose study can provide "*example information*" useful for conservatives and restorers. Since manufacturing, metals and their alloys (except gold), react with the environment and start a corrosion process that leads to more stable compounds. Before applying various techniques of conservation, knowledge of corrosion products (resulting from exposure to different environments) is essential for restorers. The nature of corrosion products determines the most effective procedures and techniques that can be used.

The use of non-invasive and non-destructive analyses techniques is *a must*, when we are dealing with artifacts, with different elemental compositions. Determination of the surface corrosion layers and coin composition is important both for understanding compounds that form different alloys (which can be considered support material for important objects, such as numismatic artifacts), and also for helping in their conservation.

The selection of analytical techniques has great importance, as it is a strict condition that the structure of the artifacts should not be affected. The techniques must be non-destructive, rapid, quantitative and with high sensitivity [3,4]. Considering those

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requirements, the best methods are represented by the nuclear analytical techniques (X-ray fluorescence, X-ray diffraction, Particle induced X-ray emission).

The use of XRF for the analyses of numismatic artifacts has represented for several decades a viable alternative to the use of conventional destructive methods. The technique has almost all the properties required for cultural heritage artifacts analysis: it is completely non-destructive, fast and multi-element and has good sensitivity [5]. Its main drawbacks are related to the strong influence on the obtained results of impurities from the sample, inhomogeneity and also irregular surface or corrosion products present on the surface of the samples [5].

Similarly, X-ray Diffraction, even though it implies the use of much more expensive instruments, represents another very important technique, offering information on the products' corrosion phases, as well as on the samples' composition [6].

Particle Induced X-ray Emission (PIXE) emerged in the last decades as one of the most appropriate method in the study of cultural heritage artifacts [7–9]. The method can be applied for determining the metal sources, evaluating the trace elements present in the sample or just for a complex characterization of the artifacts [7–11].

In the present paper, we propose a complex methodology for the evaluation of metallic artifacts, consisting of combined use of micro-area and *bulk* XRF, micro-area and *bulk* XRD, PIXE and optical microscopy for the characterization of seven silver coins, with different origins and mintage years [12]. The coins were selected, considering several aspects: all the coins were found in Romania; all the coins are part of a single collection, being preserved in the same conditions for over one hundred years; finally, the different grade of silver allows testing the proposed methodology on a large concentration range.

2. Material and methods

2.1. Analyzed coins

The coins subjected to study are presented in the Supplementary Material Fig. S1. Table 1 presents their general characteristics (with the inscriptions detailed in Table S1, Supplementary Material). All the coins belong to authors' private collection. The analyses were performed without any cleaning, in order to evaluate both the composition and the corrosion products. The samples were first visually inspected and identified using reference works for numismatic area [13–16]). Further details are presented in Supplementary Material.

2.2. Methods of analysis

The samples were analyzed using four different techniques: optical microscopy, X-ray fluorescence, X-ray Diffraction and Proton induced X-ray emission.

The optical microscopy evaluation was performed using a Kruss MBL3000 microscope, at different magnifications [17].

Two types of instruments were used for the X-ray Fluorescence measurements: the *bulk* measurements were performed using an energy-dispersive spectrometer, EDXRF PW4025, type MiniPal 2 (PANalytical, B.V., The Netherlands), with a Si-PIN detector, at 20 kV and automatic current intensity, measurement time 300 s, in Helium atmosphere (beam spot area 81.7 mm^2) [18,19]; the micro-area measurements were performed using a small spot (under 1 mm) energy dispersive X-ray fluorescence (ED-XRF) spectrometer, optimized for precious metal testing (Spectro Midex, SPECTRO Analytical Instruments GmbH, Germany), equipped with a 50 kV Mo-anode tube and a Peltier cooled Si-drift chamber detector; besides a very good precision and accuracy over a wide range of concentration levels, the spectrometer offers short testing times (30–40 s) [20].

X-ray diffraction analyses were performed using a Rigaku SmartLab equipment, operating at 45 kV and 200 mA, using Cu Kα radiation (1.54059 Å), in parallel beam configuration (2θ/θ scan mode), from 3 to 90 2θ degrees for bulk determinations; for micro-area X-ray diffraction the same instrument was used, but in a different configuration (point focus with CBO-f optics, estimated beam size – 400 μm, between 5 and 90 2θ degrees); the components were identified using the Rigaku Data Analysis Software PDXL 2, database provided by ICDD [21].

Proton induced X-ray emission (PIXE) measurements were performed using the "In-Air" PIXE setup, recently developed at the 3MV Tandetron from "Horia Hulubei" National Institute for Physics and Nuclear Engineering. The used beam was 3 MeV protons obtained by the sputtering ion source and accelerated through the IBA (Ion Beam Analysis) chamber [22,23].

Using this facility, fragile and large samples can be analyzed without the risk of damaging, caused by the vacuum chamber conditions and its sample dimensions limitations. All the samples were carefully positioned onto the 3 axe positioning system, in order to be driven in front of the proton beam.

A proton beam of approximately 2.735 MeV (SRIM simulations, starting from the 3 MeV beam in high vacuum conditions) was extracted in-air and directed toward the samples. The proton beam spot size on the sample was about 1 mm in diameter (experimental set-up presented in Fig. S2, Supplementary Material). The resulting characteristic X-ray spectra were recorded using a Silicon PIN (SiPIN, Amptek, USA) and analyzed with the GUPIX software.

The performance of these methods for artifacts analysis was already presented in previous published works [17,19–21].

3. Results and discussions

The microscopic evaluation of the samples reveals both the general characteristics of the analyzed samples (shape of the letters), and the aspect of the corrosion points. The corrosion products of

Table 1
The coins analyzed in the study and their main characteristics.

No	Sample encoding	Inscriptions	Year	Source	Diameter (mm)	Weight (g)
1	Sample A	*PHS DG HIS REX DUX BR/DOMINVS:MI – HI:ADIVTOR*	1569	Spanish Netherlands/ Antwerp	32.62	12.43
2	Sample B	*SIGISMVNDVS BATHORI/PRINCEPS TRANSSYLVANAE 1593*	1593	Transylvania/Nagybanya	39.70	28.71
3	Sample C	*MO:ARG:CON FOE:BELG:PRO:TRAI /CONFIDENS*DNO*NON*MOVETVR*	1647	Netherlands/Utrecht	42.22	26.36
4	Sample D	*MO.NO.ARG. CIVIT. DAVENTRIAE/CONCORDIA.RES.PARV.CRESCVUNT*	1662	Netherlands/Deventer	42.48	22.74
5	Sample E	*Tughra of Mustafa III in center/Year: AH1171, regnal year 5*	1762	Turkey	37.21	19.12
6	Sample F	*Sultan Mustafa bin Ahmed Han dame mülke Darebe fi Islambol AH1187, regnal year 4/Sultan ül berreyn ve hakan ül bahreyn es sultan ibn es sultan*	1777	Turkey/Istanbul	43.82	27.44
7	Sample G	*Second type tughra/Darebe fi Islambol 1203*	1793	Turkey/Istanbul	42.45	23.74