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The origin and chronology of medieval silver coins based on the analysis of chemical composition

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Abstract. Medieval Central Europe coins – the Saxon coins, also called as the Otto and Adelheid denarii, as well as the Polish ones, the Władysław Herman and Bolesław Śmiały coins – were examined to determine their provenance and dating. Their attribution and chronology often constitute a serious problem for historians and numismatists. For hundreds of years, coins were in uncontrolled conditions and in variable environment. Destructed and inhomogeneous surface were the effect of corrosion processes. Electron microscopy with energy dispersive X-ray analysis (scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS)), X-ray fluorescence (XRF) analysis (energy dispersive X-ray fluorescence (EDXRF) and total reflection X-ray fluorescence (TXRF)), and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) were applied. The results of these investigations are significant for our knowledge of the history of Central European coinage, especially of Polish coinage.

Key words: elemental composition • medieval Central Europe coins • scanning electron microscopy (SEM) • laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) • numismatists

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Introduction

The aim of the presented work was to determine the provenance and dating of a few groups of the early medieval Central European coins. The widely known and already described types of coins have been chosen for investigations. However, their attribution and chronology often constitute a serious problem for historians and numismatists.

The Saxon coins, also called as the Otto and Adelheid denarii, as well as the Polish ones, the Władysław Herman and Bolesław Śmiały coins, were examined. Totally, about 200 coins excavated from 19 archaeological stations and the so-called hoards were studied. The ores from selected deposits such as Upper Silesia, Góry Świętokrzyskie, and Rammelsberg were also analyzed to determine a provenance of metals used for manufacturing coins. For hundreds of years, coins were in uncontrolled conditions and in variable environment. Destructed and inhomogeneous surface were the effect of corrosion processes.

Electron microscopy with energy dispersive X-ray analysis (scanning electron microscopy with energy dispersive X-ray spectroscopy, SEM-EDS), X-ray fluorescence (XRF) analysis (energy dispersive X-ray fluorescence, EDXRF, and total reflection

X-ray fluorescence, TXRF), and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) were applied. All limitations that arise from a complex structure of the historical artifacts were taken into consideration.

The main goal of using SEM was detailed localization and precise selection of interesting and important micro-areas of the coin surface. Elemental analysis was carried out inside a small (about 50 μm wide) crater after the LA-ICP-MS investigations. Analyses were made at the coin surface and inside – along and across – the crater. Obtained results proved the higher concentration of silver at the surface as compared with silver concentration in the bulk of the samples. Opposite phenomenon was observed for copper concentration. These results were the successive effect of the long-time corrosion processes.

The results of these investigations are significant for our knowledge of the history of Central European coinage, especially of Polish coinage. An interpretation of the results of the statistical methods allowed us to differentiate the artifacts in relation to the various production centers (mints), various recipes, as well as various raw materials and their purification methods.

Experimental procedure

Investigated material

Denarii, which were struck approximately from Xth century to XIth century in Central Europe, were found in great number of hoards excavated in Poland. Individual characteristic of these coins is cross picture and legend on obverse and reverse sides. Iconography of denarii has not included information about mints [1–4]. On the iconography, criterion is possible differentiation of eight main types of denarii:

- type I – the oldest, with a temple picture, cross and pseudo-legend on the sides, and 23 mm in diameter, struck during the period 960–1000 A.D.;
- type II – smaller size, struck during the period 1000–1030 A.D.; individual letters occurred often in pseudo-legend;
- type III – named interim denarii, rare;
- type IV – named Deventer, grouped denarii with letters S, A, and Ω, emission during the period 1002–1024 A.D.;
- type V – emission during the period 1030–1024 A.D. with Maltese cross and patriarchal cross with three pearls on the sides;
- type VI – emission during the period 1015–1100 A.D. with Maltese cross and right isosceles cross on the sides;
- type VII – emission during the period 1025–1100 A.D. with Maltese cross and crosier picture on the sides;
- type VIII – similar to type VII, emission after 1070 A.D.

For comparison, Otto and Adelheid denarii (991–995 A.D.) [5], dirhams (XIth century), Hungarian and Czech denarius, as well as the Polish ones, the Bolesław Chrobry, Bolesław Śmiały, Władysław Herman, and the Palatine Sieciech coins, were also examined. Examples of investigated coins are presented in Fig. 1.

Experimental methods

Technological studies, studies of manufacturing techniques, of the appearance of aging and methods for determining the age of objects are performed, first, to determine the authenticity of works of art; second, to obtain information on the technology

Saxon coin type I, subtype 1 – obverse, reverse

Saxon coin type I, subtype 2 – obverse, reverse

Saxon coin type II, subtype 1 – obverse, reverse

Saxon coin type V, subtype 1 – obverse, reverse

Saxon coin type VI, subtype 1 – obverse, reverse

The Otto and Adelheid denarius, example 1 – obverse, reverse

Fig. 1. Examples of investigated coins.

and techniques that were used by a given master; and third, to indicate the optimum conservation techniques that should be used during renovation and conservation work of a given object. The specific feature of such research is the use of multiple methods, mainly physiochemical, to study the objects of unique nature and of high artistic and market value. Often it is impossible to collect material, or even a small analytical sample, for testing. In such instances, portable equipment and various methods that do not cause any damage to the object and do not require sampling are used. The terms 'destructive' and 'nondestructive' must be understood – in this context – as relating to the whole work of art and not only the analytical sample taken. Taking an analytical sample could lead to a risk to the historical monument – could disfigure it or reduce its artistic or market value, and so on.

The objects themselves are often very heterogeneous. This is due, among other things, to the composite materials they are made of, their complex technological construction, and natural aging processes. Their external layers, that is, the layers to which we usually have unrestricted access and which we see when viewing an object, do not fully represent the material from which the object was initially manufactured. Also the chemical components of the external layer often differ significantly from the chemical composition of the material from which the object was produced. This leads to serious problems concerning interpretation, and taking samples from the deeper, noncorroded layers could lead to even greater damage to the object. The selection of the research method used must each time be well thought out, taking into consideration mainly the purpose of the test and the nature of the tested object. As the Saxon denarii are particularly rare and, therefore, of high value, it was intended to perform analysis without sampling or with very small interference.

Three methods were applied for studying the characterization of coins: electron microscopy with energy dispersive X-ray analysis (SEM-EDS), XRF analysis (EDXRF, TXRF), and LA-ICP-MS.

XRF was used without sampling in order to determine the silver contents and also minor (Cu, Pb, Bi) and trace element (Au, Hg, Zn). The XRF analysis was carried out with the aid of spectrometer (EG&G ORTEC) with Si(Li) detector of 180 eV resolution at the Mn K_α and ring ^{109}Cd and ^{238}Pu excitation sources [6]. Analysis of the obtained characteristic X-ray spectrum was carried out by means of AXIL-QXAS (IAEA) program. Certificated standards (133X AGQ3, 133AGQ2, 132X 925Zn1, 132X 925Zn3, and 131X AGP1 A) produced by MBH Analytical Ltd, Great Britain, were used for quantitative XRF analysis.

Method that enables the source of origin of the materials to be assessed is the analysis of the lead isotopic ratios ($^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$, $^{206}Pb/^{204}Pb$) using LA-ICP-MS. In this study, the Pb isotopic composition was measured using ICP-MS ELAN DRC II, PerkinElmer, equipped with LSX-500 laser ablation system, CETAC. The NIST NBS 981 Pb was applied to correct for instrumental mass bias [5, 7–11].

Owing to corrosion processes, which changed the chemical composition of the surfaces of the coins, investigations of crater after the LA-ICP-MS analysis were necessary using SEM-EDS analysis [12–15]. Morphology of compounds and elemental composition analysis in micro-areas was carried out by means of SEM DSM 942 (Zeiss, Germany) and EDS microanalysis system Quantax 400 (Bruker, Germany). Different options of signal collection were used and analyzed: from area of about 0.01 mm^2, point analyses, Line Scan profile (LSP) from coins surface, inside and across of the LA-ICP-MS crater.

Results and discussion

The first step is to determine the elemental composition of the coins by X-ray fluorescence analysis. This technique allows rapid qualitative and quantitative multielemental analysis. Using this method, 230 coins were analyzed. The minor and trace elements such as gold, mercury, lead, bismuth, and zinc were

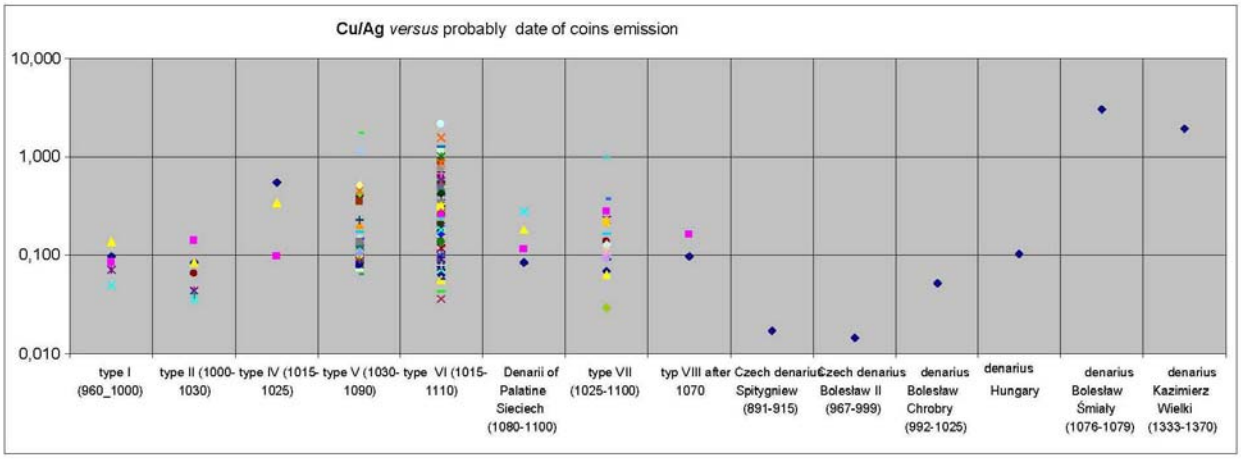

Fig. 2. Change in composition of the Saxon coins type I, II, IV, V, VI, VII, and VIII; Bolesław Chrobry, Bolesław Śmiały, Palatyn Sieciech and Kazimierz Wielki denarii; and Czech and Hungarian denarii vs. probably date of coins emission. The coins are listed in the chronology of mintage. Different color marks are connected with different finding place of hoards such as Brzozowo Nowe, Cieszyków, Dzierzążnia, Górki, Grójec, Jastrzębniki, Naruszewo, Słuszków, Wodzierady, Wodzin, Zakrzew, Zalesie, and Zbiersk.

determined. The silver content of coins was found to vary in the range 22.5–98.0 wt% and copper content was changed from 1.5 to 68.7 wt%. Figure 2 shows the Cu/Ag ratio in the coins plotted against most probably date of emission because Cu is a good indicator of debasement. During the minting period of investigated denarii, the copper content in the coins was enhanced, devaluating the coins at the same time. Detailed results of these investigations have been published elsewhere [16].

The second step of investigations was the determination of lead isotope ratios ($^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$, $^{206}Pb/^{204}Pb$) by means of LA-ICP-MS. Two hundred and forty-five objects were analyzed – coins and Pb ores from areas of Upper Silesia (Olkusz), Góry Świętokrzyskie, and Rammelsberg (Harz Mountains). Following conventions established in archaeometallurgy, the lead isotope compositions of ores and metal artifacts are plotted in binary diagrams using different lead isotopes normalized to ^{206}Pb or ^{204}Pb [17]. An example for such provenance analysis was presented in Fig. 3. Starting with comparison of denarii with lead ore deposits, it becomes obvious that parts of the coins, mainly type V, VI, and VII, overlap with lead isotope data of galena from Upper Silesia (Olkusz) and Góry Świętokrzyskie. Rammelsberg deposit should be excluded as potential source for the studied denarii because only one denarius (type VI) from hoard 'Słuszków' has Pb isotope data similar to that of Rammelsberg galena. Detailed descriptions of these coins' provenance study are given elsewhere [16].

Finally, SEM observation allowed us for quality of surface assessment. Introductory observations were made with small magnification. It allowed us to surface homogeneity determination, characteristic areas presence and description of both sides of coins – obverse and reverse. Surface of the coins was corroded with clearly visible corrosion products. The local cracks and crevices were present at the surface. Using SEM method, the accurate localization and precisely choosing micro-area of interest on the sample were possible. Two important areas of the coins were investigated with details: homogeneous areas at the surfaces and areas inside of craters after LA-ICP-MS investigations. Magnification of 1000× was used, so the analyzed areas were about 0.01 mm^2. The small craters were visible at the coin (Fig. 4). Sizes of trace formed after laser ablation were in the range of about 100–200 μm in length and about 50 μm

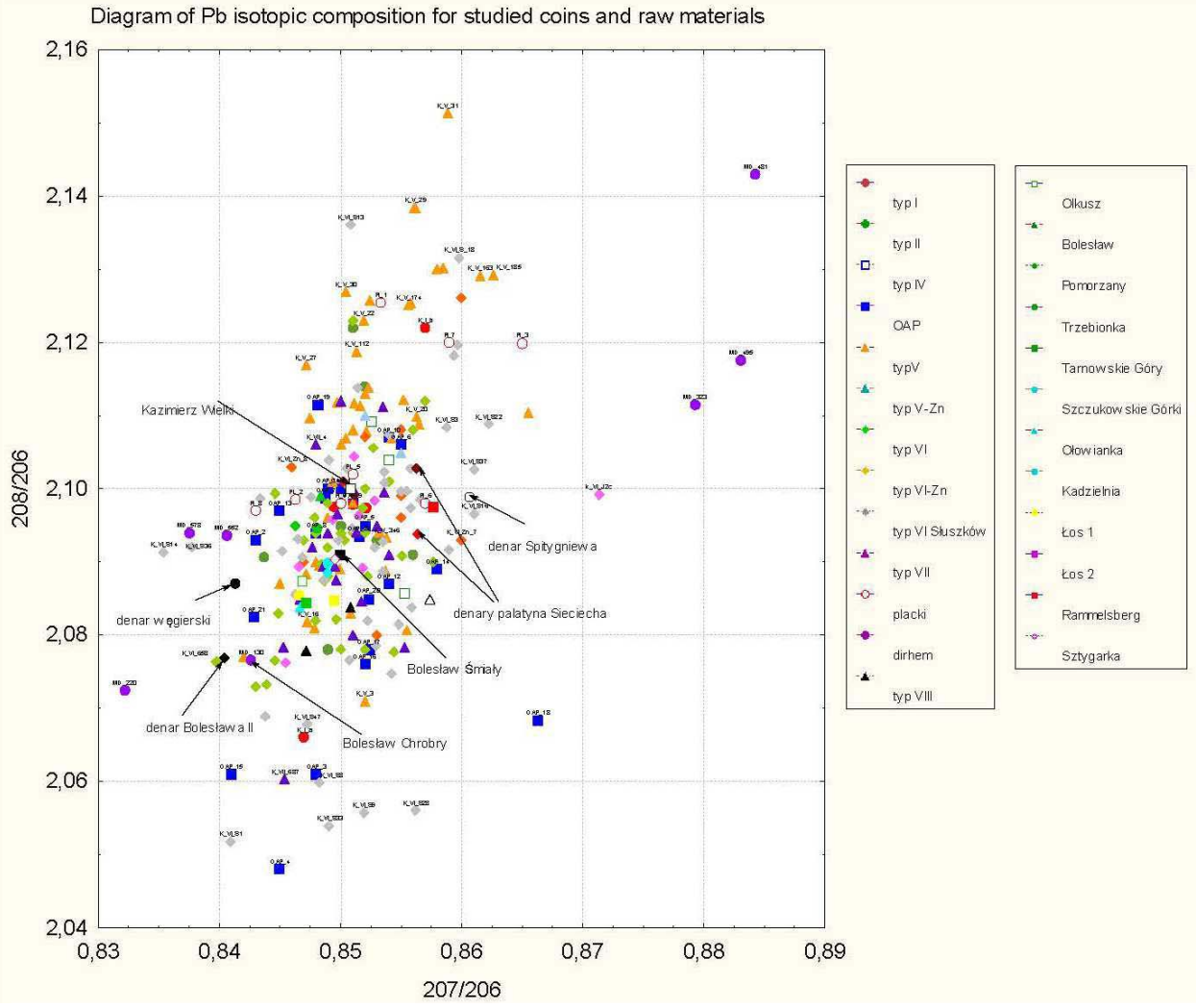

Fig. 3. $^{208}Pb/^{206}Pb$ vs. $^{207}Pb/^{206}Pb$ diagram for the Saxon denarii type I, II, IV, V, VI, VII, VIII, the Otto and Adelheid denarii, dirhams, as well as Pb ores from areas such as Olkusz, Góry Świętokrzyskie, and Rammelsberg (245 objects).

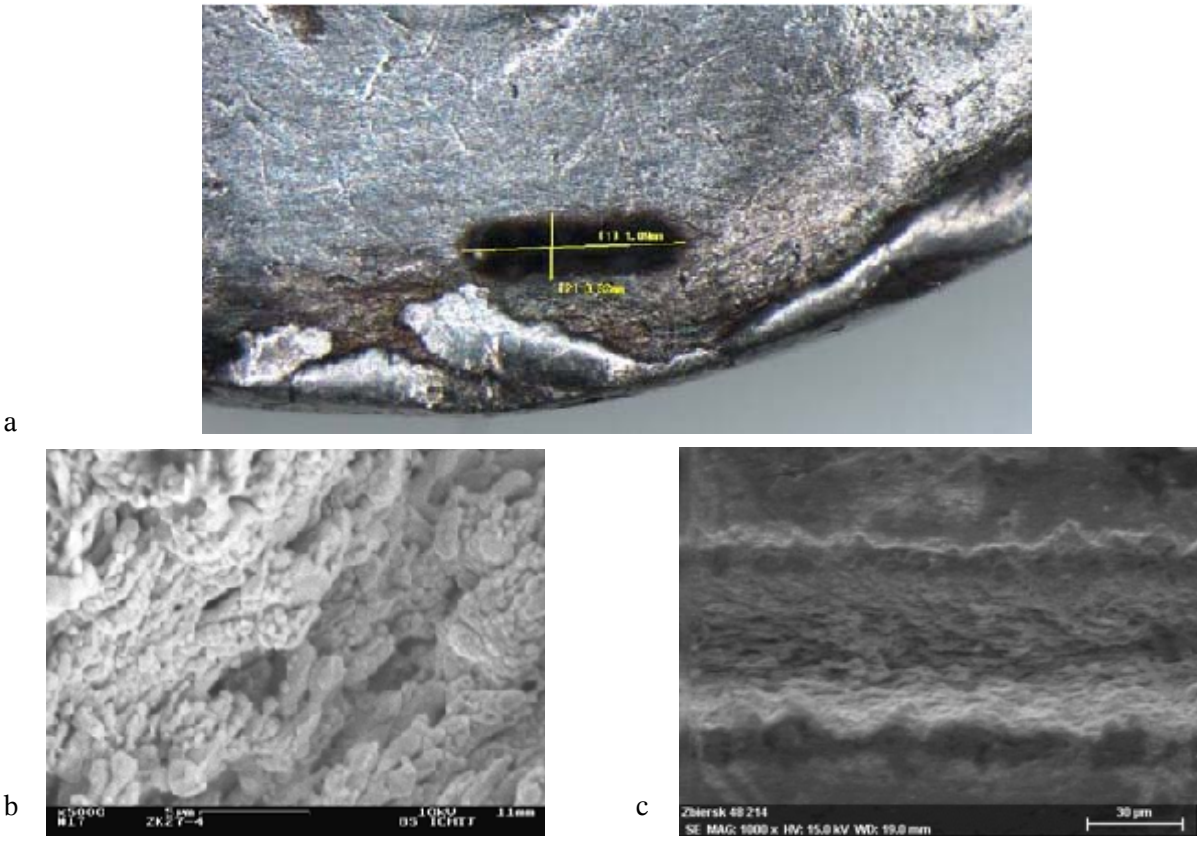

Fig. 4. Trace on the coin surface after laser ablation (method LA-ICP-MS): (a) visible crater and surrounding carbon deposit and example of investigated crater after laser ablation on coin surface. (b) Saxon coin type V Zbiersk 48 (magnification 1000×). (c) Saxon coin type V Zbiersk 27 (magnification 5000×).

in width (Fig. 4b). Visible grains are the results of high-energy laser beam interaction with the material of the coins' (Fig. 4c). Elemental analyses were carried out inside the small crater area. Figure 5 presents example of typical EDS spectra. Elements identified in collected spectra were Ag, Cu, and Zn, attributed for main elemental composition of coin, and Si, C, and O – attributed as effects of long-time corrosion of coins.

Results of LSP analysis consists of three spectra taken along: the line at the coin surface, the line inside the crater after LA-ICP-MS investigations, and the line across the crater. The set of mentioned spectra for the Saxon coin type V Zbiersk 55 is presented in Fig. 6. Material at the coin surface consisted of about 80 wt% of silver and small amounts

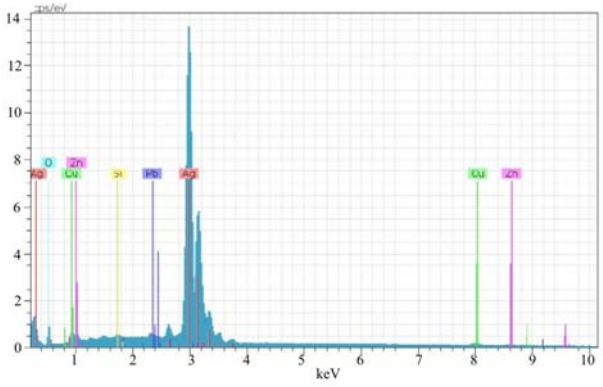

Fig. 5. EDS of coin surface (Saxon coin type VI Zbiersk 55).

of other elements – mainly Cu and Zn, Si, O, C (Fig. 6a). The elemental composition of material inside the crater is different: there were about 60 wt% silver and about 40 wt% copper (Fig. 6b). Authors assumed that these results correspond with the elemental composition of material used for coin manufacturing process. This was confirmed by elemental composition analysis along the line across the crater. There were about 80 wt% of silver at the coin surface, about 60 wt% inside the crater, and again about 80 wt% at the surface. In the same time, the amount of copper was small, then increased significantly, and then decreased again (Fig. 6c). Obtained results proved the changes in elemental composition. These were caused by leaching and diffusion of copper by corrosion process during the long-time stay in the uncontrolled environment.

Comparison of Cu or Ag determined by means of XRF and SEM-EDS analysis on coin surface and inside of the crater after laser ablation is presented in Fig. 7. The quantitative results obtained by XRF and SEM-EDS were compared. The concentrations of silver obtained by SEM-EDS at the crater after laser ablation in the noncorroded core of the coins were lower than those determined by XRF. This study confirmed that quantitative bulk analysis via nondestructive XRF may not be directly applied in the determination of the fineness of silver-copper coins. This fact ought to be taken into consideration especially when the thickness of corroded layer is equivalent to the depth of the fluorescence radiation of the Ag K_α line.

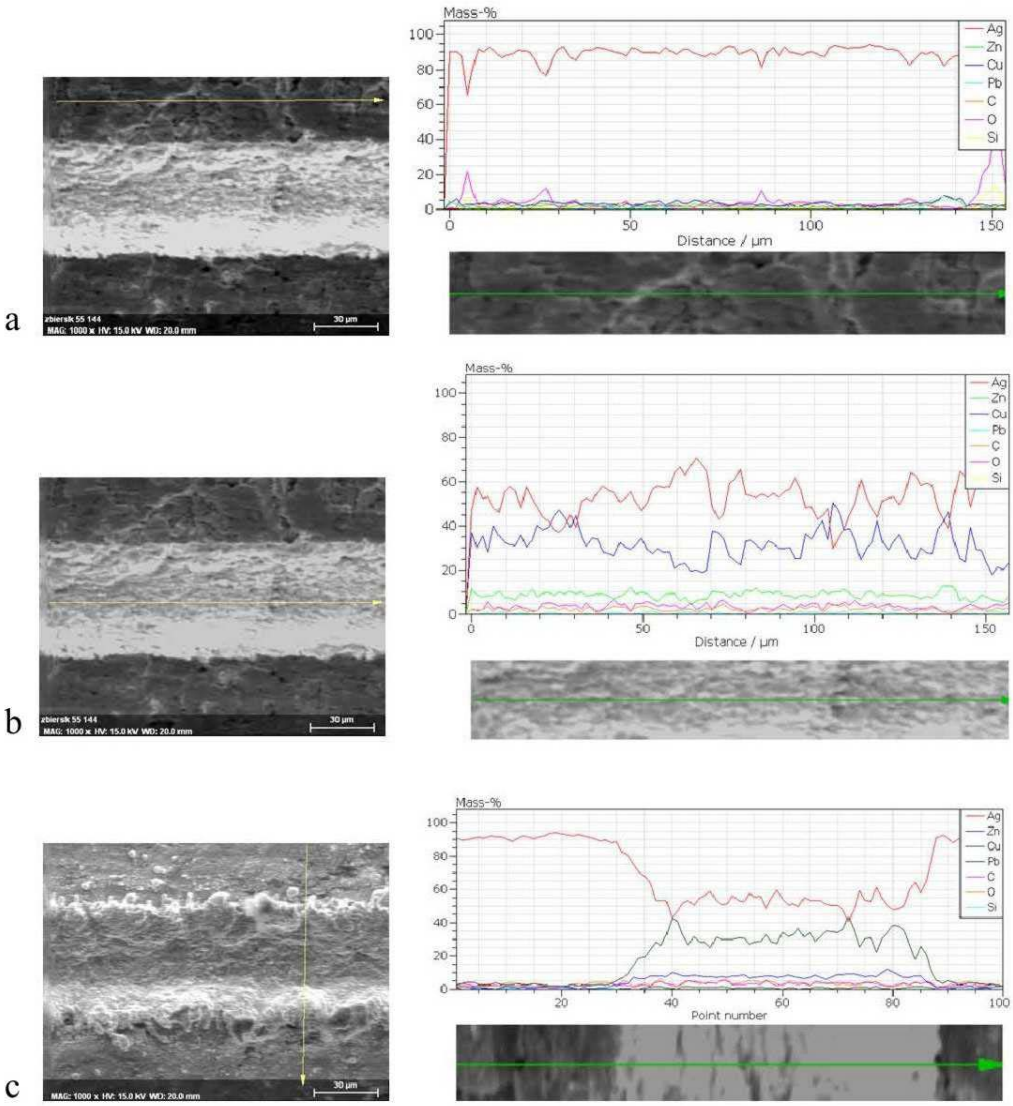

Fig. 6. Results of the scan along the line (LSP) are shown in photo, measuring the concentration of elements (Saxon coin type V Zbiersk 55) (a) on the coin surface, (b) along the crater bottom, and (c) across the crater.

It is important to mention that during coins investigations, the limitations that arise from a complex structure of the historical artifacts were taken into consideration.

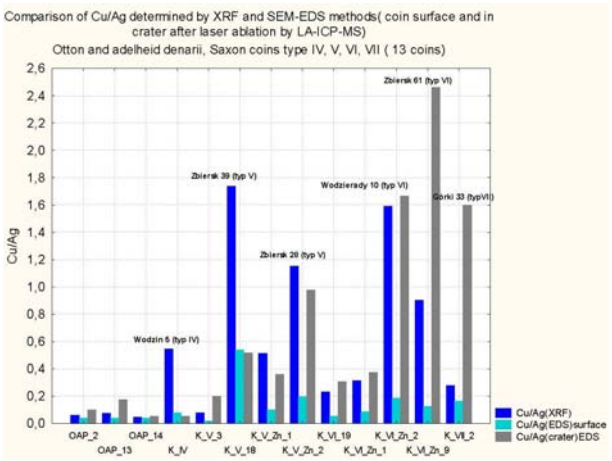

Fig. 7. Comparison of Cu or Ag determined by XRF and SEM-EDS methods (on the coin surface and in the bottom of the crater after laser ablation by LA-ICP-MS) in Otto and Adelheid denarii and Saxon coins type IV, V, VI, and VII (13 coins).

Conclusions

- Obtained results of the carried out investigations are significant for our knowledge of the history of Central European coinage, especially of Polish coinage.
- Unique documentation and database for different types of coins is the result of these studies.
- The work illustrates the usefulness of an integrated range of analytical techniques in approaching a problem of presented type of investigations.
- Interpretation of the results was allowed to differentiate the artifacts in relation to the various types of denarii, various recipes, as well as various raw materials.
- The obtained data show that it is not easy to completely and correctly identify or reproduce the materials used in the past and their deterioration processes.

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References

1. Kiersnowski, R. (1960). *Pieniądz kruszcowy w Polsce wczesnośredniowiecznej*. Warsaw: PAN Instytut Historii.
2. Suchodolski, S. (1971). *Początki mennictwa w Europie Środkowej, Wschodniej i Północnej*. Wrocław: Zakład Narodowy im. Ossolińskich Wydawnictwo PAN.
3. Jammer, V. (1952). *Die Anfänge der Münzprägung im Herzogtum Sachsen (10. und 11. Jahrhundert)*. Hamburg: Museum für Hamburgische Geschichte Abt. Münzkabinett.
4. Gumowski, M. (1939). *Corpus Nummorum Poloniae*. Kraków: Druk. „Powściągliwość i Praca".
5. Hatz, G., Hatz, V., Zwicker, U., Gale, N. H., & Stos-Gale, S. A. (1991). Otto-Adelheid-Pfennige. Suecia repertis. *Nova Series, The Rogal Swedish Academy of Letters, History and Antiquities*, 7, 1–146.
6. Kierzek, J., Kunicki-Goldfinger, J., & Małożewska-Bućko, B. (2000). Rentgenowska analiza fluorescencyjna w badaniu dzieł sztuki. Wybrane zagadnienia. *Ochrona Zabytków*, 2, 166–181.
7. Large, D., & Wachler, E. (1999). The Rammelsberg Massie sulphide Cu-Zn-Pb-Ba-Deposit, Germany: an example of sediment-hosted, massive sulphide mineralization. *Mineralium Deposita*, *34*, 522–538.
8. Zartman, R. E., Pawłowska, J., & Rubinowski, Z. (1979). Lead isotopic composition of ore depositis from the Silesia-Cracow mining district. *Prace Instytutu Geologicznego*, *XCV*, 133–151.
9. Wedephol, K. H., & Baumann, A. (1997). Isotope composition of Medieval lead glasses reflecting early silver production in Central Europe. *Mineralium Deposita*, *32*, 292–295.
10. Bielecki, K. H., & Tischendorf, G. (1991). Lead isotope and Pb-Pb model age determination of ores from Central Europe and their metallogenetic interpretation. *Contrib. Mineral Petrol.*, *106*, 440–461.
11. Ponting, M., Evans, J. A., & Pashley, V. (2003). Fingerprinting of Roman mints using laser ablation MC-ICP-MS lead isotope analysis. *Archaeometry*, *45*, 591–597. DOI: 10.1046/j.1475.2003.00130.x.
12. Goldstein, J. I., Newbury, D. E., Echlin, P., Joy Jr, D. C., Romig, A. D., Lyman, C. E., Fiori, C., & Lifshin, E. (1992). *Scanning electron microscopy and X-ray microanalysis. A text for biologists, material scientists and geologists*. New York: Plenum Press.
13. Lee, R. L. (2007). *Scanning electron microscopy and X-ray microanalysis*. PTR, Prentice Hall.
14. Hawkes, P. W., & Spence, J. C. H. (2007). *Science of microscopy*. Springer.
15. Health, J. P. (2005). *Dictionary of microscopy*. John Wiley & Sons, Ltd.
16. Waliś, L., Pańczyk, E., Sartowska, B., Kierzek, J., Dudek, J., Widawski, M., & Weker, W. (2016). *Ustalenie pochodzenia i chronologii wybranych grup monet srebrnych wytworzonych w mennicach polskich i Europy Środkowej na podstawie składu chemicznego, źródeł surowców i technologii wytworzenia*. (in preparation).
17. Stos-Gale, Z. A., & Gale, N. H. (2009). Metal provenancing using isotopes and the Oxford archeological lead isotope database (OXALID). *Archeol. Anthropol. Sci.*, 1, 195–213. DOI: 10.1007/s12520-009-0011-6.