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MULTI-TECHNICAL STUDY OF SILVER DENARS FROM MEDIEVAL POLAND FOR AN IMPROVED UNDERSTANDING OF THEIR ARCHAEOLOGICAL CONTEXT AND PROVENANCE*

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This paper discusses a methodology that involves the use of X-ray fluorescence (XRF), high-energy particle-induced X-ray emission (HE-PIXE) and high-energy particle-induced γ-ray emission (HE-PIGE) spectroscopies for the study of historic denars with the aim of describing the advantages and limitations of each technique as well as arriving at an archaeometric interpretation of the compositions. A total of 39 medieval Polish denars minted by kings Bolesław the Brave and Mieszko II Lambert were analysed for their elemental composition. While XRF is limited to the analysis of the material close to the object's surface, high-energy ion-beam analysis (HE-IBA) was used to obtain information from Cu at a relatively larger depth. The major elements detected were Ag and Cu, while the minor elements were Pb, Au, Bi and Zn. An evaluation of the results obtained with the different techniques shows that the content of Cu near the surface is different from the bulk composition of the coins. The obtained elemental composition was used to proliferate the understanding of chronological changes in the production of early medieval Polish denars.

KEYWORDS: SILVER DENARS, COINS, XRF, PIXE, PIGE, NUMISMATICS, MEDIEVAL POLAND

INTRODUCTION

The use of physico-chemical analyses applied to the study of historic coins has significantly increased over the last decades (Rosenberg 1985; Denker *et al*. 2004; Bachler *et al*. 2016). The materials that constitute these objects can reveal important technological and environmental features that enhance knowledge about their history, manufacturing, style and archaeological environment. For example, the chemical composition of the alloy may provide insights into the manufacturing procedure (Pitarch *et al*. 2011), the presence or absence of trace elements might point to possible sources of raw material or mints (Linke *et al*. 2004; Šmit and Šemrov 2006;

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Birch *et al*. 2019), while chronological and quantitative analyses of groups of coins from a particular period may serve to clarify economic evolution and development of production processes (Uzonyi *et al*. 2000).

Several analytical approaches have been employed over the years to provide qualitative or quantitative answers to archaeologists, historians and numismatic researchers. These have included destructive (Nir-El 1997) or non-destructive procedures (Linke *et al*. 2004; Pitarch *et al*. 2011), surface (Uzonyi *et al*. 2000; Šmit and Šemrov 2006) or all-encompassing (Gordus 1967; Rosenberg 1985) methods, or various combinations of them. Earlier studies on the physico-chemical properties of historic coins involved the use of neutrons to perform analyses of entire coins (Brown and Tindall 1979). Particle-induced X-ray emission (PIXE) continues to be one of the preferred methods for studying the chemical composition of historic metal alloys (Uzonyi *et al*. 2000; Denker *et al*. 2004; Šmit and Šemrov 2006), mainly due to its good accuracy, high sensitivity and low detection limits (Linke *et al*. 2003). X-ray fluorescence (XRF) spectrometry has become an essential tool in the cultural heritage field for studying the composition of metal alloys (Sándor *et al*. 2000; Milazzo 2004; Constantinescu *et al*. 2005), mainly due to its rapid, multi-elemental and non-destructive nature. Its relatively high availability and portability compared with the previously mentioned methods makes XRF a preferred technique among heritage scientists. The application of XRF spectrometry to numismatic collections has been controversial mainly because of compositional deviations originating from surface irregularities, non-homogeneity of the alloys and measurement geometry (Trojek *et al*. 2010). Elemental differences between the surface and the bulk material caused by the difference in the electro potential between Ag and Cu have been evidenced (Linke and Schreiner 2000; Sándor *et al*. 2000; Beck *et al*. 2004; Ager *et al*. 2013; Hrnjić *et al*. 2020). This effect will depend on the coins' production process, how the coin was treated or kept in the past, and how affected the material is by alterations, such as corrosion.

The approach employed in this work consisted of the combined use of several XRF methods and high-energy ion-beam analysis (HE-IBA) to study of a group of 39 denars minted by kings Bolesław the Brave and Mieszko II Lambert. A similar methodology was employed on coins of the same type by Lekki *et al*. (2017). These denars form part of a larger Central European collection of about 250 items. Since these are the first denars minted in Polish territory in the Middle Ages, their historical and political importance is unprecedented (Kiersnowski 1962; Suchodolski 1967). The two techniques proposed provided simultaneous and multi-elemental analysis, offered the detection of trace elements, did not require any form of pretreatment of the objects, and were therefore considered suitable for the analysis of these historic denars. The aim of the study was to develop an optimized methodology to study the surface properties of historic denars and discuss the advantages and limitations of these techniques when applied to the study of these objects.

Two different XRF spectrometers were used: micro-X-ray fluorescence (μ-XRF) and handheld X-ray fluorescence (HH-XRF). The data acquired by μ-XRF were evaluated by two different quantitative approaches. The data from the applied XRF methods were compared to evaluate which methods gave the most coherent results.

As mentioned above, the near-surface composition obtained by the X-ray spectroscopic techniques may not be representative for the bulk of the coin. The HE-IBA with a 68 MeV proton beam provides analytical data from greater depths of the coins compared with X-ray spectroscopy since the high energetic protons travel deeper into the material and the excited γ- and high energetic X-rays have the ability to escape from greater depth. At the HE-IBA

facility two analytical methods were used: particle-induced X-ray emission (PIXE) and particle-induced gamma-ray emission (PIGE). Whereas the μ-XRF was used in mapping mode to ensure a good average of the coins surface, the HE-IBA results were acquired as point analysis because of the long measurement times required for the accumulation of the spectral data for this technique.

Since the differences in the bulk and near-surface composition can originate from material alteration, that is, corrosion, the preservation state and corrosion products on the surface of the coins were studied by visual examination, Raman spectroscopy, HE-IBA and μ-XRF. The results of this study will be published elsewhere because this article focuses on the comparison of the analytical methods and the archaeometric interpretation of the results.

Denars of the Piasts

The present study was focused on 39 denars minted between 995 and 1020 from the collection of the Münzkabinett Staatliche Museen zu Berlin (Numismatic Cabinet of the National Museums Berlin). These denars were minted by two of the first Polish kings from the early Piast dynasty, namely Bolesław the Brave (Bolesław Chrobry) and Mieszko II Lambert. The rule of Bolesław the Brave and his son, Mieszko II Lambert, was characterized by the creation of a modern state through the unification of the Polish people, a political voice at the European level and the development of commerce. It is widely accepted that Bolesław the Brave (992–1025) created and established the first Polish monetary system. The PRINCES POLONIE denar, minted by Bolesław the Brave (e.g., object number 18246625) (Fig. 1, a), is probably the most important coin in Polish history. The inscription POLONIE is remarkable for being the first reference to Poland on a metallic object destined for circulation and exchange. Mieszko II Lambert struck his denars as co-governor next to his father. These denars were most likely struck in Greater Poland, since the majority of them have been recovered from this geographical area. The end of Mieszko's coinage is dated to *c*.1020, before his accession to the throne. Based on their iconography, they can be divided in two groups: Bolesław the Brave (27 items) and Mieszko II Lambert (12 items). These two groups can be further subdivided into 18 categories based on the iconographic classification system proposed by Suchodolski (1967). It was found that 13 of the 18 types existent were represented in the denars evaluated. Some denars are shown in Figure 1 (for images of all studied denars, see in the additional supporting information); object numbers, general descriptions and a classification of the denars is provided in Table 1.

METHODS

XRF spectrometry

The instrument used for μ-XRF analysis was a Röntec (now Bruker Nano, Germany) ARTAX PRO spectrometer. The measurements were non-invasive and did not contact the denars. The instrument was equipped with a molybdenum (Mo) target and polycapillary optics. The X-ray tube has about an 80 μm spatial resolution and uses a silicon drift detector (SDD) with an active area of 10 mm^2 and energy resolution of about 165 eV for the Mn Kα at 100 kcps. Each point was analysed at 45 kV and 500 μA for a live-time count of 30 s. The beam was focused on the analysis spot with the help of a laser and a camera. Acquisition and evaluation of the XRF spectra

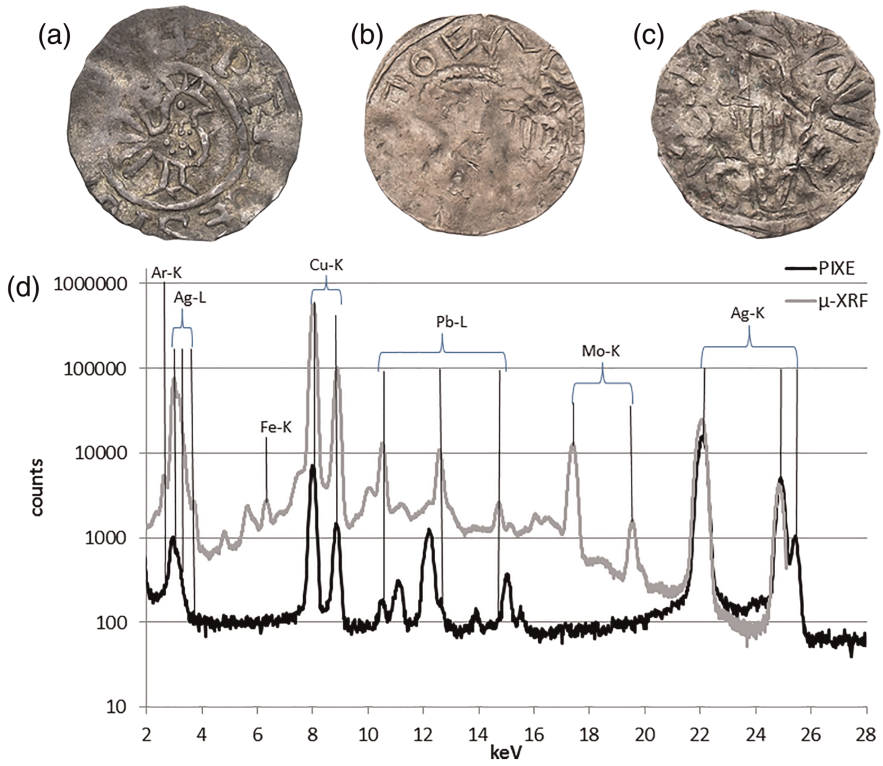

FIGURE 1 *(a) PRINCES POLONIE denar, minted (1000–10) by Bolesław the Brave; object number 18246625, 20 mm diameter; (b) denar minted (995–1005) by Bolesław the Brave; object number 18246643, 18 mm diameter; (c) denar with a hand on the obverse, minted (969–92) by Mieszko I; object number 18225385, 19 mm diameter; and (d) overlay of micro-X-ray fluorescence (μ-XRF) and high-energy particle-induced X-ray emission (HE-PIXE) spectra obtained for denar object number 18246643. [Colour figure can be viewed at wileyonlinelibrary.com]*

was carried out using a Spectra 5.3 (Bruker Nano, Germany). Based on the size of the denar, μ-XRF maps covered areas in the range of 270–500 mm^2; the step size used was 2 or 3 mm. The obverse and reverse of each denar were analysed, and the total estimated collection time for a single denar was approximately 4 h. Around 50–80 points were measured on each side of a denar, resulting in total spectra collection times of 1500–2400 s. Alongside elemental composition, the intensities of the Ag Kα and Lα peaks areas were extracted from the spectra to determine if any coin exhibited surface enrichment (Linke and Schreiner 2000).

The μ-XRF spectroscopic data were acquired and evaluated in the following two different ways:

- The calibration method proposed by Sándor *et al*. (2000) was employed to obtain the Ag, Cu and Pb concentrations. This method uses peak area ratios (PARs) to determine the concentration ratio of the elements. For Ag and Cu, the net peak areas of Kα-lines were employed, while for determination of Pb, the Lα-line was used. This methodology was used in a previous work discussing the analysis of denars from this period (del Hoyo-Meléndez *et al*. 2015). The reported percentages for major elements were based on the average obtained for all measurements carried out on both sides of the coins. The average relative uncertainty for the concentration of Ag is 2.0%, while those obtained for Cu and Pb were

Table 1 *Combined results of ion-beam analysis (IBA) and micro-X-ray fluorescence (μ-XRF) analysis by class and denar type*

No.	*Ruler*[*]	*Coin type*[†]	*Weight (g)*	*Diameter (mm)*	*Minting date*	*Ag K (PIXE)*	*Cu (PIGE/ PIXE)*	*Pb L (μ-XRF)*	*Bi L (μ-XRF)*	*Zn K (μ-XRF)*	*Au L (μ-XRF)*	*Hg L (μ-XRF)*
18225143	B	I.1	1.08	21	?	89.6	7.0	1.10	0.15	0.16	0.27	< LOD
18246635	B	III/IV.8	1.17	20	995–1005	88.1	10.8	0.69	0.26	0.45	0.35	< LOD
18246636	B	III/IV.8	0.85	20	995–1005	80.1	19.3	0.76	0.22	< LOQ	0.38	< LOD
18246637	B	III/IV.8	0.75	18	995–1005	95.4	4.5	0.15	0.16	< LOQ	0.38	< LOD
18246638	B	III/IV.8	0.82	18	995–1005	77.4	21.8	0.59	0.21	< LOQ	0.39	< LOD
18224253	B	III.3	1.02	19	?	84.8	14.4	0.92	0.16	0.11	0.35	< LOD
18246643	B	IV.4	1.09	18	995–1005	65.9	33.0	1.50	< LOQ	< LOQ	0.00	< LOD
18231523	B	V/VI.10	1.74	19	995–1005	95.0	4.6	0.18	0.12	< LOQ	0.34	< LOD
18246621	B	VIII.13	1.44	19	995–1005	85.5	13.7	0.16	< LOQ	< LOQ	0.17	< LOD
18246622	B	VIII.13	1.50	19	995–1005	80.9	18.0	0.48	0.18	0.27	0.22	Trace
18246623	B	VIII.13	1.04	19	995–1005	84.6	14.2	0.40	0.2	0.25	0.30	< LOD
18246625	B	IX.14	1.15	20	1000–1010	93.0	6.2	0.84	< LOQ	0.15	< LOQ	< LOD
18246626	B	IX.14	1.66	20	1000–1010	96.7	0.9	1.60	< LOQ	< LOQ	< LOQ	Strong
18246627	B	IX.14	1.71	20	1000–1010	97.4	1.9	0.86	< LOQ	< LOQ	< LOQ	< LOD
18246624	B	IX.15	1.44	20	After 1010 (?)	95.9	3.5	0.51	< LOQ	< LOQ	< LOQ	< LOD
18246628	B	IX.15	1.92	19	After 1010 (?)	96.5	3.2	0.52	< LOQ	< LOQ	< LOQ	< LOD
18246629	B	IX.15	1.90	20	After 1010 (?)	94.4	4.4	0.60	< LOQ	0.17	< LOQ	Strong
18246630	B	IX.15	0.71	19	After 1010 (?)	94.5	4.0	1.50	< LOQ	< LOQ	< LOQ	< LOD
18246619	B	XI.17	1.20	20	1000–1010	86.1	12.8	0.76	< LOQ	< LOQ	< LOQ	< LOD
18246620	B	XI.19	1.18	19	1000–1010	82.4	16.0	0.74	0.16	0.15	0.30	< LOD
18246631	B	XII.20	0.74	21	1005–1015	87.1	12.6	0.32	0.19	< LOQ	0.40	< LOD
18246632	B	XII.20	1.69	20	1005–1015	98.8	0.1	0.84	< LOQ	< LOQ	< LOQ	< LOD
18246633	B	XII.20	0.99	21	1005–1015	97.0	1.7	1.20	< LOQ	< LOQ	< LOQ	< LOD
18246634	B	XII.20	1.10	21	1005–1015	93.1	6.1	0.72	< LOQ	0.11	< LOQ	< LOD
18246639	B	XIII.21	1.06	18	?	93.0	6.2	0.60	< LOQ	< LOQ	0.60	< LOD
18246640	B	XIII.23	0.79	17	?	96.6	2.4	0.41	0.24	< LOQ	1.77	Trace
18246641	B	?	1.11	20	?	85.9	12.3	1.40	< LOQ	< LOQ	< LOQ	< LOD
18246613	M	I.1	1.36	22	1010–1020	95.4	4.2	0.33	< LOQ	< LOQ	< LOQ	< LOD
18246614	M	I.1	2.07	23	1010–1020	96.2	3.4	0.38	< LOQ	0.14	< LOQ	< LOD
18246615	M	I.1	1.99	20	1010–1020	96.2	3.4	0.36	< LOQ	0.11	< LOQ	< LOD

(*Continues*)

Table 1 *(Continued)*

No.	*Ruler*[*]	*Coin type*[†]	*Weight (g)*	*Diameter (mm)*	*Minting date*	*Ag K (PIXE)*	*Cu (PIGE/ PIXE)*	*Pb L (μ-XRF)*	*Bi L (μ-XRF)*	*Zn K (μ-XRF)*	*Au L (μ-XRF)*	*Hg L (μ-XRF)*
18246616	M	I.1	1.58	20	1010–1020	95.3	4.3	0.38	< LOQ	< LOQ	< LOQ	< LOD
18246617	M	I.1	1.63	20	1010–1020	95.0	4.9	0.26	< LOQ	< LOQ	< LOQ	< LOD
18246618	M	I.1	1.56	21	1010–1020	95.5	3.0	0.60	< LOQ	< LOQ	< LOQ	< LOD
18237843	M	II.2	1.47	20	1010–1020	94.6	4.7	0.46	< LOQ	< LOQ	< LOQ	< LOD
18246611	M	II.2	1.71	20	1010–1020	96.5	2.8	0.59	< LOQ	< LOQ	< LOQ	< LOD
18246612	M	II.2	1.11	17	1010–1020	95.3	4.2	0.33	< LOQ	< LOQ	< LOQ	< LOD
18246610	M	II.3	1.54	21	1010–1020	93.8	5.6	0.66	< LOQ	0.1	< LOQ	Trace
18246642	M	III.4	1.42	19	?	75.6	19.9	1.00	< LOQ	3.43	< LOQ	< LOD
18225385	M	III.4	1.37	19	?	81.4	18.1	0.26	0.19	< LOQ	0.28	< LOD

Notes:

[*]Ruler: B, Bolesław; M, Mieszko II.

[†]Classification after Suchodolski (1967).

LOD, limit of detection; LOQ, limit of quantitation.

11.1% and 13.9%, respectively. This estimation was based on the method proposed by Rousseau (2001) and was previous described by del Hoyo-Meléndez *et al*. (2015).

- Additionally, a fundamental parameter (FP) method conducted with Bruker M-Quant software was used. As for the PAR method, the accumulated spectra obtained from the scans of the obverse and reverse of a coin were used. From the scan data some individual spectra were omitted in order to improve the data. The omitted spectra had atypical large amounts of Ca, Cu, Cl and Si originating from the corrosion and/or environmental depositions on the surface of coins, and therefore were not being representative for the coins' alloy. For quantification, Ag, Cu, Fe and Zn K-lines were used, and for Au, Hg, Pb and Bi L-lines were used. The relative uncertainty of Ag was 3% and for Cu and traces 15%. For analytical values for Ag and Au alloys of known composition, see Table S2 in the additional supporting information. The limit for quantification (LOQ) was estimated to be 0.1% for the trace elements.

An S1 Titan HH-XRF spectrometer (Bruker, Germany), equipped with a Rh tube and an X-Flash® SDD detector, was also employed to carry out quantitative analysis of the denars. The S1 Titan has an analysis spot of 5 mm and operates at 50 kV and 15 μA, while the acquisition time employed was 30 s. The percentages are averages from four measurements, two on each side. This instrument has several internal calibrations for metal alloys that are based on the FP method. The X-ray-lines used for quantification were the same as for the FP of the μ-XRF. S1RemoteCtrl and the S1Sync software were employed for instrument control, while Artax software (Spectra 5.3) was also used for qualitative analysis of the spectra. The average relative uncertainty, as given by the manufacturer, for the concentration of Ag was 0.3%, while those obtained for Cu and Pb were 1.0% and 4.0%, respectively.

HE-IBA spectroscopy

HE-PIXE/PIGE measurements were performed on the experimental area (Denker *et al*. 2005a, 2005b) of the HZB cyclotron. The measurements were non-invasive and there was no direct contact with the denars. Protons with an energy of 68 MeV were extracted from the vacuum of the beam-line via an 80 μm-thin Kapton foil. The diameter of the beam was verified with a luminescent quartz and was < 2 mm. Proton intensity was measured using an ionization chamber from PTW (Freiburg Physikalisch-Technische Werkstätten Dr. Pychlau GmbH, Germany). The X- and γ-rays were detected with a high-purity Ge detector (HPGe) from Eurysis with an active area of 30 mm^2 with a resolution of 180 eV at 5.9 keV. The measurement time was 200 s. Due to the low cross-section of nuclear reactions compared with the production of X-rays, the measurements were repeated and the spectra were added. Quantitative analysis was performed off-line with the code GUPIXWIN (Campbell *et al*. 2010) using the X-ray-lines of Fe K, Ni K, Cu K, Zn K, Ag K, Au K and Pb L. The accuracy of the experimental parameters was verified by Ag alloy of known composition (see Table S3 in the additional supporting information). The average relative fit errors as given by GUPIXWIN based on the counting statistics were 0.2% for Ag K, 2.7% for Cu K, and 14.0% for Pb L and Au L. The Cu concentration given by the PIGE was determined via the 67.4 keV γ-line, which can be received from a greater depth compared with Cu K X-rays. A higher content of Cu at the large depth indicates surface enrichment resulting in the depletion of Cu from the surface. Due to the self-absorption of the Cu X-ray-lines in the Ag matrix, the analytical depth for the X-rays is in the order of 10 μm, whereas the 67.4 keV γ-line provides an analytical depth of about 400 μm. The thickness of the coins varied between 200 and 600 μm. Thus, at least half the thickness fits into the analytical depth. For quantification, the area of this γ-line was compared with the area measured on Ag samples from Degussa with a certified

Cu content. As the count rate for this γ signal is relatively low, a limit of about 10% by weight and a relative error of 30% rel. was estimated for the quantification of Cu by HE-PIGE (see Fig. S3 in the additional supporting information).

A comparison of spectra obtained from μ-XRF and PIXE for one denar (18246643) is shown in Figure 1. The μ-XRF spectrum shows the signals of the elements Ag, Cu, Pb and some Fe. Besides the characteristic signals from elements in the sample, also Raleigh scatter signals of the X-ray anode material (Mo) and the typical bremsstrahlung continuum are present. The spectral underground shows some unusual structure. This structure can be observed when metals are analysed with the ARTAX PRO. The structured underground is due to diffraction signals for energies (wavelength) which fulfil the Bragg conditions for the geometry defined by the beam paths of the spectrometer and the atom spacing in the sample (Bronk *et al*. 2001). The PIXE spectrum has a much lower spectral noise level compared with the XRF spectrum. The background does not exceed 100 counts, resulting in an advantageous signal-to-noise ratio. The high-energetic protons generate a higher X-ray yield for the higher energetic lines, but relatively weak excitation of lower energetic lines, for example, the Ag K-line is much better excited compared with the Ag L-line. The lines of Pb L were comparatively weak in the PIXE spectrum and superimposed partially with other signals that were not present in the μ-XRF spectrum. These signals were escape lines at 11.0, 12.2, 15.0 and 13.8 keV generated by the Ag Kα and Kβ signals reduced by the Ge Kα and Kβ energies. Unfortunately, these lines were superimposing partially with characteristic X-ray-lines of elements that were present in the coin such as Pb, Bi and Au.

RESULTS AND DISCUSSION

X-ray spectroscopic analysis

The spectra of the evaluated denars showed the dominance of Ag and Cu, while minor and trace elements may consist of different combinations of Pb, Fe, Zn, Au, Hg and Bi. The results of the μ-XRF (FP) quantification are given in Table S4 in the additional supporting information. The main element contents obtained by different XRF are compared in the additional supporting information.

The μ-XRF spectrometry maps provide an overview about the homogeneity of the coin material. Figure S2 in the additional supporting information presents examples of maps obtained for denar 18246610. The net peak intensity distributions of lines of Ag-L and Cu-K confirm a certain degree of heterogeneity of the denar. The distribution for the Au Lα, Pb Lα and Bi Lα-lines indicate a higher degree of heterogeneity.

To evaluate the homogeneity in depth, the peak intensity ratios of Ag Kα/Ag Lα obtained from denarii were compared with the intensity ratios obtained from the Ag-Cu standard of a similar composition (see Table S4 in the additional supporting information). From the 39 denarii analysed, only four coins (three Bolesław and one Mieszko) showed a negative ratio, which suggests a disparity between the concentrations of Ag and Cu in the bulk and on the surface of a coin, that is, a surface enrichment.

Comparison of the μ-XRF and HE-IBA results

The values of the HE-PIXE/PIGE analyses are shown in Table S5 in the additional supporting information. While the HH-XRF and μ-XRF (FP) gave similar results for Ag and Cu, the HE-PIXE showed a systematic difference. Based on the analyses of the reference materials,

the HE-PIXE results were of higher accuracy and had a smaller relative error for Cu in high Ag alloy compared with the XRF.

For a large number of coins, the HE-PIGE resulted in Cu values different from the μ-XRF (FP) (see Fig. S5, d, in the additional supporting information) or HE-PIXE data (see Table S5 online). As expected, the HE-PIGE gives higher Cu values than the X-ray near-surface methods. For coins, where the HE-PIGE results indicated Cu contents of $> 10\%$ (limit of quantification—LOQ) the HE-PIGE values were used instead of the PIXE results.

Only one of the four denarii where surface enrichment was detected by ratios of Ag Kα/Ag Lα had a larger content of Cu in the bulk (18246642 more than twice larger). The general observation of the enriched Ag contents at the objects surface is coherent with the observation of other studies (Linke and Schreiner 2000; Sándor *et al*. 2000; Beck *et al*. 2004; Ager *et al*. 2013). Since the counting rate of the γ signal is small, the HE-PIGE can only detect the enriched layers, with a high relative error and a Cu content above the LOD of 10%. However, for seven coins, the HE-PIGE detected a Cu content in the bulk $> 1.5\times$ higher compared with the surface (18246636, 18224253, 18246621, 18246622, 18246619, 18246620, 18246641 and 18246642). Thus, the Ag enrichment observed by the Ag Kα/Ag Lα ratio and PIGE is only partially in accordance. The Ag Kα/Ag Lα ratio method might not be applicable to very thick Cu-depleted layers and the presence of corrosion products interfering with the fluorescence line intensities of Ag, preventing μ-XRF from detecting the surface enrichment.

For the unevenly distributed trace elements, the high number of μ-XRF measurements is advantageous to compensate for the heterogeneity of the denars, and the results can be considered the best representation for the denars' near-surface material characterization. For Pb, the results of the μ-XRF (FP) were about 15% higher than for the HE-PIXE. The analysis of the reference materials did not indicate such a difference, and this effect might therefore be related to the Pb distribution on the coin (e.g., see Fig. S2, d, in the additional supporting information). Additionally, the μ-XRF (FP) values have a lower relative analytical error for Pb and are therefore preferred over the HE-PIXE data.

Comparison of the Au HE-PIXE and μ-XRF results gave a very weak correlation (see Fig. S5, c, in the additional supporting information). The μ-XRF evaluated the Au-L-lines, whereas the HE-PIXE uses the Au-K-line at 68.8 keV (for the $K_{\alpha 1}$-line). The quantitative results obtained using these methods showed that the μ-XRF results are on average slightly higher. This could suggest a lower Au concentration in deeper layers compared with the near surface, in agreement with previous publications where the Au concentration was larger in the enriched area, that is, surface (Borges *et al*. 2017; Hrnjić *et al*. 2020). This effect might have partly contributed to the spatial inhomogeneous distribution of the Au. The HE-PIXE technique only analysed one spot on the surface compared with the μ-XRF that analysed a larger area of the surface. The μ-XRF results also have the smaller relative analytical error and were deemed more representative for the coins' surface.

The values used for the archaeometric interpretation of the denars are the HE-PIXE results for Ag-L and Cu-K with Cu from the HE-PIGE if a high Cu content was detected. These values were combined with the μ-XRF (FP) for trace elements (Table 1).

Composition of the denars

Denars minted during the reign of Bolesław have a high content of Ag, averaging to $92.25\% \pm 4.1\%$ (excluding outlier 18246643). They can be divided into two main groups: denars minted between 995 and 1005 and those believed to be produced later. Older denars are less fine than

younger ones, consisting on average of 89.53% ± 5.3% Ag, while younger coins contain 94.40% ± 2.2% Ag. The quantity of Cu is reciprocal to the content of Ag in both cases, which for older denars amounts to 9.10% ± 5.1% and 3.91% ± 2.5% for younger denars (Fig. 2, a, b). Mieszko II denars have a more uniform composition than denars associated with Bolesław—with the exception of two denars (Table 1 and Fig. 2, a). These two denars, 18225385 (Fig. 1, c) and 18246642, are the only ones of the Mieszko II type III.4 (unknown minting date). The Mieszko II type I and II denars (probably minted *c*.1010–20) contain on average 95.6% ± 0.5% and 95.1% ± 1.0% Ag and 3.9 ± 0.7% and 4.3 ± 1.0% Cu, respectively. The increase in fineness and the more uniform content of Ag in younger Piast mints suggests a more regulated minting practice. The transition to controlled production is already evident in younger Bolesław denar types IX, XI and XII, and continues during the reign of Mieszko II.

Pb is almost always present in historical Ag coins because argentiferous lead ores were the most common source of Ag, and due to the Ag separation process of cupellation (Pernicka and Bachmann 1983; Meyers 2003). The amount of Pb varies independently of other elements, but there is a tendency for Bolesław denars to have larger content of Pb than Mieszko denars. The quantity of Pb is $< 1.6\%$, and in 32 of the denars is $< 1.0\%$. Figure 2 (c) shows the dispersion in Cu with respect to the Pb of the older Bolesław denars dating to 995–1005 (coin types III/IV, IV, V/VI, VIII and III/IV). Denars minted later than 1000 by Bolesław, types IX, XI, XII, have a

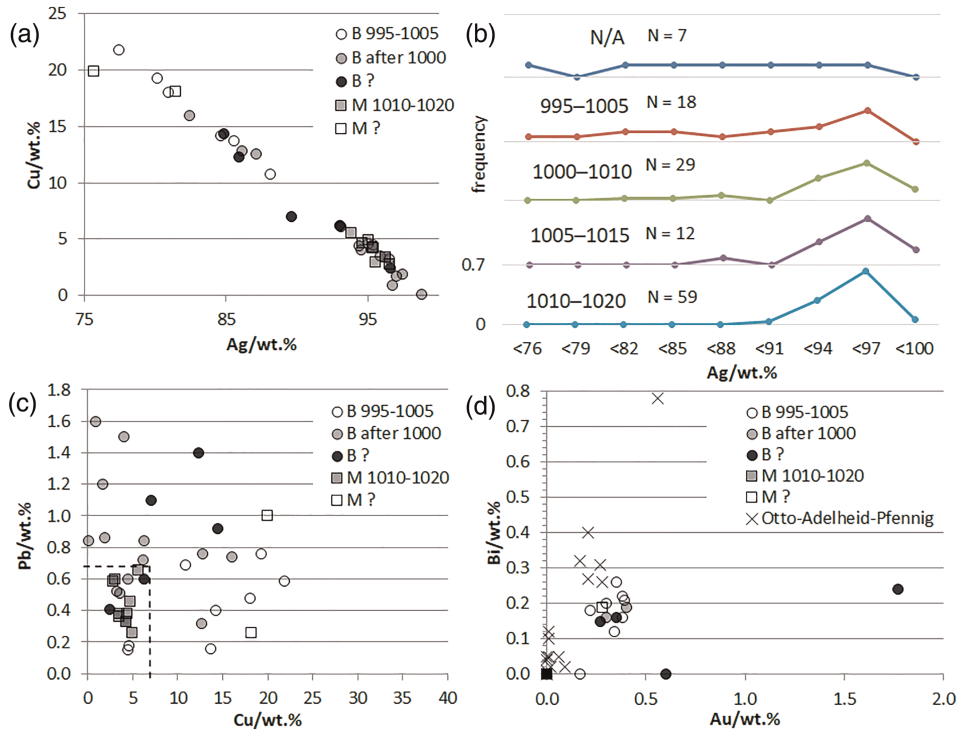

FIGURE 2 *(a) Cu and Ag results, data points labelled by ruler (B, Bolesław; M, Mieszko II) and supposed minting date; (b) frequency of Ag results by minting date, data from both this study and del Hoyo-Meléndez et al. (2015), Młodecka and Chabrzyk (2010a, 2010b); (c) Pb and Cu results (this study) data points labelled by ruler (B, Bolesł aw; M, Mieszko II) and supposed minting date; and (d) Au and Bi results (this study) and Otto-Adelheid pfennigs analysed by Matzke (2003) and Merkel (2016). [Colour figure can be viewed at wileyonlinelibrary.com]*

tendency to higher Pb contents. Only three of the 13 later (after 1000) Bolesław denars remain within the area indicated by discontinuous lines which contains all Mieszko II denars of types I and II, dated to 1010–20. Most of the Bolesław denars with an uncertain minting date (three denars out of four group B? in Fig. 2, c) fall outside this area.

This pattern was observed in the previous XRF analysis of other denars from these two kings and was associated with a change in technology during the minting of denars with a later chronology (del Hoyo-Meléndez *et al*. 2015). Particularly variations in Au and Bi content were observed. Au was usually detected together with Bi, with only a few denars as exceptions. High Au and Bi values are more often found in the older denars that show a high dispersion in Cu and Pb (del Hoyo-Meléndez *et al*. 2015). This observation can be confirmed specifically for the Bolesław denars from 995 to 1005. Most denars (six of nine) have a significant Bi and Au content (Fig. 2, d).

Another representation of the data shows the difference between them more clearly. Figure 3 shows the plot of Pb/Ag and Cu/Ag ratios of the coins from Polish collections using data from del Hoyo-Meléndez *et al*. (2015), Młodecka and Chabrzyk (2010a, 2010b) and the current study. With the exception of two coins from the Münzkabinett which are of type III.4, the plot of Pb/Ag and Cu/Ag ratios shows a smaller dispersion for coins minted by Mieszko II (particularly types I and II) relative to those of Bolesław (Fig. 3). Arguably one can state that Bolesław coins exhibit a slightly lower quality of Ag after evaluating their Pb/Ag and Cu/Ag ratios. The dominance of Pb in some Bolesław coins is clearly highlighted, indicating ineffective refining during Ag purification processes (Kantarelou *et al*. 2011).

Hg was detected in five denars. In two (18246629 and 18246626), it was found in higher quantities by μ-XRF. The presence of Hg in medieval Ag denars can be related to the amalgam silvering and mercury blanching applied on the surface of an object (Anheuser 1996). However, as Hg is a very volatile element, most of it is removed from the silver after the process of cupellation (Merkel 2016). An experiment on amalgam silvering performed by Anheuser (1996) suggests that this process leaves 10–40% of Hg on the object's surface, while another study indicated that the content may be lower (Uhlir *et al*. 2016). The small quantities of Hg could also be interpreted as contamination or as an indicator of surface treatment that occurred after making the denar. Therefore, Hg was not considered for the archaeometric interpretation (Table 1) (for initial μ-XRF values, see Table S4 in the additional supporting information). Zn was mainly detected

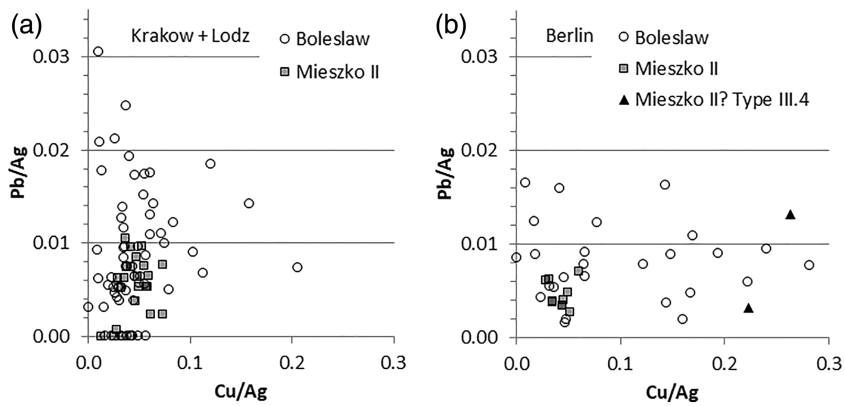

FIGURE 3 *(a) Plots of Pb/Ag and Cu/Ag ratios calculated for early Piasts denars in Polish collections (data from del Hoyo-Meléndez et al*. 2015; Młodecka and Chabrzyk 2010a, 2010b); and (b) and data from the Münzkabinett Berlin.

in Bolesław denars minted between 995 and 1005, which perhaps indicates that at least some of older coins were alloyed with brass.

DISCUSSION OF THE COMPOSITION OF THE DENARS IN THE CONTEXT OF OTHER EARLY MEDIEVAL SILVER COINS

Historical silver contains impurities present as minor and trace elements such as Pb, Au or Bi, which can be indicators of ore types or the ore deposit from which it was extracted or technological processes used during extraction. Determining the provenance of metals by their trace element pattern can be challenging since metallurgical processing, alloying, reuse and mixing of metals from various deposits influence the trace element content (Pernicka 2014). Among trace elements relevant for discerning different silvers, only Au is not affected by technological processes and it maintains the same ratio with Ag as in ores (Pernicka and Bachmann 1983). Bi, for example, is affected by the purification and separation process of cupellation (L'Héritier *et al*. 2015). The ratios of Pb isotopes are less affected by technological processes (excluding the mixing of different silvers), but Pb isotope analysis was not possible within the frame of this study.

The compositional comparison of early medieval denars carried out by Młodecka and Chabrzyk (2010a, 2010b) suggested that Islamic dirhams are likely the source of Ag used by the early Piasts. The proposed the similarity relied on comparing the trace elements and Ag content of Piast denars, and 11 dirhams minted in different Islamic centres dated to between 796/7–802 and 976. While Ag coins from Central Asia and the Middle East were a dominant source of silver during the ninth and 10th centuries, a collapse of the trading network that connected Central Asia with Europe caused a gradual downscaling of Ag import in Northern and Eastern Europe starting from the 980s—commonly referred to as the silver famine (Noonan 1992). While such change is especially noticeable in Northern Europe (Kilger 2008), hoard and coin finds from Poland suggest that an alternative route was established connecting Central Asia and the Baltic zone through the West Slavic territories. Most dirhams found in Poland are dated to the 10th century (Kiersnowski 1960), and their introduction is connected with redirecting trade routes between the caliphate and the Northern and Eastern Europe through the Black Sea via Dnieper, reaching Krakow on its way to the Baltic area (Kiersnowski 1960). Despite the large number of Islamic coins, Central European silver started to come into circulation around this time, due to larger silver mining operations undertaken in the Harz Mountains under Ottonian rulership. Moreover, at the end of 10th century, the flow of dirhams was coming to a halt and Polish markets were flooded with Saxon coins: the Otto-Adelheid denars and unnamed cross denars (Bogucki 2014).

In the study by del Hoyo-Meléndez *et al*. (2015), two groups of Piast denars were discerned on the basis of their trace element composition, which suggests that there are at least two types of silver used for making the coins. For the younger denar types (most minted after 1010), the authors also suggested that due to the geographical vicinity, as well as political and diplomatic ties between the early Polish state and the Ottonian realm, the earlier Piast coins were manufactured from silver from the Harz Mountains, while the composition of the later Bolesław denars might be matching with Islamic silver, as suggested by Młodecka and Chabrzyk.

In the 10th century, the most productive minting centres in the Islamic world were Samarqand and al-Shāsh, which is also confirmed by the vast number of dirhams found in hoards in Eastern and Northern Europe (Kovalev 2003). If dirhams were remelted for making Piast denars, the most likely candidates would be coins from Samarqand and al-Shāsh. A large archaeometric study of the surface composition of dirhams by energy-dispersive X-ray fluorescence (EDXRF)

was carried out by Ilisch and Schwarz (2003) in which about 2800 dirhams from different regions of the Islamic world were analysed. From that number, 244 dirhams were minted in Samarqand and 166 in al-Shāsh. A smaller but significant study of the composition and Pb isotopes of 37 Samanid coins was performed by Merkel (2016). The results of the studies show that one characteristic of 10th-century Transoxanian Ag is its unique high content of Bi. The content of Bi varies greatly between the coins. In coins from Samarqand analysed by Ilisch and Schwarz (2003), the average content of Bi was around 0.7%. In al-Shāsh coins, the Bi average was 0.9%, with a high standard deviation. The amount of Au in both mints studied by Ilisch and Schwarz was around 0.2%. From the Merkel analyses on Samanid coins, it can be observed that both Samarqand and al-Shāsh coins have a similar average composition of Bi at around 0.6% and Au of 0.08%. The Bi and Au contents of the oldest Bolesław denars have Bi and Au averages of 0.18% and 0.34%, respectively. The values of both Bi and Au are quite different from the contemporary Samanid coins. While the amount of Au does not change during the process of cupellation or melting, it is still possible to argue that Bi could be partially reduced during cupellation (Pernicka and Bachmann 1983; L'Héritier *et al*. 2015). A relevant contemporary group is coins minted in the Viking settlement of Hedeby. Pb isotope analysis confirmed that they were made from Samanid silver (Merkel 2016). These coins belong to the groups KG9–11 and are dated to between 965 and 980 by Malmer (1966). While the Bi content is on average lower than in Samanid coins, in a few cases the value of Bi is $> 5.0\%$. Even when the Samanid coins were remelted for the production of new coins, they kept a significant amount of Bi.

The higher amount of Au, the small standard deviation of Bi in Bolesław denars and the lower Bi amount than in either coins from al-Shāsh or Samarqand suggest that the dirhams were not used for production of the oldest Bolesław denars. Del Hoyo-Meléndez *et al*. (2015) suggested that Islamic dirhams were the potential raw material for the Piast denars due to the detection of Hg on some of the Piast denars. Hg is a very volatile element and would completely evaporate during the remelting process (Merkel 2016). Dirhams minted in Samarqand, al-Shāsh, Andaraba and Bukhara show high Hg contents, which most likely indicate the practice of Hg blanching. However, Hg stops appearing in significant amounts in these dirhams at the end of the ninth century (Ilisch and Schwarz 2003). This shows that the application of Hg blanching to Ag coins significantly decreased in Central Asia at the end of the ninth century. Most of the dirhams arriving in Eastern Europe can be dated to the mid-10th century (Noonan 1992) and have a low Hg content. As an alternative, the presence of Hg in the Piast denars can be explained by potential surface contamination, for example, in a buried environment (Kantarelou *et al*. 2011).

Moving away from Samanid coins, the other active large-scale silver extraction area in the 10th century was the Harz Mountains in Northern Germany. A coin type closely connected with the Ag production in Harz are the Otto-Adelheid pfennigs frequently found in hoards of the late 10th and early 11th centuries (Hatz 1961). It is assumed that these coins are made from local silver extracted from the Harz Mountains and are a very important case study for studying the composition of Ottonian silver (Zwicker *et al*. 1991). A comparison of the two main trace elements associated with silver (Au and Bi) shows that the composition of Bolesław and Mieszko II coins is close to Otto-Adelheid pfennigs thought to be minted in Goslar, a town in the Harz region (Fig. 2, d). The Otto-Adelheid pfennigs (Hatz types III–V) are dated to the last quarter of the 10th and first half of the 11th centuries. The analyses by Matzke (2003) and Merkel (2016) show that there are two distinct compositional groups: one with very low Au and Bi, and the other with Au and Bi ranging from 0.2% to 0.4% (Zwicker *et al*.'s, 1991, analysis was not considered because of an overestimation of Bi). The composition reflects the different Ag deposits in the Harz Mountains, Rammelsberg (higher Au and Bi) and Upper Harz (low Au and Bi). While the

Otto-Adelheid pfennigs from the last decades of the 10th century suggest they were produced from silver mined from the Rammelsberg deposit, the later mints have Au and Bi contents that suit the composition of the Upper Harz silver. The provenance of Ag for the Otto-Adelheid pfennigs and the connection with the silver deposits of the Harz Mountains was also confirmed by Pb isotope analysis, even though it is likely that the Pb used for cupellation in Rammelsberg came from the Upper Harz (Zwicker *et al*. 1991; Merkel 2016). The compositional variation in the coins from Harz is similar to the Piast denars and they overlap chronologically with the minting of the first Polish denars. The Au versus Bi plot (Fig. 2, d) shows that many of the older Bolesław denars overlap with the Otto-Adelheid pfennigs associated with the Rammelsberg deposit. A similar resemblance applies for the younger Piast coins mainly minted under Mieszko II and pfennigs related to the Upper Harz silver. Rather than proposing an eastern origin of silver used for producing older types of Bolesław denars, the contents of Au and Bi suggest that the two types of silvers identified in denars from Berlin and Krakow could come from two different deposits extracted from the Harz Mountains: Rammelsberg and Upper Harz. Again, as mentioned above, trace elements alone are not an appropriate tool for the determination of Ag provenance; they can only give a direction about likely candidates. In order to discuss the provenance with more certainty, it is necessary to perform Pb isotope analysis.

CONCLUSIONS

The analytical protocol of XRF and HE-PIGE/PIXE provided complementary data that lead to conclusive results which were interpreted in the historic context.

The two XRF methods with FP quantification (μ-XRF and HH-XRF) gave very similar results. A larger discrepancy had been found for the values determined by the PAR method. The HE-IBA allowed the further evaluation of materials from deeper inside the denar by evaluating the Au K-lines and Cu γ-line. A disadvantage of the HE-IBA is that only spot analysis was carried out, which can be problematic for the heterogenetic distributed trace elements. The FP μ-XRF underestimated the Cu content in the high Ag matrix by about 10% rel. The difference for trace elements (Au and Pb) between the methods of approximately 15–25% was estimated from the gradients of the correlation lines. For these elements, because of the larger surface analysed and the smaller analytical error, the μ-XRF values were deemed to be more reliable. For the prediction of an Ag-enriched surface, the agreement of the results from the evaluation of the ratio of Ag Kα/Ag Lα with the results of the HE-PIGE was unsatisfactory. The HE-PIGE values of a Cu content in greater depth suggest more and different coins to be affected by the Ag-enriched surface compared with the results of the Ag Kα/Ag Lα ratio.

The analysis confirmed the overall compositional trends observed for Piast denars from Krakow. Coins minted by both Bolesław and Mieszko II show a high content of Ag and an increasing purity of coins over time. The data suggest that from *c*.1010, both Bolesław and Mieszko II coins were made through a more regulated minting policy. On the basis of trace elements, it is possible to suggest that at least two types of silver were used. The Piast coins were compared with Otto-Adelheid pfennigs. Silver coins that were circulating in Central and Eastern Europe in the 10th and 11th centuries. These pfennigs form two compositional groups that both originate from silver derived from the Harz Mountains in northern Germany. The Harz Mountains area holds several argentiferous-rich deposits. The largest two, namely Upper Harz and Rammelsberg, have a different ore composition, which is also reflected in Ottonian coins in the 10th and 11th centuries. The younger Piast denars with a low Au and Bi content are similar to the Otto-Adelheid coins made from silver derived from the Upper Harz mines. The older

Bolesław denars have an Au and Bi content that closely matches Otto-Adelheid pfennigs, which are also associated with the Harz Mountains silver, but with a different silver deposit: Rammelsberg. It should not be excluded that Central Asian coins were also remelted in the making of the Piast denars, but at present no compositional indicators can provide an argument for such a claim. However, matching compositions of different coin groups cannot provide a definite answer about the provenance of silver. This uncertainty may be used as a direction for future studies. A more reliable method to determine the provenance of silver is Pb isotope analysis. Such an analysis would provide a clearer answer to the origin of silver used in the production of the oldest Piast denars.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

Figure S1a. Obverse and reverse view of 39 denars given in the same order as in Table 1.
Figure S1b. Obverse and reverse view of 39 denars given in the same order as in Table 1.

Figure S2. X-ray fluorescence (XRF) maps obtained for denar 18246610 showing the net peak areas of (a) Ag Kα, (b) Ag Lα, (c) Cu Kα, (d) Pb Lα, (e) Au Lα and (f) Bi Lα.
Figure S3. Regression for the linear calibration of the particle-induced γ-ray emission (PIGE).
Figure S4. Correlation of the results obtained through area scans calculated by the fundamental parameter (FP) and peak area ratios (PAR) methods for (a) Ag, (b) Cu and (c) Pb; and correlation of the results obtained by micro-X-ray fluorescence (μ-XRF) (FP method) and handheld X-ray fluorescence (HH-XRF) for (d) Ag, (e) Cu and (f) Pb. The error bars for the μ-XRF FP method are: Ag 3% rel., Cu 11% rel. and Pb 7% rel.; and for the μ-XRF PAR method: Ag 2% rel., Cu 1% rel. and Pb 13% rel. For HH-XRF, error bars are Ag 0.3% rel., Cu 1% rel. and Pb 4% rel.
Figure S5. (a–c) Correlation of the results between micro-X-ray fluorescence (μ-XRF) (fundamental parameter (FP) method) and high-energy particle-induced X-ray emission (HE-PIXE) for Cu, Pb and Au, respectively; (d) correlation of the Cu results between μ-XRF and particle-induced γ-ray emission (HE-PIGE) plotted for each denar with $>$ 10% Cu in the HE-PIGE result. The straight solid line indicates a correlation factor of 1. The error bars for the μ-XRF FP method are: Cu K 11% rel., Pb L 7% rel. and Au L 3% rel.; for HE-PIXE Cu: 2.7% rel., Pb 14% rel. and Au K 35% rel.; and for HE-PIGE Cu gamma 30% rel.
Table S1. Summary of the results from the analysis of reference materials using the empirical calibration method proposed Sándor *et al*. (2000) with the Artax instrument.
Table S2. Micro-X-ray fluorescence (μ-XRF) results (fundamental parameter (FP) method) and values of samples with known composition (wt%).
Table S3. Particle-induced X-ray emission (PIXE) results (fundamental parameter (FP) method) on samples with known composition.
Table S4. Micro-X-ray fluorescence (μ-XRF) results (wt%) (fundamental parameter (FP) method). Note: [a]Pear intensity ratios of Ag K/Ag L are presented as the percentage deviation with respect to the values obtained from the AgCu standards.
Table S5. Comparison of the Ag, Cu and Pb results of the analytical methods applied in this study

