



Investigation of surface silver enrichment in ancient high silver alloys by PIXE, EDXRF, LA-ICP-MS and SEM-EDS



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ABSTRACT

Surface elemental analysis presenting high silver (Ag) contents have been regarded as reliable for original bulk composition of silver coins which are accordingly referred as being produced from very pure Ag alloys. Also, the extent in which the surface elemental composition analytical results are influenced by surface Ag enrichment has been disregarded in coins alloys with Ag finenesses greater than the Ag content indexed to the maximum value of copper (Cu) solid solubility in Ag – 91.2 wt.%. PIXE and EDXRF results obtained on Portuguese 11 *dinheiros* silver coins issued in the 16th century with a legal Ag fineness of 916.6 thousandths, show 4 to 7% higher Ag surface contents. As identified by LA-ICP-MS and μ -PIXE through coins thicknesses, the overestimation of the superficial measured Ag is associated to a Cu depletion gradient representing as much as 50% less Cu on surface than on the bulk of the coins. The subsurface microstructural characterization by SEM-EDS reveals the presence of an important superficial layer depleted of Cu-phase, with a thickness < 70 μ m, resulting primarily from intergranular corrosion during the coin manufacturing process. These layers can only be accessed by destructive or invasive analysis, as thicknesses beyond the information emission depth obtained with EDXRF could not be identified by Ag $K\alpha/L\alpha$ ratios. As showed by the combination of different methods of analysis, EDXRF, PIXE, SEM-EDS and LA-ICP-MS, the results obtained by surface analytical techniques may differ from the original bulk compositions for these high Ag content coins and should be taken cautiously together with historical context and information.

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1. Introduction

Depending on the previously production and environmental conditions to which Ag alloy coins were subjected during its existence, Cu is depleted from their surface and originates higher Ag compositional content of surface layers with variable thicknesses, which are not representative of the original Ag alloy [1–9].

This Cu depletion mainly due to the technological monetary production process [2–3,5,7,10–14], to previously conservation treatments [7, 15–16] or to the former corrosion/archaeological history [2–4,7,10–11, 14,17] have a larger effect on Cu-rich coins and pose challenges to the characterization of the original fineness of these coins with non-destructive analytical techniques as PIXE and EDXRF.

Until now, most of the studies which relate the surface composition to the microstructure [3–5,12,14,18–22] have focused particularly on Ag-Cu alloys mostly with Ag finenesses under that indexed to the

maximum value of Cu solid solubility in Ag, i.e., 91.2 wt.%. In these alloys significant Ag and Cu differences between the coin core and surface are expected, as there was a well-known intentional alteration of the coin surface Ag content during the monetary production process [7,10–12, 14] in order to create an Ag-rich surface layer, while giving the metallic silver brightness to which a high perceived coin value was associated. In these lower fineness coins, Ag enrichment assessment is complicated once previous research has considered the cut section of coins found in archaeological contexts where, depending on the alloy composition, very variable thicknesses of Ag enriched layers were detected, that could extend from 50 to 250 μ m in depth, associated in most cases with corrosion processes resulting from the burial conditions to which the coins were subjected [3–4,6,12,22–23]. In some cases, compositional Ag differences between the core and the surface of the coins attain values up to 100% [3–4] as a result of the metallurgical history of the coins. The existence on these coins of this altered surface layer, irrespective of the far depth useful penetration reachable by surface analytical techniques, that in the majority of the cases is insufficient to reach the unchanged core, will always give elemental Ag composition values different from the core metal due to its contribution to the analysis [4–5, 22,24]

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The Ag K and L X-ray lines and their emission depth differences can be used to determine variations in surface composition of Ag alloys. According to Linke et al. [4] the determined Ag K_{α}/L_{α} ratios on the coins may be compared with those obtained on a standard of similar composition to estimate the error that occurs while determining the fineness of coins by EDXRF analysis, allowing estimating the deposition of corrosion products or Ag enrichment on a Ag surface. Linke et al. [18] determined up to 20% K/L ratios variations for differences between the core and the surface composition reaching almost 100%. Kantarelou et al. [24] determined that the K/L ratio may change approximately 10% for a homogeneous Ag alloy in the range of 80–100% Ag, and was not able to make a clear assessment of the existence of Ag surface enrichment in coins with high Ag EDXRF results, 87.6–99.4%, due to the high error associated with these ratios. This Ag K_{α}/L_{α} intensity ratio method has been used, however, to classify coins with high Ag compositions (above 90%) as not possessing detectable Ag enrichment, assuming therefore the values of the analysis to be consistent of the original fineness of the coins [25].

This research focuses on a large program analysis of Portuguese high Ag alloy coins, mainly from the 16th century. The impossibility to clean the coin's surface before analysis, avoiding possible effects of surface Ag enrichment, had constrained the elemental composition analysis to the use of nondestructive and noninvasive analytical techniques available, as Particle Induced X-Ray Emission (PIXE) and Energy-Dispersive X-Ray Fluorescence (EDXRF). These techniques have been extensively applied in numismatics in silver coins characterization [4,9,18–20,22,24–28] and allow an expedite quantitative multi-elemental nondestructive analysis, albeit obtaining information from a limited surface depth in an Ag matrix. The results from the surface analytical techniques, EDXRF and PIXE, were then complemented by μ -PIXE analyses along the thickness sections of some coins to determine the core original fineness and the composition gradients of major and minor chemical elements, and by Scanning Electron Microscopy with Energy Dispersive Spectrometry (SEM-EDS) and X-ray Diffraction (XRD) analyses in order to understand microstructure features and to gather information related to the coin manufacturing process or to evaluate any corrosion development. This complementary analytical methodology has been the traditional approach to investigate microstructure and composition of silver coins, due to differences of composition between the surface and the bulk [3–4,12,14,18–19,21]. However, to clarify the previous EDXRF, PIXE and SEM/EDS analysis, Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) analysis was conducted to obtain elemental content profiles in the near-surface thickness in order to elucidate the overestimation of Ag content in coins by surface analytical techniques. LA-ICP-MS has been applied to characterize Ag alloys in objects [29–30] and coins [6,31], and has a wide potential of application in the ancient metals examination due to no need of sample preparation, low detection limits, a spatial resolution associated to a micro-sampling with very small size of ablated material, and the possibility to carry out depth compositions profiling, which provides the information about the distribution of elements in the structure, and a compositional fingerprinting.

As the metallurgical history impacts the current state of the coins, the present investigation aimed to understand in what way the coins microstructure and the analytical limitations of the used methods could affect the determination of the Ag fineness on the surface of high Ag alloys. The knowledge of the coins silver fineness is fundamental to numismatics and to economic historians as permits to verify if the monetary production strictly followed the monetary laws, and to understand the monetary policies of the monarchs and their relations with political and economic events.

2. Experimental

2.1. Coins samples

Analyzes were carried out in a group of coins taken from a set of 200 coins minted by the sixteenth century Portuguese monarchs and

selected among those existing in the *Lisboa* Mint House numismatic museum collection (INCM, SA), aiming that the coins presented the lowest surface alteration, i.e., corrosion or patina. The coins show generally a good state of preservation with a more or less dark patina of unknown thickness on the surface, and present different degrees of engraving wearing. A small number of coins (labeled as C1 to C4) without any intrinsic value and/or numismatic interest, in some cases with great wear of the engravings, were provided by some collectors for destructive analysis.

2.2. Coins preparation

The coins were cleaned with acetone and were placed in an ultrasonic bath for 3 min to remove any contamination particles adhered to the surface. In all coins, EDXRF analyses were made on the obverse and reverse, and PIXE analysis on two points on the obverse of each coin, in a surface that presented the lowest degree of alteration or patina. The coins subjected to destructive analysis were cut to a half-diameter and examined along the thickness to characterize the microstructure and to determinate any elemental composition variation.

2.3. EDXRF

A KeveX 771 EDXRF spectrometer with a primary beam of photons from a 200 W Rh X-ray tube was used in the secondary target excitation mode (Ag and Ga secondary targets) for EDXRF analysis. The radiation produced by the secondary target and filter induces the emission of the characteristics X-ray lines of the coins constituents. The source-detector system has a 45° incidence angle and a 45° output angle. The EDXRF beam cross-section permitted only a global analysis on each face. The characteristic X-rays from the sample spot area close to 2.5 cm in diameter, are acquired by a Si (Li) detector cooled by liquid nitrogen after being collimated to 90° in a 5 mm in diameter collimator. The coins were irradiated with a beam of monochromatic X-rays under low vacuum conditions, using two different excitation conditions: (a) to detect Cu, Zn, Ni, Au, Hg, Pb, Bi it was used a silver secondary target with a voltage of 35 kV, a current intensity of 0.5 mA during 300 s, and (b) to detect silver it was used a gadolinium secondary target with 57 kV, 1.0 mA and 300 s. The spectra were processed using a Gaussian deconvolution, and the elemental composition was determined using the EXACT computer program based upon a fundamental parameter method. The certified reference material 133X AGQ2 (batch C) from MBH analytical® (England), a quaternary silver alloy, was used to determine experimental calibration parameters.

2.4. PIXE

The coins were irradiated in vacuum with a 2 MeV proton beam produced by the 2,5 MV Van de Graaff accelerator from C²TN, using a 1,5 mm diameter beam collimator and a beam current intensity of 15 nA for a total accumulated charge of 10 μ C. A 145 eV resolution Si(Li) detector placed at 70° relative to the proton beam direction was used together with a 350 μ m Mylar filter for strongly reducing the Ag L lines intensity enhancing the Ag K lines contribution to the spectra. Spectra analysis and elemental quantification was performed through the GUPIXWIN computer program. Process validation was accomplished through the analysis of the MBH analytical® certified reference material.

The composition analysis along the thickness of the coins was realized with a nuclear microprobe from Oxford Microbeams. The 2 MeV proton beam was focused on the section of the coin with a spatial resolution of 3 \times 4 μ m². Successive 70 \times 800 μ m² scanings were carried out along the section of the coin in vacuum conditions, using an X-ray detector SDD with a resolution of 145 eV and positioned at 45° relative to the incident beam, and a 50 μ m Mylar filter to suppress the low

energies signals. Spectra analysis and elemental quantification was performed as above mentioned.

2.5. SEM-EDS, XRD

The microstructural characterization was conducted with SEM-EDS in backscattering electron imaging mode using a scanning electron microscope with a conventional tungsten filament (Zeiss DSM 962). This equipment has an energy dispersive spectrometer Oxford Instruments INCAx-sight. The analyses were performed at a working distance of 25 mm, with an accelerating voltage of 20 kV, a filament current of approximately 3A and an emission current of 70 μ A. Other analyses were realized with a Hitachi S3700N SEM-EDS using a high vacuum, with an accelerating voltage of 30 kV and an optimum working distance of 10 mm. The EDS compositional data were obtained using a Bruker AXS microanalysis system with a XFlash Detector 5010.

XRD microstructural identification of the Ag and Cu phases on the diametral section of the coins was made using a X-ray diffractometer system XPERT-PRO. XRD patterns were recorded directly on samples using a non monochromatized Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$), operating with a 45 kV accelerating voltage and a 40 mA current. The scanning was made over the angular range $20^\circ \leq 2\theta \leq 140^\circ$, with a step size of 0.03° and a sampling time of 50 s.

2.6. LA-ICP-MS

LA-ICP-MS analyses were performed using an Agilent 8800 ICP-MS Trip Quad coupled to a CETAC LSX-213 G²⁺ laser ablation system. The equipment was calibrated and tuned prior to the analysis with the certified reference material NIST 612. Elemental fractionation was monitored using the ²³⁸U/²³²Th and the oxide formation was evaluated using the ²⁴⁸ThO/²³²Th ratio. ICP-MS was performed in TRA mode (Time Resolved Analysis) and with the scan type MS/MS mode (no gas in the collision/reaction cell). The monitored isotopes were: ⁶³Cu; ¹⁰⁷Ag with dwell times of 10 ms, and ¹⁹⁷Au, ²⁰¹Hg, ²⁰⁸Pb, ²⁰⁹Bi with dwell times of 20 ms. The ICP plasma has operated at 1550 W of RF Power, 1.4 V of RF matching, sample depth of 4.0 mm and dilution gas (Ar) at 0.7 L/min. The laser conditions used for the analysis were 50 μ m laser beam diameter, 5% energy, 60 μ m/s of scan rate (for lines with about 1300 μ m), frequency of shot 5 Hz, and He flow 1 L/min.

3. Results and discussion

3.1. PIXE versus EDXRF

The mean elemental composition obtained with PIXE and EDXRF for 40 “11 *dinheiros*” coins minted by *Dom Sebastião I* (1557–1578) (Table 1) identify the metal as being a Ag-Cu alloy with an unexpected high fineness, with low contents of minor and trace elements, as gold (Au), mercury (Hg), lead (Pb) and bismuth (Bi), associated to the ores from which the silver was extracted or to the process of silver extraction. The obtained results are comparable in all the investigated coins showing a trend to higher Ag contents than the nominal value imposed by the known sixteenth century monetary laws for these coins. The Portuguese silver coinages were issued then with a 11 *dinheiros* Ag alloy,

corresponding to a fineness of eleven parts of Ag in twelve of metal, i.e., 916.6 thousandths, but these results present positive deviations from the standards, 4% up to 7% higher, something which wouldn't be feasible for the Portuguese monetary production from this century.

As seen in Table 1, the major as well as the minor elements have a similar content and standard deviation magnitude irrespective of the used analysis method, and the high standard deviation values express the composition heterogeneity present on the sample of analyzed coins. The good accuracy of PIXE and EDXRF quantification method was ascertained by analyzing the certified reference material 133X AGQ2 (batch C) from MBH analytical® with a composition close to the expected coins composition (Table 2).

The occurrence of iron (Fe), almost always present on the spectra of the silver coins, is attributed to outdoor pollution manifested with varying degrees of surface contamination that causes Fe enrichment in the surface of the coins due to encrusted dust [15,26]. Fe is virtually insoluble in solid Ag, immiscible with Ag in the liquid phase and was not found as inclusions on the Ag matrix microstructure, and for these reasons its surface content was not taken into account for the overall composition of the coins.

Fig. 1 shows a similar trend for the Ag and Cu contents measured by PIXE and EDXRF on each of the 11 *dinheiros* coins, with a slightly surface Ag enrichment due to Cu depletion, evidencing the heterogeneity present on the sample of analyzed coins. Also, the individual surface analyses on different areas of the same coins have indicated no significant variation in composition revealing a material homogeneity within each coin.

The Ag K α /L α ratios determined using the intensities of EDXRF Ag K α and Ag L α X-ray lines on the obverse and reverse of a representative group of 41 coins, minted during the sixteenth century period by *Dom Manuel I*, *Dom João III* and *Dom Sebastião I*, were compared with the same ratio obtained on the MBH analytical® reference Ag alloy in Table 3.

The mean K/L values obtained on the obverse and reverse of the coins are very close to the acquired on the reference alloy. Knowing that for a 92% Ag composition alloy the information depth for Ag L α intensity does not exceed a thickness of about 2 μ m and that 90% of the Ag K α intensity (higher energy emission) comes from a layer with 40 μ m thickness [24], the comparison between the EDXRF quantification using Ag K α and L α lines on this group of coins (Fig. 2) reveals a slightly lower Ag content due to the tarnishing layer present on the surface of the coins, not supporting the direct existence of a subsurface Ag enrichment and still not explaining the up to 98% Ag content measured.

It is known that tarnishing submicronic layers with a more or less dark coloration could influence the quantitative compositional surface analysis of Ag alloys. Mass and Matsen [8] have reported for an incipient tarnished sterling Ag coupon, XRF Ag compositional deviations 0.1 wt% lower than the content of the Ag alloy after polishing, and a lower Ag content in the range of 0.5–0.9 wt% for a fully tarnished surface in some objects. Kallithrakas-Kontos et al. [32] investigated the elemental compositional differences on tetradrachms silver coins by EDXRF, before and after a cleaning patina procedure, stating that this layer should have a small influence on the contents of several elements, as Ag, Au, Pb

Table 1

Mean values and standard deviation of silver, copper, gold, lead, mercury and bismuth expressed as weight percent obtained with PIXE and EDXRF on the 11 *dinheiros* coins minted by *Dom Sebastião I* (1557–1578).

	Ag	Cu	Au	Pb	Hg	Bi
11 <i>dinheiros</i>	91.67	–	–	–	–	–
Coin PIXE	96.37	2.79	0.13	0.42	0.19	0.09
	± 1.60	± 1.34	± 0.07	± 0.25	± 0.90	± 0.04
EDXRF	95.82	3.30	0.12	0.54	0.13	0.10
	± 1.51	± 1.32	± 0.05	± 0.33	± 0.60	± 0.04

Table 2

Obtained values and uncertainty (wt.%) for certified reference material 133X AGQ2 (batch C) from MBH analytical®.

Element	Ag	Cu	Au	Pb
Certified value	92.745	5.808	0.978	0.469
		± 0.072	± 0.003	± 0.007
PIXE obtained value	92.88	5.63 ± 0.23	1.04 ± 0.03	0.46 ± 0.03
	± 0.26			
PIXE error (%)	0.14	3.16	6.05	1.99
EDXRF obtained value	92.94	5.67 ± 0.13	0.98 ± 0.01	0.46 ± 0.02
	± 0.16			
EDXRF error (%)	0.21	2.45	0.35	2.69

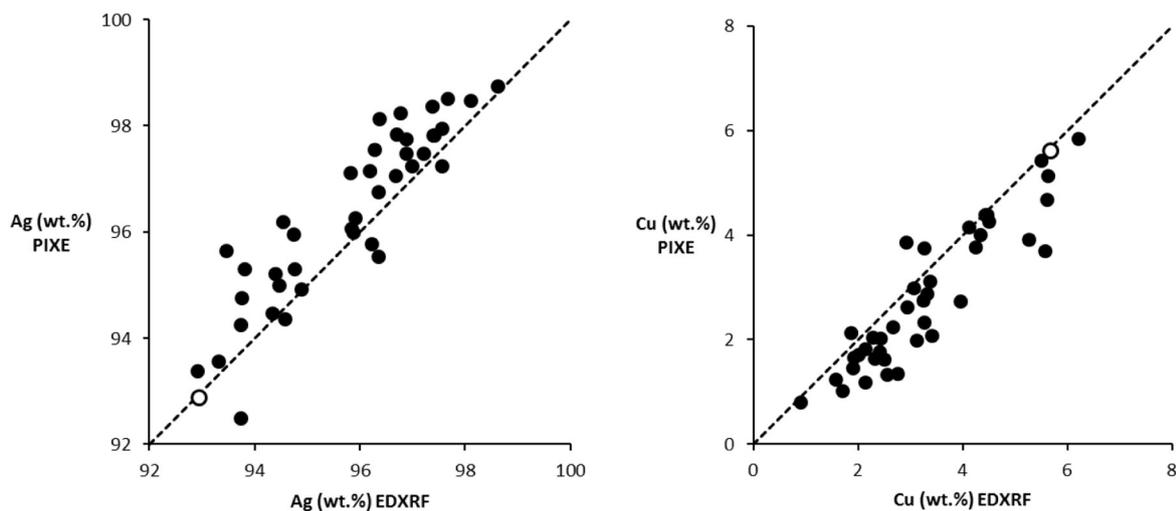


Fig. 1. PIXE and EDXRF Ag and Cu compositional values obtained for *Dom Sebastião I* “11 dinheiros” coins. A dotted line of equal content was drawn for purposes of clearness and the open circle represents the mean data from the certified reference material.

and Bi. However, these former investigations do not correlate the obtained data with the subsurface microstructure of the coins, or to the degree of oxidation/corrosion on the surface.

The variation found in the coins K/L ratio could be related to the amount of a submicrometer tarnishing layer on the surface of each of the coins, or to the influence of the surface roughness in the measurements of Ag L intensity, as the rough or flat regions would give large count rates variations, contrary to the Ag K intensity [11]. Also, in agreement with the results, the MHB analytical® reference Ag alloy K/L ratio is nearly the same as the one reported by Kantarelou et al. [24] for the CNR-141 reference standard (81.1 ± 1.1) with a very close Ag content (92.5% Ag, 7.5% Cu).

3.2. PIXE versus LA-ICP-MS

To provide an estimation of the Ag bulk content of the coins and to investigate if the surface composition has been modified by the minting operations, the composition was determined with a nuclear microprobe on the cross-sections along the thickness. Table 4 indicate the composition obtained by μ -PIXE on approximately 70 μm thick successive layers taken along the diametral cross-sections of four coins (C1 to C4) minted in *Lisboa* (C1 and C3) and in *Porto* (C2 and C4).

The surface Cu depletion results in an overestimation of the superficial measured Ag, with a value 2.5 to 5% higher. This Cu depletion represents 45–50% less Cu on surface than on the bulk of the coins, and originates in most cases from the first 70 μm thickness subsurface layers.

The coins minted during *Dom João II* reign present higher Au and lower Bi contents than the coins minted by *Dom Manuel I*, pointing to different provenances of the minting silver bullions in these different reigns. The mean coin bulk analysis (Table 5) indicate for three of the coins a Ag content slightly higher, and for the other one slightly lower, than that for the maximum Cu solubility on Ag, i.e., the silver content below which it is possible an Ag-Cu eutectic formation on equilibrium cooling conditions (91.2 wt.%).

Table 3
Ratio between Ag-K α and Ag-L α intensities measured on the MBH analytical® reference silver alloy and on obverse and reverse of the coins.

Sample	Number of measurements	AgK α /AgL α
MBH 133X AQQ2	9	80.63 \pm 4.81
Silver coins (obverse)	41	78.57 \pm 7.06
Silver coins (reverse)	41	79.16 \pm 7.41

Albeit the obtained Ag bulk content in three of the coins is under the fineness fixed by the monetary law (91.7%), but nevertheless very close, this value does not directly reveal the coinage fineness of the alloy that was mixed in the melting furnace and the precision with which the founders adjust the silver melting's with copper, nor the exactitude with which the assayers tested the silver ingots. On the beginning of the sixteenth century, the silver assays were made at *Lisboa* Mint House virtually by the touchstone, and not by the cupellation test, a test much more fallible and influenced by the weather and ambient conditions, depending of the available amount of light as attested in 1509 by the *Lisboa* Mint House technicians [33].

After adding Cu to adjust the monetary Ag fineness all the minor elements present on the entry Ag bullion remained in the melted Ag metal with the same residual quantities. The Ag bullion content (Table 5), that is, the perceived Ag content assayed at the mint house is more realistically related as the sum of the Ag, Cu, plus all the minor elements present in the Ag alloy [12,34] such as Au, Hg, Pb and Bi, which the moneymen were unaware and weighed as Ag, and in case of the coins minted in *Lisboa* corresponds closely to the values of the pretended Ag fineness of 11 *dinheiros*. The higher bullion fineness encountered on the *Porto* minted coins must be an evidence of poor minting control related to the fact that this monetary workshop worked with long inactive periods and without a continued production, which adversely affects the alloy preparation as well the assaying expertise.

The investigation of concentration gradients between the surface and the bulk of four coins were realized by LA-ICP-MS elemental concentration depth profiles (Figs. 3–4) with the determination of intensity ratios of Cu and four minor elements, Au, Hg, Pb and Bi, with reference to Ag. It should be noted that the first data on the LA-ICP-MS profiles are influenced by the tarnishing layer on top of the surface, and that the duration of the analysis was long enough to reach the core of the coins.

A very significant finding was the confirmation of important Cu depletions on the near surface region of the two coins minted in *Lisboa*, C1 (*Dom João II*, 1481–1495) and C3 (*Dom Manuel I*, 1495–1521), and one coin minted in *Porto*, C4 (*Dom Manuel I*, 1495–1521), resulting in important Cu composition differences between the surface and the bulk of the coins of approximately 40%. Albeit the subsurface Cu profile was found to be different on these coins minted in successive reigns and on different chronological periods of currency emission, they show a consistency of the minting executed in both mint houses over time and indicate a distinctive feature of the subsurface region possibly introduced by the monetary production process. The other coin minted in *Porto*, C2

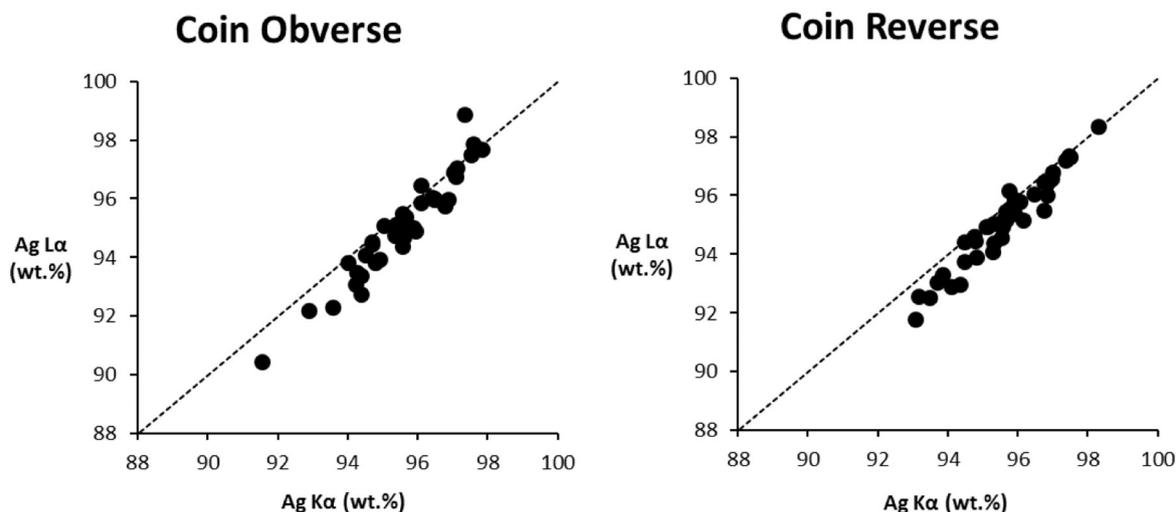


Fig. 2. Comparison of EDXRF Ag quantification using $K\alpha$ and $L\alpha$ lines for the obverse and reverse of the coins minted during the sixteenth century by *Dom Manuel I*, *Dom João III* and *Dom Sebastião I*. A dotted line of equal content was drawn for purposes of clearness.

(*Dom João II*, 1481–1495), does not show significant surface Cu depletion on the analyzed location, and has a Ag content on the internal layers similar to that measured on the other coins. μ -PIXE results indicate also

Table 4

Composition obtained by μ -PIXE on diametral cross-sections taken on four coins minted in *Lisboa* and *Porto* by *Dom João II* (C1, C2) and *Dom Manuel I* (C3, C4).

Position	%		ppm					
	Ag	Cu	Zn	Ni	Au	Hg	Pb	Bi
C1 - Dom João II (1481–1495) – Lisboa Mint								
Obverse	94.65	4.00	n.d.	n.d.	7524	n.d.	5834	n.d.
Obv. subsurface	93.75	4.97	n.d.	n.d.	6158	n.d.	6675	n.d.
Depth obverse	90.84	7.82	n.d.	n.d.	7067	n.d.	6305	n.d.
Bulk	90.11	8.62	n.d.	n.d.	7179	n.d.	5528	n.d.
	89.63	8.96	n.d.	n.d.	7500	n.d.	6561	n.d.
	89.75	8.86	n.d.	n.d.	7290	n.d.	6604	n.d.
	90.29	8.46	n.d.	n.d.	6238	n.d.	6254	n.d.
Depth reverse	91.56	7.12	n.d.	n.d.	6984	n.d.	6213	n.d.
Rev. subsurface	92.68	5.81	n.d.	n.d.	8158	n.d.	6849	n.d.
Reverse	94.26	4.25	n.d.	n.d.	8030	n.d.	6067	n.d.
C2 - Dom João II (1481–1495) – Porto Mint								
Obverse	93.95	4.04	n.d.	n.d.	9824	n.d.	9975	n.d.
Obv. subsurface	94.08	3.99	463	n.d.	8657	n.d.	10,181	n.d.
Bulk	93.12	4.57	393	n.d.	10,741	n.d.	11,936	n.d.
	93.16	4.55	342	n.d.	10,717	n.d.	11,871	n.d.
	93.28	4.51	496	n.d.	10,061	n.d.	11,538	n.d.
	92.64	4.96	497	n.d.	10,733	n.d.	12,717	n.d.
	92.69	5.08	422	n.d.	9485	n.d.	11,907	n.d.
	92.75	4.98	370	n.d.	10,858	n.d.	10,807	n.d.
Rev. subsurface	93.99	4.04	390	n.d.	8871	n.d.	11,236	n.d.
Reverse	95.98	2.44	284	n.d.	7961	n.d.	7608	n.d.
C3 - Dom Manuel I (1495–1521) – Lisboa Mint								
Obverse	95.64	4.02	52	37	165	49	1267	1856
Obv. subsurface	92.53	6.93	n.d.	n.d.	n.d.	n.d.	1400	4000
Bulk	91.07	8.32	n.d.	n.d.	n.d.	n.d.	1900	4200
	91.21	8.19	n.d.	n.d.	n.d.	n.d.	2200	3900
	91.77	7.46	n.d.	n.d.	n.d.	n.d.	2600	5100
	91.77	7.46	n.d.	n.d.	n.d.	n.d.	2600	5100
Reverse	93.91	5.39	n.d.	34	108	113	1839	3319
C4 - Dom Manuel I (1495–1521) – Porto Mint								
Obverse	93.61	4.26	446	n.d.	3938	n.d.	15,682	1065
Obv. subsurface	94.63	3.68	408	n.d.	2659	n.d.	13,023	775
Bulk	92.52	5.43	442	n.d.	2589	n.d.	16,336	1145
	91.92	6.00	526	n.d.	3063	n.d.	15,909	1253
	90.82	6.92	565	n.d.	3142	n.d.	17,815	1101
	91.16	6.69	683	n.d.	3370	n.d.	16,644	766
	90.40	6.77	625	n.d.	3163	n.d.	17,658	1214
	91.06	6.62	599	n.d.	3449	n.d.	18,038	1089
Reverse	93.40	4.44	437	n.d.	3870	n.d.	16,153	1061

n.d. – not detected.

that the LA-ICP-MS Cu compositional profile from C2 coin was realized in a non-representative region of this coin.

The minor elements Au, Hg, Pb and Bi (Fig. 4) also show superficial contents distinct from the internal layers, which are in most cases not representative of the original composition of the coins. All coins present compositional Au profiles decreasing from the surface, in correspondence with the μ -PIXE data obtained along the thickness of the same coins, being the coins minted by *Dom João II* (C1, C2) more richer in this element than the coins minted by *Dom Manuel I* (C3, C4). Coins with low contents of Pb or Bi show relatively uniform compositional profiles of these elements along the thickness, but coins with larger contents have important lower compositions on surface, when compared to the bulk, revealing the propensity for these elements for being lost from the surface during the metallurgical history of the coins. Also, PIXE results confirm generally the compositional profiles for Pb and Bi obtained by LA-ICP-MS. The Au and Pb variation trend agree with the data reported by Carter [1].

The Hg, present in these coins in very low contents under the limits of detection by PIXE, rapidly decreases in the initial outer layer (first two measures) but remains almost constant in the rest of the inner core.

3.3. SEM-EDS

Fig. 5 shows representative high magnification examples of back-scattered scanning electron micrographs obtained on thickness diametral cross-sections taken from C2 and C3 *Vintém* coins. These images

Table 5

PIXE obverse, reverse and average bulk compositions from four coins minted in *Lisboa* and *Porto* by *Dom João II* (C1, C2) and *Dom Manuel I* (C3, C4).

Coin		%		ppm						Bullion (%)
		Ag	Cu	Zn	Ni	Au	Hg	Pb	Bi	
C1	Obverse	94.65	4.00	n.d.	n.d.	7524	n.d.	5834	n.d.	91.27
	Bulk	89.95	8.73	n.d.	n.d.	7052	n.d.	6237	n.d.	
	Reverse	94.26	4.25	n.d.	n.d.	8030	n.d.	6067	n.d.	
C2	Obverse	93.95	4.04	n.d.	n.d.	9824	n.d.	9975	n.d.	95.18
	Bulk	92.94	4.78	439	n.d.	10,249	n.d.	12,008	n.d.	
	Reverse	95.98	2.44	284	n.d.	7961	n.d.	7608	n.d.	
C3	Obverse	95.64	4.02	52	37	165	49	1267	1856	92.01
	Bulk	91.35	7.99	n.d.	n.d.	n.d.	n.d.	2233	4400	
	Reverse	93.91	5.39	n.d.	34	108	113	1839	3319	
C4	Obverse	93.61	4.26	446	n.d.	3938	n.d.	15,682	1065	93.46
	Bulk	91.36	6.36	568	n.d.	3065	n.d.	16,872	1096	
	Reverse	93.40	4.44	437	n.d.	3870	n.d.	16,153	1061	

n.d. – not detected.

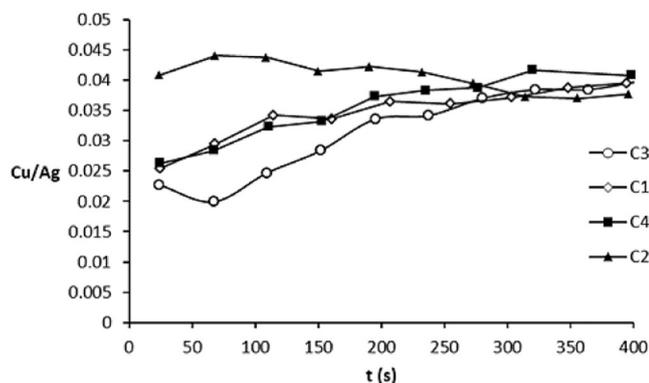


Fig. 3. Cu compositional depth profiles determined by LA-ICP-MS on obverse of coins C1, C3 and C4 and on reverse of coin C2.

reveal a banded structure composed of a fine and darker Cu-rich solid solution phase, clearly identified by EDS and XRD analysis, in a brighter Ag-rich matrix, and an inhomogeneous subsurface region with a different Cu to Ag phase proportion when compared to the existent on the core of the coin. This near surface altered region almost without Cu-rich phase could vary in the same cross-section from approximately 25 to 60 μm deep. According to Table 5, it seems that this altered subsurface layer should be in most cases enclosed in a subsurface thickness under 70 μm . These images would hardly reveal this banded structure with lower magnifications leading to the erroneous interpretation of the coins being only constituted by the Ag-rich phase.

Also, all microstructures show no clear surface layer indicating that Cu have been completely stripped out at the subsurface regions, no intergranular corrosion, and no presence of voids replacing zones of the prior Cu-rich phase, aspects related to Cu oxidation and leaching due to corrosion processes associated in most cases with burial environments, as presented in several investigations concerning coins with lower Ag contents [3–4,12,17–19,23] and that could extend to significant deeper thicknesses or to the entire coin.

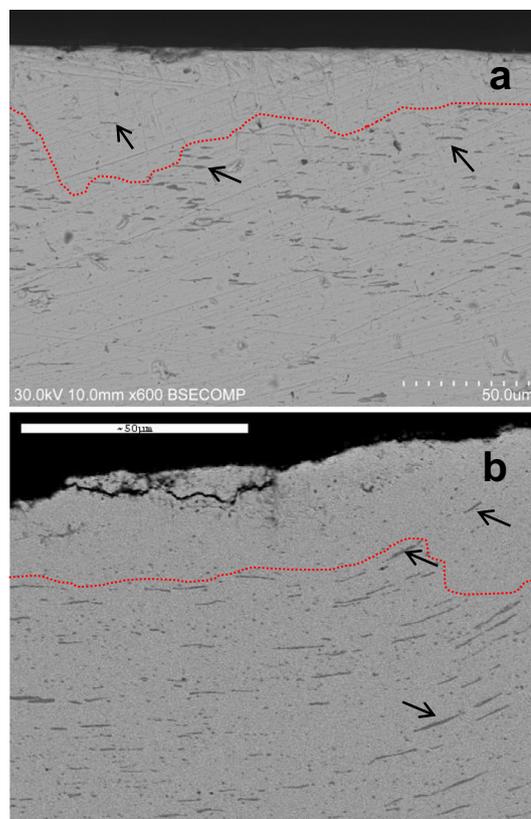


Fig. 5. SEM-BSE images in diametral section on *Vintém* coins minted (a) by Dom João II (C2) and (b) by Dom Manuel I (C3). The dotted line identify a subsurface area nearly devoid of the Cu-rich phase, which on the upper left of (a) extends from a depth of about 60 μm to as lower as 20 μm on the remaining image. This region extends also in (b) from about 25 μm on the left to about 40 μm on the right. The arrows identify examples of the Cu-rich phase banded structure.

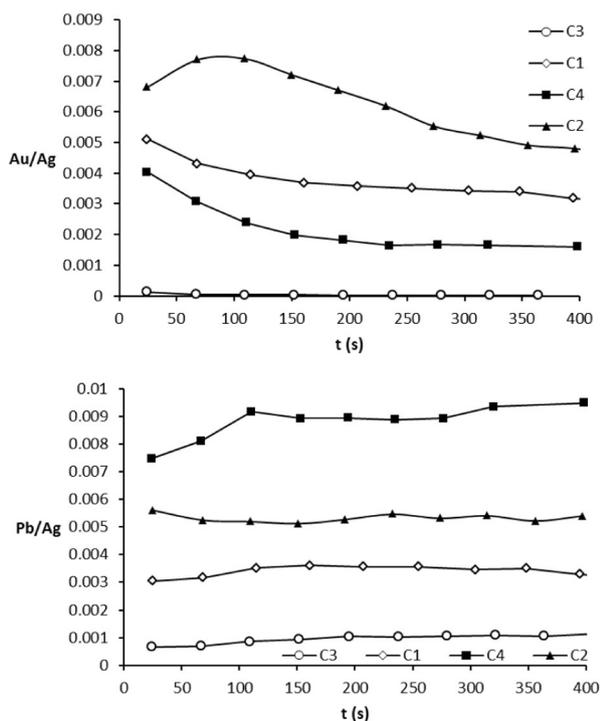


Fig. 4. Au, Hg, Pb and Bi compositional depth profiles determined by LA-ICP-MS on obverse of coins C1, C3 and C4, and on reverse of coin C2.

SEM-EDS analysis in the darker phase regions of two coins (C1 and C2) belonging to the same chronological period of *Dom João II* gave an elemental composition very close to the eutectic composition, revealing that the metallurgical process led, in these cases, to the formation of small eutectic inclusions due to the solidification process of the alloy. SEM-EDS analysis of the light phase shows compositions of a Cu supersaturated Ag phase with Cu contents lower than that related to the maximum Cu content in Ag solid solution. The Ag and Cu contents determined continuously by an EDS line scan from the bulk metal to the surface edges indicated a rather homogeneous elemental distribution in each phase without a concentration gradient.

3.4. Results discussion

The depth of information on Ag-Cu alloy coins depends on the matrix chemical composition and on the primary radiation and fluorescence radiation energy, with the greatest amount of Ag characteristic fluorescence radiation being emitted from the nearest surface layer. Linke et al. [4] has determined EDXRF relations between different compositions of Ag-Cu alloy matrixes and Ag $K\alpha$ and Cu $K\alpha$ radiation depth of information. From these relations, we could roughly obtain for a *11 dinheiros* Ag-Cu alloy depths of information for Ag $K\alpha$ and Cu $K\alpha$ radiation of about 20 μm and <4 μm for 63.2% intensity, and between 60 and 70 μm and <10 μm for 95% intensity, respectively. PIXE is known to have an information depth of 5–10 μm [4,27].

Influenced by the effect of the metallurgical microstructure, EDXRF and PIXE obtain near identical Cu contents as both methods are getting information coming mostly from a layer with the same microstructural morphology. Also, much of the Ag detected by EDXRF analysis will come from this near surface region with a depth of some tens of micrometers with restricted proportions of Cu-rich phase in the microstructural arrangement adjacent to the surface, resulting on a higher Ag EDXRF analysis content when compared to the core of the coin.

As expected, Ag-rich phases with similar compositions will give similar Ag- $K\alpha$ and Ag- $L\alpha$ intensities ratios, and the difference between Ag and Cu contents measured at the surface and bulk of the coins, results therefore in these coins from the contribution of the Cu-rich phase present in each of these regions. It derives apparently from the existent lower proportion of the Cu-rich phase in the near surface region and not from the depletion of Cu in solid solution on the Ag-rich phase present in this area, as indicated by the homogeneous elemental distribution in the Ag-rich phase detected by SEM.

The conjunction of all the above results lead us to assume that the coin manufacturing process involved intergranular dry corrosion in the annealing operations, primarily related to the preferential leaching of the Cu-rich phase in the subsurface layer depth. Also, to support this, there was not detected a Ag gradient for the Ag-rich phase across this region and the inner core, which is in agreement with the Ag- $K\alpha$ and Ag- $L\alpha$ intensities ratios on coins and standards regardless of the higher Ag surface contents.

The monetary production process after ingot casting originate important Ag compositional differences between surface and bulk in Cu-rich Ag alloys [10–13], and also in the case of these Portuguese silver coins, a characteristic microstructure morphology results from the multiple hammering and annealing/quenching stages involved in the thickness reduction of the silver bar after casting, previously to obtaining the metal blank for minting, associated with the blanching on the end of the monetary process. All these operations contribute to the depletion of Cu near the surface impacting the Ag fineness obtained by superficial analytical methods. The fact that coins from different chronologies and different metallurgical histories have comparable microstructural features suggests that these resulted from similar manufacturing operations or treatments during the minting process.

It is also important to relate the thickness of this altered subsurface region with the monetary production process. According to experiments made with modern Ag alloys [11], the thickness of a replicated

Cu depleted layer obtained by annealing and blanching before striking coins was reported to be in the range of 20 to 30 μm . Also, an archaeometric replication with four steps of thickness reduction and an annealing temperature of 700 °C originated a layer of about 15 μm thick in a eutectic Ag-Cu alloy [13]. In addition, Butcher and Ponting [12] found a 120 μm Ag enriched layer on a Nero denarius with a core composition of 78.4% Ag alloy, assuming that without an intentional prolonged oxidation with the removal of the Cu oxidation by acids, this layer would be approximately 20 μm depth. However when compared to these replicated results, it seems that the observed microstructural subsurface distribution of phases on these high Ag alloy coins originates an unexpected higher thickness on this altered subsurface layer.

The lack of published data relative to possible surface Ag enrichment in high Ag content coins has hampered the understanding of this phenomenon for Ag contents higher than 91.2%, not allowing to know in what extent the surface elemental composition investigated by surface analytical methods will be influenced. Measured surface Ag contents higher than 94% have been considered relevant for coins bulk composition [35]. Also, for Ag-Cu alloys expected to have >91.2% Ag the Ag surface composition has been regarded as following the composition of the Ag-rich primary phase, wherein no significant surface and bulk Ag composition differences are assumed [5].

In Table 6 we present a collection of compositional data for these high Ag alloys published in literature. For very pure roman silver coins, over 98%, the obtained results have been considered reliable by Butcher and Ponting [12] once the coins were produced without the employment of Cu depletion and used the Ag bullion composition that was regarded as pure silver at the time of coin production, which includes Au, Bi, Pb and small amounts of Cu from the ores. According to the results presented on this table, there are no significant compositional surface/bulk differences (<1%) in coins having low Cu content under 3%, i.e., bulk analysis higher than 97% Ag, and the determined surface concentration can be considered reliable for the original bulk composition in most cases.

However, Ag compositional differences increase with the percentage of Cu in the alloy, and represent up to almost 7% deviation for alloys with Cu contents near the maximum value of solubility of this element in Ag, well in correspondence with our results. Alloys with Ag contents under 91.2% show maximum compositional differences between the bulk and surface.

Also, high purity Viking Age silver ingots with an Ag composition higher than sterling silver present significant compositional differences measuring 4% less Cu by XRF due to Ag enrichment [37], and PIXE results obtained on an eighteenth century Belgian fork [38] with a very similar Ag content (bulk - 91.8%, surface >94%) to the *11 dinheiros*

Table 6
Surface and bulk silver content data of high fineness coins taken from published literature.

Reference	Coin	Ag% bulk	Ag% surface	Surface/bulk difference (%)	
Civici et al. [20]	7922	99.00	99.05	0.1	
	Surface XRF, bulk PIXE	7890	89.95	95.65	6.3
		7882/7	88.75	96.50	8.7
Gitler et al. [34,36]	Surface XRF, bulk	JR18	98.1	98.1	0.0
	ICP-AES	JR4	98.1	98.6	0.5
		JR28	98.0	98.3	0.3
		IM26154	97.7	98.3	0.6
		JR26	96.0	96.7	0.7
		JR11	95.4	96.8	1.5
		JR17	94.8	98.9	4.3
		PC	93.8	96.0	2.4
		JR21	93.2	99.4	6.7
		JR2	92.3	96.3	4.3
Ager et al. [22]	Surface XRF, bulk	JR3	90.0	97.5	8.3
	micro-XRF	N2	97.1	97.9	0.8
		N8	97.2	97.5	0.3
		N9	96.2	98.3	2.2

coins, has presented an altered depth layer of 20 μm , disclosing a great correspondence with our results. However, more investigation is needed to clarify the microstructural effects.

4. Conclusions

This interdisciplinary approach focused on the surface Ag enrichment of high Ag alloys based on the microstructural and compositional characterization of Portuguese 11 *dinheiros* silver coins. In these high Ag alloys, the minting process induces a subsurface microstructurally modified layer, with a different proportion of Cu and Ag phases than the core of the coins, with an unknown elemental compositional gradient and depth, <70 μm . This subsurface layer originates through PIXE and EDXRF analysis an Ag overestimation of 4 to 7% higher than the bulk of the coins. EDXRF Ag K_{α}/L_{α} ratios cannot identify this layer when its thickness exceeds the information emission depth obtained with this method.

Due to the unpredictable variability of this subsurface microstructure arrangement, the compositional differences between the surface and the core of the coins can only be determined by using additional microdestructive or micro-invasive analytical techniques, as is difficult to find evidences of the effects of the minting process based only on the surface of the coins. This subsurface Cu depleted layer is caused by the hammering, annealing and quenching operations of the silver bar during the minting process, and probably originated from high temperature intergranular copper corrosion, with formation of copper oxides advancing from surface to the interior, later associated to the preferential lexiviation of the Cu-rich phase.

There is a lack of information related to surface metallurgical microstructure on ancient high Ag alloys and therefore more research is needed, including experimental replications, to understand the effects of the minting operations and processes on the surface of these alloys. This study shows however that important metallurgical information resulting from the minting process may be missed when analyzing high silver alloys relying only on the judgment of surface analysis methods, as EDXRF or PIXE, which results could incur in potential erroneous interpretations of the coins fineness and thereafter of the numismatic and the economic history.

The information obtained on coins covering the entire range of the Portuguese sixteenth century can uncover interesting aspects of the minting methods as well about the silver used for their coinage. It can be said that the Portuguese *Lisboa* Mint House had rigorously implemented the 11 *dinheiros* standard imposed by the monetary law.

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