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Micro-XRF analysis of silver coins from medieval Poland

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ABSTRACT

X-ray fluorescence (XRF) analysis has become a standard method in archaeological science due to its non-invasive and non-destructive nature. This technique has extensively been used for the study of numismatic collections since the data derived from it can be correlated with manufacturing processes, provenance of raw materials, and geographical distribution of ancient mints. A group of 71 silver coins of the first Piasts: Boleslaus the Brave (996–1025) and Mieszko II Lambert (1025–1034) belonging to the collections of the National Museum in Krakow have been characterized using micro-XRF spectrometry. This is the most numerous collection of their coins representing nearly 30% of all known coins from these rulers. The research has focused on evaluating the use of this technique as a screening tool for elemental surface characterization of the alloys. Surveyed coins are mainly constituted by Ag, Cu and Pb along with trace levels of Fe, Ni, Zn, Au, Hg, Bi, and Br. Quantitative analyses have revealed Ag contents in the 81.6–97.5% range for all the evaluated coins. This study had the goal of providing information about the elemental composition of these objects, which will serve to enhance the existing knowledge about geographical and chronological diversification of Polish numismatic collections.

1. Introduction

Archaeometallurgical research often has the goal of correlating temporal and spatial distribution of ancient metal objects and their chemical composition [1–3]. Analogously, chemical analysis of numismatic collections has become an important area of research since it may provide significant information about the manufacturing process [4], the provenance of raw materials [5,6], the geographical distribution of ancient mints [7], and the minting periods [8]. This information is of enormous value for archaeologists and historians since the correlation between the chemical composition of the objects and their political, social, and economic contexts can be examined. In the numismatic field, chemical characterization has typically involved the use of global analyses to study the elemental composition of historic coins [9–11]. Moreover, X-ray fluorescence (XRF) spectrometry has been extensively employed for evaluating the surface composition of the alloys [12–17]. Although a qualitative and quantitative analysis of numismatic collections is possible through the use of XRF spectrometry, the quantitative part has a few disadvantages including surface irregularities and measurement geometry [18] as well as elemental differences between the surface and the bulk material [19]. The latter can be due to corrosion processes, which evidently alter the surface composition of the coins.

Corrosion of metal alloys is a common occurrence in archaeological objects. The two main factors accountable for these processes are: the chemical composition of the alloy [20,21] and the environmental elements interacting with the object [22]. Of these processes, Ag enrichment at the surface of Ag–Cu coins is a common occurrence and very well studied phenomenon [23–27]. This process usually takes place in alloys that contain metals that exhibit significant differences in electronegativity such as Ag and Cu. The higher electronegativity of Cu relative to Ag results in preferential corrosion of the former one producing a depletion effect of Cu and enrichment of Ag [23]. Visible signs of Cu corrosion in Ag–Cu coins are typically associated with silver surface enrichment effects. However, it should be emphasized that this process is not homogeneous and the Ag–Cu ratio will vary depending on the area selected for analysis. Some authors have also indicated that Ag enrichment can be deliberately carried out during the manufacturing processes [24]. This occurrence evidently presents problems at the time of

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performing accurate chemical analysis of cultural heritage objects using XRF since it may result in overestimation of the Ag content. Previous research on numismatic collections has included micro-destructive [28] and destructive [26,29] methods of analysis or the use of conservation cleaning protocols prior to performing the chemical analyses [30]. However, most museum professionals consider that the analyses must be performed in a non-destructive way and without performing any prior cleaning treatment of the historic object. Accordingly, numismatic researchers at the National Museum in Krakow discouraged the employment of destructive analyses and recommended the exclusive use of XRF spectrometry even though this technique only provides surface information.

As mentioned earlier, a typical problem faced when interpreting XRF data is to assume that the object is homogeneous and that the composition at the surface is similar to that of the bulk. It is widely known that the depth of penetration of X-rays is influenced by the density of the material, the fluorescence energy of the chemical elements in the object, and the energy of the X-ray beam [31]. In XRF analysis, the photons emitted by the X-ray source are usually absorbed by the object's surface, limiting the information range to about 10–100 μm [17]. Moreover, the corrosion layer often found on historic coins is not always uniform and it may exhibit different thicknesses throughout a single object. Therefore, quantitative analysis by XRF is limited since it is very likely that the thickness of the corroded layer exceeds the depth of penetration that can be achieved by XRF. For example, a study of medieval Ag coins by means of energy dispersive X-ray fluorescence (EDXRF) and scanning electron microscopy coupled with energy dispersive X-ray microanalysis (SEM/EDX) revealed that it is possible to have differences of about 50% between leached surfaces and non-corroded areas [32]. For this reason, various authors have indicated that relating surface and bulk information is not always a straightforward task [33]. In contrast, Beck et al. [24] developed a model based on the analysis of Ag–Cu standards of various compositions that were evaluated in the context of global and local analyses of Ag–Cu coins. The model indicates that Ag contents above 92% show a linear correlation between surface and core compositions. Nevertheless, the authors emphasize that XRF analysis alone should not be used to determine the fineness of ancient Ag–Cu coins.

In Poland, the increasing number of publications in this field indicates that numismatic research continues to be a high priority. Studies about the establishment of the first monetary system in this country during medieval times have important implications not only at the national level, but also from a European perspective. It can be highlighted that the rule of Mieszko I and his son Boleslaus the Brave (Bolesław Chrobry) during the X–XI centuries was characterized by the creation of a modern state through the unification of Polish tribes, the political influence at the European level, and the development of trade. It is widely accepted that King Boleslaus the Brave (992–1025) created and established the first Polish monetary system. Boleslaus the Brave pennies, struck probably from circa 995, were based on the Western European monetary system established by Charlemagne (768–814). These coins are represented by approximately 20 types, some of which are imitations of coins from other countries. Most probably they were struck by mints located in Greater Poland, Kuiavia or northern Masovia.

The PRINCES POLONIE denar, minted by Boleslaus the Brave, is arguably the most important coin in Polish history. The inscription POLONIE is remarkable for being the first reference to Poland in a historical source. Although there is no absolute confirmation that Mieszko I minted his own coins, some researchers believe that as the first historical ruler of Poland the production of the first Polish coins could be attributed to him [34]. According to this out-of-date hypothesis [35], the first Polish denar consisting of an Ag coin depicting the top of a chapel and having the inscription MISICO with a cross on the verso side was probably minted around 980. If this was the case, then it is likely that King Boleslaus the Brave, Mieszko's I son, continued minting the coin that was originally developed by his father. In contrast, Suchodolski [36] has indicated that the appearance of coins during the reign of Mieszko I is less probable and has proposed that coins with the MISICO inscription were more likely minted by Boleslaus' son, Mieszko II Lambert during his reign in 1025–1031. The hypothesis postulated by Suchodolski seems to be generally accepted by Polish numismatic researchers and his classification system is employed in several publications including this work. Mieszko II Lambert did not strike coins on his own, but only as a co-governor at the side of his father – Boleslaus the Brave. Mieszko started to issue pennies most probably due to his increase in importance after marrying the prominent Richeza of Lotharingia (1025–1063), the granddaughter of Otto II (973–983). Probably the coins of Mieszko II, just as the rest of his father's issues, were struck in Greater Poland. The majority of the coins found so far came from this geographical area. The end of Mieszko's coinage is dated to ca. 1020, before his independent accession to the throne. It has been estimated that 60 specimens of three types out of about 15,000 pennies struck by this ruler have been preserved to this day.

The nomenclature used to designate the coin type uses the abbreviation Such (for Suchodolski) followed by a Roman and a cardinal number. The present research aims to address some of these issues by providing chemical data that can be used towards a better understanding of these objects when evaluated in conjunction with historical information. Although a small group of similar objects consisting of 11 coins has been analyzed using XRF spectrometry [37], the majority of numismatic reports are generally based on historical and archaeological analysis. This indicates that additional compositional studies are needed in order to expand the existing knowledge about medieval coinage in Poland.

This research examined a group of 71 early Piast Polish coins using micro-XRF spectroscopy with the aim of evaluating the use of this technique as a screening tool for surface characterization of the alloys. The aim of the present study is to offer complementary elemental information about these heritage objects that will help clarifying the different points of view concerning the origins of the Polish state.

2. Materials and methods

2.1. Objects

A collection of 71 Ag coins (Table 1), minted between 995 and 1020 AD, from the Numismatic Cabinet of the National Museum in Krakow was examined. In general, the evaluated objects can be divided into two large groups, namely Boleslaus the Brave (52 coins) and Mieszko II Lambert (19 coins). For simplification purposes, only the names Boleslaus and Mieszko are employed throughout the text. According to Suchodolski [36,38], these two groups can be further subdivided into 18 categories based on an iconographic classification system. It was found that only 10 types out of 18 existent are represented in the 71 coins evaluated. For Boleslaus coins the distribution is a follows: two type II, six type III/IV or IV, one type V/VI, four type VIII, 29 type IX, one type X, five type XI, and four type XI. A more even distribution was found for coins minted by Mieszko (12 type I and seven type II). Four representative examples of the evaluated coins, namely Mieszko Type I (Such.I.1), Boleslaus Type IX PRINCES POLONIE (Such.IX.14), Boleslaus Type XI DVX INCLITUS (Such.XI.17), and Boleslaus Hybrid Type III and IV (Such.III/IV.7), are presented in Fig. 1. Images on the left and right side of the Figure correspond to obverse and reverse, respectively. The examined coins vary in diameter