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Study of Portuguese Coins Issued During the Reign of D. João with pXRF Technique and Multivariate Analysis

Estudo de Moedas Portuguesas Emitidas Durante o Reinado de D. João com Técnica pXRF e Análise Multivariada

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ABSTRACT

Portable energy dispersive X-Ray Fluorescence (pXRF) technique was applied for the study of 113 Portuguese coins minted during the reign of D. João I (1385-1433). Multivariate analysis was also employed to obtain more information about the coin set. These coins are part of a collection that belongs to the National History Museum in Rio de Janeiro (MHN). Different Portuguese currencies were studied such as *Real Branco*, *Real de 10 Soldos*, and ½ *Real Cruzado*. The coins were minted with an alloy known as billon, which is made of copper and silver. The reigns of D. João I (1385-1433) and his predecessor, D. Fernando (1367-1383), had intense warlike activity. This activity affected the economy, mainly during the reign of D. João I where the legal content of silver in coins was lower (2.78% weight) in contrast, for instance, with the reign of D. Fernando (8.33% weight). It was verified that some coins have a concentration below the legal value, while an expressive number of coins did not present silver in their composition. A Principal Component Analysis (PCA) was able to separate one monetary value coin regarding the city that it was minted.

keywords pXRF, billon alloy, silver base coin

RESUMO

A técnica de Fluorescência de Raios X Dispersiva de Energia com equipamento portátil (pXRF) foi aplicada para estudar 113 moedas portuguesas cunhadas durante o reinado de D. João I (1385-1433). A análise multivariada também foi empregada para extrair informações adicionais sobre o conjunto de moedas. As moedas fazem parte de uma coleção mantida pelo Museu Histórico Nacional no Rio de Janeiro (MHN). Diferentes moedas portuguesas foram examinadas, incluindo o Real Branco, o Real de 10 Soldos e o ½ Real Cruzado. As moedas foram cunhadas usando uma liga conhecida como bilhão, composta principalmente de cobre e prata. Os reinados de D. João I (1385-1433) e seu antecessor, D. Fernando (1367-1383), foram marcados por intensa atividade militar. Essa atividade impactou significativamente a economia, especialmente durante o reinado de D. João I, quando o teor de prata legalmente obrigatório nas moedas era menor (2,78% em peso), em comparação com, por exemplo, o reinado de D. Fernando (8,33% em peso). Observou-se que um número substancial de moedas não continha prata em sua composição, enquanto outras apresentavam concentrações abaixo do limite legal. A Análise de Componentes Principais (ACP) foi capaz de distinguir uma denominação monetária com base na cidade em que foi cunhada.

palavras-chave pXRF, moedas bilhão, moedas de prata

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Introduction

The Energy Dispersive X-Ray Fluorescence (EDXRF) technique has been widely applied in studies involving cultural heritage, such as archaeological artifacts and historical objects (Bugoi et al., 2002; Milazzo, 2004; Neiva et al., 2005). This technique is particularly useful when samples cannot be destroyed or must be preserved. In the case of coins, EDXRF can be used to determine the chemical composition of the metal alloys employed in the minting process. Several studies have presented insightful analyses and results regarding ancient coins (Guerra, 2000; Parreira et al., 2009).

Coins are of great historical significance, as they carry information about the period in which they were issued. Moreover, they can be considered "vehicles of ideas." Florenzano (1989) notes that authorities deliberately chose specific symbols to be printed on coins in order to convey precise meanings, essentially using coins as a form of marketing.

The reign of King João I (1385–1433) saw the production of a wide variety of currencies in Portugal (Cordeiro, 2021). These coins reflect aspects of religious ideology and the political structure of the country, making them valuable objects of study. This period was marked by intense military activity, which significantly impacted Portugal's economy. Monetary manipulation led to the minting of coins using a metal alloy known as billon, and after 1369, the exclusive use of silver and gold in coinage was abandoned (Valério, 1992).

In this study, a laboratory-made portable EDXRF (pXRF) system was used to analyze a collection of coins belonging to the *Museu Histórico Nacional*(MHN, National Historical Museum) in Rio de Janeiro. Portable systems are increasingly used in various studies, such as that by Felix et al. (2020), who investigated the enrichment of silver (Ag) on the surface of Colonial Brazilian coins due to corrosion processes.

The main objective of the present work was to determine the chemical composition of the metal alloys used in these coins. Elemental concentrations were calculated using the acquired X-Ray Fluorescence (XRF) spectra. Principal Component Analysis (PCA) was performed to identify potential groupings of coins based on shared characteristics. One major advantage of portable spectrometers is their ability to perform in situ measurements.

The *Museu Histórico Nacional* is affiliated with the *Instituto Brasileiro de Museus* (IBRAM, Brazilian Institute of Museums), an agency under the Brazilian Ministry of Culture, and is located in Rio de Janeiro. The museum holds approximately 6,000 Portuguese coins in its collection, from which the coins analyzed in this study were selected (Cordeiro, 2021).

Material and methods

Samples

The pXRF technique was applied to 113 Portuguese coins minted during the reign of King João I. Measurements were conducted at the *Museu Histórico Nacional* in Rio de Janeiro, and no physical or chemical treatment was applied to the coins prior to analysis. The coins were minted in Lisbon, with an amount of 79 coins; in Porto, with 30 coins; and in Évora, with 4 coins. They are also classified according to their monetary value, as presented in Table 1, along with their physical characteristics.

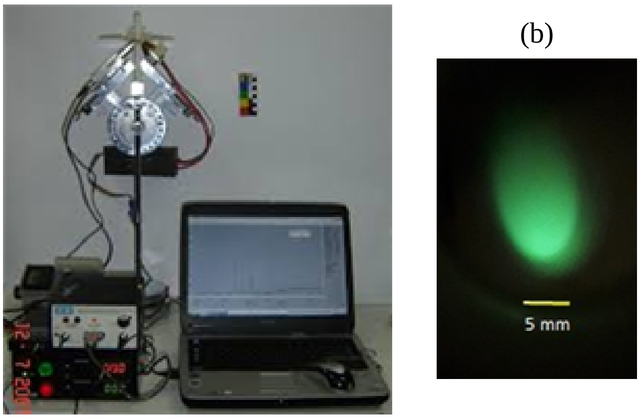
Table 1 - Coin's classification according to its monetary value.

Monetary value	**Year of minting**	**Amount of coins**	**Diameter range** (mm)	**Average diameter** (mm)	**Average irradiation area** (mm^2)
Real de 10 Soldos	1386 – 1397	10	[23.4 – 27.1]	25.8	523
½ Real de 10 Soldos	–	7	[17.4 – 19.8]	18.9	280
½ Real Atípico	1392 – 1397	5	[15.5 – 19.0]	17.4	238
Real de 3 e ½ Libras	1398 – 1407	26	[22.7 – 26.4]	24.9	487
½ Real Cruzado	1407 – 1415	19	[21.7 – 24.6]	23.1	419
¼ Real Cruzado	–	2	–	–	–
Real Branco	1415 – 1433	36	[24.5 – 29.4]	27.0	572
½ Real Branco	–	2	[17.1 – 19.6]	19.7	275
Real Preto	–	6	[21.5 – 23.0]	22.3	390

X-Ray Fluorescence measurements

A Portable X-Ray Fluorescence (pXRF) system, depicted in Figure 1, was employed for the elemental analysis.

Figure 1 - Picture of the Portable X-Ray Fluorescence system and the irradiation area of the coins (105 mm^2).



(a)

(b)

The system, Figure 1(a), includes a Si-PIN X-Ray detector (XR-100CR – AMPTEK Inc.) with an energy resolution of 221 eV for the 5.9 keV Mn line and a 25 μm beryllium window. It is equipped with a high-voltage power supply and amplifier (PX2CR - AMPTEK Inc.), as well as a multichannel analyzer (MCA8000A - AMPTEK Inc.). The samples were excited using an X-Ray mini tube featuring a silver target and a maximum power output of 4 W, operating range: $10 - 40\,\mathrm{kV}$, $0 - 100\,\mu\mathrm{A}$, with a $5\,\mathrm{mm}$ focal spot, Figure 1(b), along with a $5\,\mu$m silver filter (MOXTEK Inc.).

The experimental conditions were selected to optimize the analytical response of the pXRF technique. Following a series of preliminary tests, a standardized measurement protocol was established and applied to all samples. Each spectrum was acquired over a period of 1000 seconds, using an excitation current of 2 μA and a voltage of 28 kV in the X-Ray tube. All measurements were conducted under ambient air conditions.

The solid angle of detection covered a surface area ranging from 18.4% to 44.1% of each coin's total area. Assuming the coins are amalgamation products, the analyzed regions were considered representative of the bulk composition.

Quantification method

The concentration of each element present in the coins was determined using the Fundamental Parameter (FP), given in equation (1), which establishes a relationship between the intensity of the characteristic X-Ray emission (I_i) and the concentration (C_i) of a given element i, and can be expressed as:

$$I_i = C_i \cdot S_i \cdot A, \tag{1}$$

where I_i is the intensity of element (i), defined as the total number of detected photons divided by the measurement time (counts per second, cps); C_i is the concentration of element (i), expressed in micrograms per gram ($\mu g/g$); and S_i is the analytical sensitivity of element (i), given in cps$\cdot(\mu g/g)^{-1}$.

The matrix absorption factor (A), which accounts for the attenuation of both the excitation beam (with energy E_0) and the emitted characteristic X-Rays (with energy E_i), is given by:

$$A = \frac{1 - e^{-\chi \cdot \rho_0 \cdot D}}{\chi \cdot \rho_0 \cdot D}, \tag{2}$$

where ρ_0 is the matrix density, D is the total thickness of the sample, and χ is the absorption coefficient, defined as:

$$\chi = \frac{\mu_0}{\sin\theta_0} + \frac{\mu}{\sin\theta}, \tag{3}$$

with μ_0 is the mass absorption coefficient of the matrix at the incident photon energy, θ_0 is the X-Ray angle of incidence, μ is the mass absorption coefficient of the matrix at the characteristic energy, and θ is the output angle of the characteristic X-Ray.

The analytical sensitivity depends on different physical factors and can be written as:

$$S_i = G \cdot \varepsilon \cdot \tau \cdot w \cdot f \cdot \left(1 - \frac{1}{j}\right), \tag{4}$$

with G being the system geometry, ε the detector efficiency, τ the photoelectric effect coefficient, w the fluorescence yield, f the intensity of emission for a given Kα line, and $\left(1 - \frac{1}{j}\right)$ the jump ratio, representing the ionization of a shell in relation to other shells.

To apply this method effectively, it is essential to determine both the analytical sensitivity (S_i) of each element and the matrix absorption factor (A), which accounts for the attenuation of X-Rays within the sample. To simplify the determination of (S_i), ultrafine standards, samples with negligible matrix effects, are used. In these cases, the absorption factor (A) can be approximated as 1, allowing direct calculation of sensitivity from known concentrations.

By analyzing certified reference materials with known elemental concentrations, a sensitivity curve can be constructed by plotting (S_i) versus the atomic number (Z). This curve enables the derivation of an empirical equation relating sensitivity to atomic number, as described by Grieken and Markowicz (2001).

In this study, the coin samples are considered to have infinite thickness relative to both the excitation energy and the energy of the emitted characteristic X-Rays. This assumption simplifies the geometry and absorption modeling. Equation (1) can be rewritten as:

$$I_i = C_i \cdot S_i \cdot \frac{1}{\chi \cdot \rho_0 \cdot D}. \tag{5}$$

Given that the incident angle of the excitation beam and the emission angle of the characteristic X-Rays are equal in the pXRF system used, the absorption path lengths are symmetric. Under these conditions, the concentration (C_i) can be written as:

$$C_i = \frac{I_i}{S_i} \cdot \left(\frac{\mu_0}{\sin\theta} + \frac{\mu}{\sin\theta}\right) \cdot \rho_0 \cdot D, \tag{6}$$

which can be simplified to:

$$C_i = \frac{I_i}{S_i} \cdot (\mu_0 + \mu) \cdot \frac{\rho_0 \cdot D}{\sin\theta}. \tag{7}$$

The relative concentration of each chemical element, denoted as $W(\%)_i$, was determined by calculating the ratio between the concentration of element i (C_i) and the total concentration of all detected elements in the sample $\left(\sum_M C_M\right)$. This allows for a normalized comparison of elemental abundances across different samples. The relative concentration can be expressed as:

$$W(\%)_i = \frac{C_i}{\sum_M C_M}. \tag{8}$$

When calculating the relative concentration of an element, the term $\rho_0 \cdot D/\sin\theta$ is eliminated from equation (7), simplifying the expression. Additionally, the matrix absorption term ($\mu_0 + \mu$) is minimized and does not significantly interfere with the determination of the major elements present in the matrix (Grieken & Markowicz, 2001).

The percentage of each element is obtained by analyzing the photopeak area corresponding to each element, provided that the signal exceeds the detection limit of the equipment. In the coins analyzed in this study, the following elements were identified: Iron (Fe), Nickel (Ni), Copper (Cu), Silver (Ag), Mercury (Hg), and Lead (Pb).

To establish the sensitivity curve, a Micromatter® set of standard samples was used in conjunction with an X-Ray tube featuring a silver anode. The operating conditions were 28 kV and 2 μA in the X-Ray tube with a silver filter of 50 μm, 2.5 gain at the amplifier, and the time of excitation-detection was 1000 s.

The sensitivity equation for elements Fe ($Z = 26$), Ni ($Z = 28$), and Cu ($Z = 29$) determined using the K lines in the pXRF spectra is given by:

$$S_i = 0.0025 \cdot Z^2 - 0.0731 \cdot Z + 0.4939, \tag{9}$$

where Z is the atomic number of the respective elements, expressed within parentheses following the chemical symbol.

For the elements determined using the L lines, Ag ($Z = 47$), Hg ($Z = 80$), and Pb ($Z = 82$), the sensitivity was calculated using the following equation:

$$S_i = 0.0002 \cdot Z^2 - 0.0211 \cdot Z + 0.6005. \tag{10}$$

The equation (10) ensures accurate quantification of heavier elements, whose characteristic X-Ray emissions are more prominent in the L spectral region. The use of standard samples and controlled excitation conditions enhances the reliability of the sensitivity calibration across both K and L lines.

Principal Component Analysis

Principal Component Analysis (PCA) is a multivariate statistical technique that enables the differentiation of objects based on their individual characteristics within a group. Its primary objective is to reduce the dimensionality of the dataset while preserving the most relevant variance in the data (Wold et al., 1987).

To perform PCA, the data are organized into a matrix $X(n \times m)$, where n represents the number of samples (rows) and m represents the number of variables or responses (columns). In the context of data obtained via the EDXRF technique, each column corresponds to the count values for a specific channel, which can be mapped to an energy value based on the instrument's calibration.

The matrix X is then decomposed into two matrices:

$$X = T \cdot P' + R, \tag{11}$$

where T is the scores matrix, representing the projection of the samples onto the new coordinate system, P' is the loadings matrix, indicating the contribution of each original variable to the principal components, and R is the residual matrix, accounting for the variance not captured by the principal components.

The decomposition in equation (11) enables the visualization and interpretation of complex datasets by identifying patterns, clusters, and outliers, making PCA a powerful tool for exploratory data analysis in compositional studies.

The scores plot provides insight into the relationships among the samples, enabling the identification of groupings, trends, or outliers. In contrast, the Loadings plot reveals how each variable contributes to the observed variance in the dataset, offering a deeper understanding of the underlying structure (Wold et al., 1987).

The PCA analysis was conducted using MATLAB® software, focusing on coins that shared the same monetary value but were minted in different cities. The entire spectra obtained from the pXRF technique were used as input for the PCA, and a mean-centering preprocessing step was applied to normalize the data and enhance interpretability.

Results

Validation

To validate the results obtained using the methodology described above, a measurement was performed on a silver alloy standard material (RAg A4) from the *Museu Histórico Nacional* collection. The certified concentration values for this sample were provided by MBH Analytical Ltd., UK. Additionally, comparative measurements were conducted by the *Instituto Nacional de Tecnologia* (INT, National Institute of Technology) using a commercial bench-top XRF system. This comparison enabled an assessment of the accuracy and reliability of the laboratory-made pXRF system. The results revealed no significant discrepancies between the two systems, confirming the validity of the portable setup for compositional analysis. The comparative results are presented in Table 2.

Table 2 - Comparison between the results obtained using pXRF and the INT results for the concentration (%) of Copper and Silver in a Standard sample.

Rag A4									
		pXRF			**INT**			**Certified value**	
Elem.	**(Z)**	**Concentration**	**SD**	**Recovery**	**Concentration**	**SD**	**Recovery**	**Concentration**	**SD**
Cu-Kα	29	18.05	0.66	90 ± 3	20.73	n.i.	103.9 ± 0.4	19.95	0.12
Ag-Lα	47	81.07	1.53	101 ± 2	79.27	n.i.	99.1 ± 0.1	79.97	0.08

Note: n.i. – Not Indicated

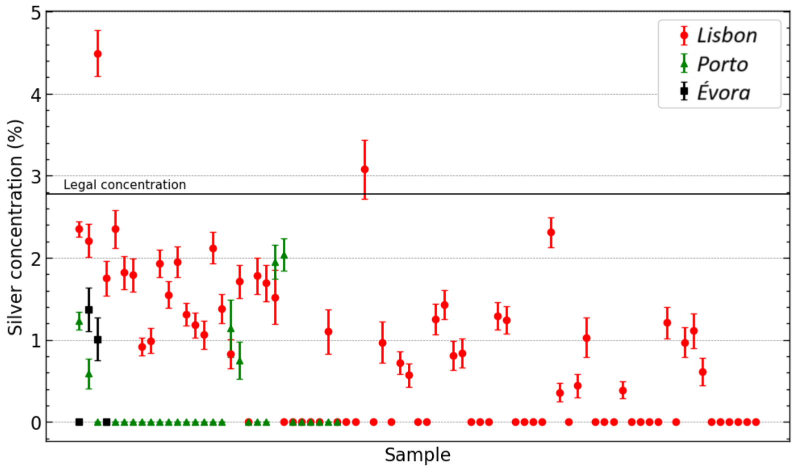
The elemental recovery rates obtained using the portable XRF (pXRF) system for the standard sample were $90 \pm 3\%$ for Cu and $101 \pm 2\%$ for Ag. These values demonstrate that the method employed is sufficiently accurate for determining the concentrations of these elements in the analyzed coins. Furthermore, the results confirm that the portable system yields measurements comparable to those obtained with commercial bench-top equipment, reinforcing its applicability for in situ compositional analysis in numismatic studies.

Quantitative results

An intriguing result emerged regarding the silver concentration in the analyzed coins. Historically, a base silver alloy known as billon was commonly employed in coin minting. Previous studies have indicated that Portuguese coins minted with billon typically contained approximately 8% silver and 90% copper (Guerra, 1995; Guerra et al., 1989; Martins & Martins, 2011).

During the reign of King Fernando (1367–1385), the legal silver content in coinage was officially reduced from 8.33% to 2.78% (Guerra et al., 1989), reflecting a significant debasement of the currency. Figure 2 presents the measured silver concentrations in coins from the subsequent reign of King João I, offering insights into the metallurgical continuity or reform following King Fernando's monetary policies.

Figure 2 - Comparative graphic of the Silver concentration in Portuguese coins minted in the different cities.



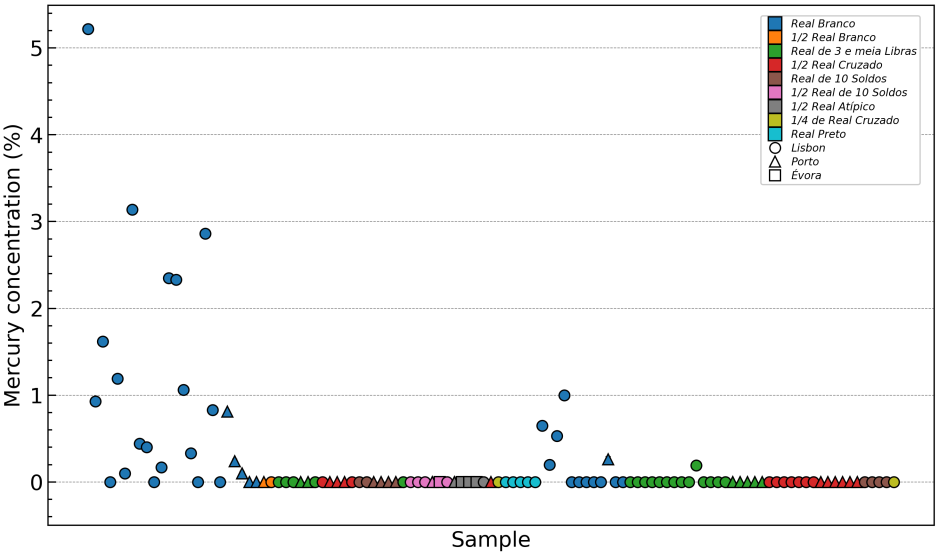
In Figure 2, the horizontal black line represents the legal silver content of 2.78%, as established during the reign of King Fernando. The data reveal that many coins lack detectable silver altogether, while several others contain silver concentrations below the legal threshold. Notably, only one coin exhibits a silver concentration within the expected legal range, and another exceeds it. The elevated silver concentration observed in that particular coin may be attributed to surface enrichment caused by corrosion processes, as suggested by (Felix et al., 2020). This phenomenon can lead to a misleadingly high surface silver content, which does not reflect the bulk composition of the alloy.

According to Oliveira (2014), the solubility of silver in copper is nearly zero at room temperature, rising to approximately 8.0% at 780 °C. This metallurgical property indicates that the absence of silver in the analyzed coins is not a consequence of the minting process, but rather reflects a true deficiency in the alloy composition. Despite this, the coins were still classified as billon coins, which traditionally implies the presence of silver.

This discrepancy supports two complementary hypotheses regarding the low silver content: economic pressures may have driven monetary devaluation, prompting the government to increase coin production to meet rising expenditures, even at the cost of reducing precious metal content; historical accounts suggest that some minters acted in bad faith, deliberately extracting silver from the coins during production (Fernandes, 1856), further contributing to the observed absence of silver. Together, these factors provide a compelling explanation for the debasement of coinage during this period, aligning metallurgical evidence with historical documentation.

The presence of mercury (Hg) and lead (Pb) was also detected in the analyzed coin samples. Mercury was identified in 24 samples, with concentrations ranging from 0.1% to 1.2%, and 90% of these fell within this range. Lead was found in 111 samples, with concentrations between 0.09% and 1.75%, encompassing 80% of the cases. The occurrence of Hg and Pb in these coins may be attributed to several factors, including impurities in the crude metals (silver and copper) used in the billon alloy, contaminants introduced during the minting process, possibly due to primitive refining techniques, or surface contamination accumulated over time (Pitarch et al., 2011). Figure 3 presents the mercury concentration data for all analyzed coins.

Figure 3 - Mercury concentration in all coins.



The presence of volatile metals such as mercury (Hg) in the coins may offer chemical evidence that the source of the billon alloy was native copper ore. One hypothesis suggests that Hg was introduced via groundwater, absorbed by the copper ore while it was buried (Oliveira, 2014). However, this explanation remains inconclusive due to the lack of consistent supporting data.

A more compelling hypothesis relates to the amalgamation process used in the extraction of silver from ore, a technique commonly employed during the period in which these coins were minted (Constantinescu et al., 2003). This process involves the use of mercury to bind with silver, facilitating its separation from other materials. A comparative analysis of the mercury (Hg) concentration, shown in Figure 3, and the silver (Ag) concentration, are presented in Figure 4.

The comparison, in Figure 4, reveals that mercury is present exclusively in samples that also contain silver. This correlation strongly supports the amalgamation hypothesis, while discrediting alternative explanations such as contamination from groundwater or crude copper, which would likely result in mercury appearing in samples regardless of silver content. This pattern was also observed by Felix et al. (2020), reinforcing the conclusion. The presence of mercury (Hg) consistently coincides with the presence of silver (Ag), lending strong support to the theory that amalgamation was the source of mercury in these coins.

Figure 5 shows the results for the concentration of Pb in all coins. Most coins present Pb in its composition.

Lead (Pb) exhibits a strong tendency to bond with other elements due to its large atomic radius and dense atomic structure. Within the copper matrix, Pb forms thin, dispersed particles, a phenomenon attributed to its low melting point and limited solubility in copper (Oliveira, 2014). These dispersed particles suggest that Pb does not fully integrate into the copper lattice, instead remaining as isolated inclusions.

Figure 4 - Mercury and Silver concentration in all coins.

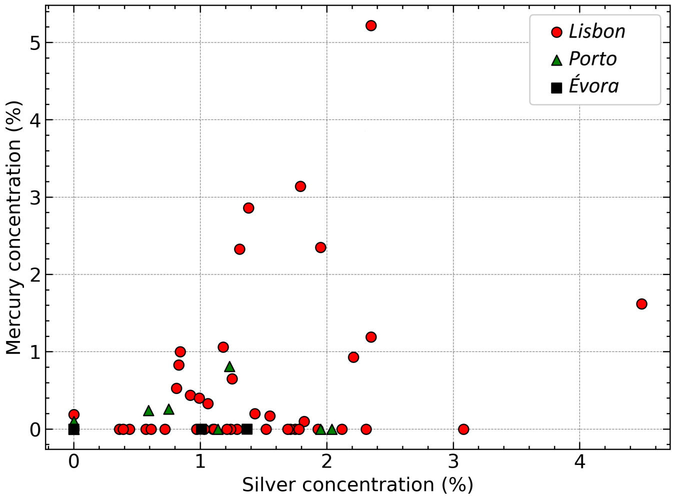
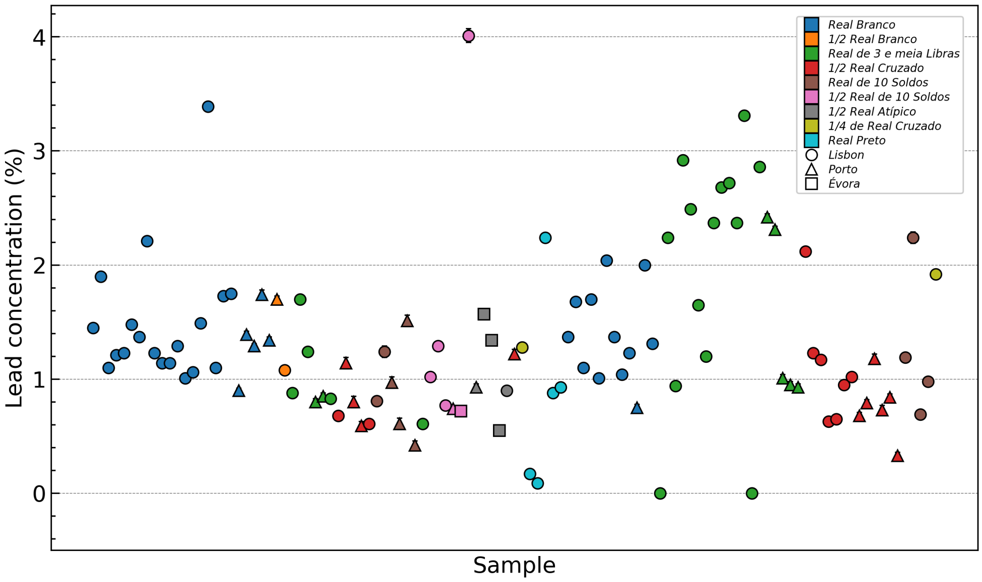


Figure 5 - Lead concentration in all coins.



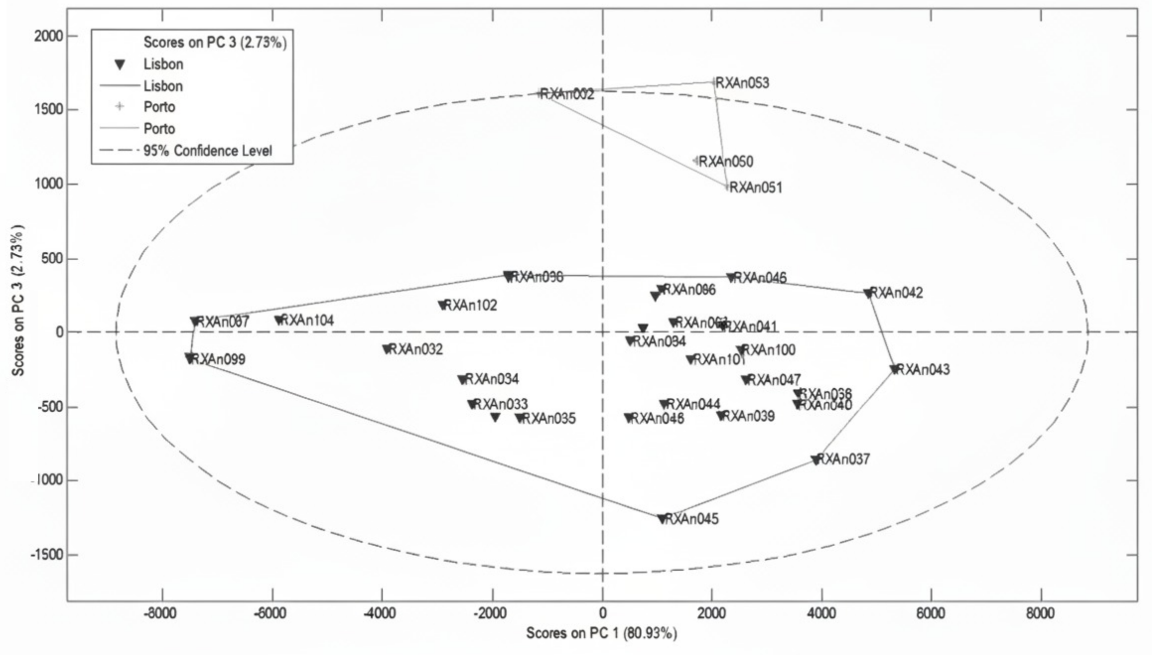
An alternative hypothesis proposes that the presence of Pb is linked to the metallurgical processes used in the extraction and refinement of silver. Lead was commonly employed in historical silver metallurgy, particularly in cupellation, where it helps separate silver from other impurities. Pb may also have played a role in the coin minting process itself, as suggested by Pitarch et al. (2011).

Importantly, the quantity of Pb detected in the coins can serve as an indicator of the refinement quality: lower concentrations of Pb typically reflect a more advanced or thorough refining process (Oliveira, 2014). Therefore, analyzing Pb levels not only informs us about the alloy composition but also provides insight into the technological sophistication of the minting practices during the period.

Principal Components Analysis results

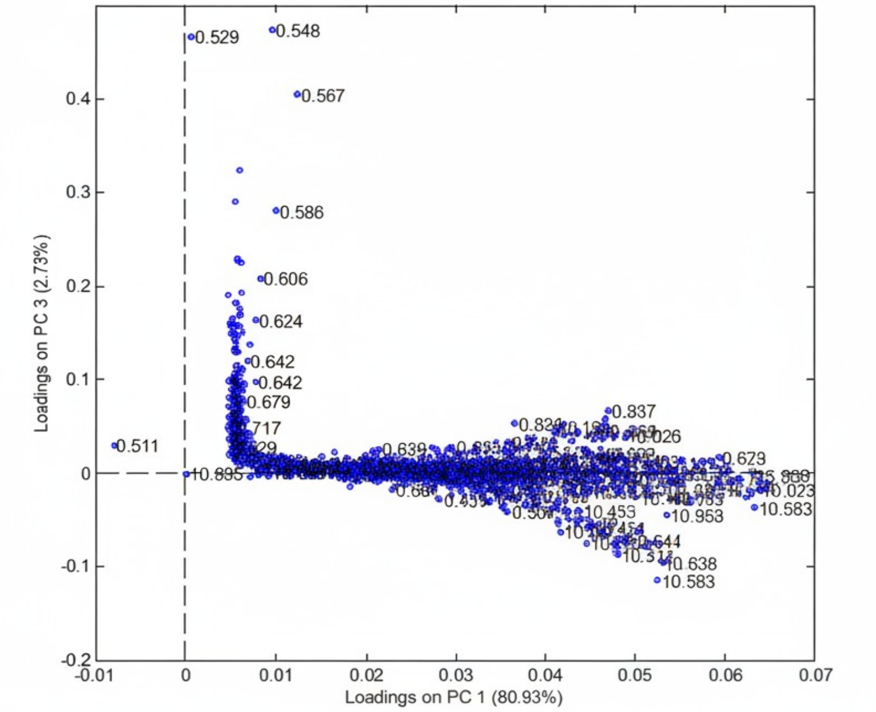
Figure 6 shows the Principal Component Analysis results for *Real Branco* coins. The PCA of the coin dataset revealed two key insights into the minting practices of the coins: the nature of the raw materials used and the possible origin of their production.

Figure 6 - Scores on *Real Branco* coins.



The scores plot in Figure 6 indicates that principal component 1 (PC1) accounts for 80.93% of the variance, effectively distinguishing the *Real Branco* coins based on their lead (Pb) content. This separation is further clarified in the Loadings plot, Figure 7, where the La line of lead at 10.552 keV emerges as a dominant contributor to PC1. This spectral feature reflects the quality of the alloy, consistent with the earlier discussion on Pb dispersion and its implications for refinement processes (Oliveira, 2014; Pitarch et al., 2011).

Figure 7 - Loadings on *Real Branco* coins.



Together, these PCA results suggest that variations in lead concentration not only differentiate coin samples but also point to differences in metallurgical techniques and material sources, offering valuable clues about the technological and geographic origins of the minting process.

In contrast to the chemical differentiation captured by PC1, principal component 3 (PC3), which accounts for 2.73% of the variance, was responsible for distinguishing coins minted in Lisbon from those minted in Porto, as shown in the Loadings plot, Figure 7. This separation is associated with a signal at approximately 0.548 keV, a region not attributable to any known chemical element detected in the measurements.

Importantly, this energy cannot be attributed to electronic noise, since such noise would produce a consistent peak across all samples, failing to generate any separation. Instead, this signal is interpreted as a physical characteristic of the coins, likely stemming from the minting process itself. Specifically, the scattering of the excitation beam in this energy range is influenced by surface roughness, which varies depending on the mechanical techniques used during coin production.

Based on the PCA findings, it can be inferred that coins minted in Porto exhibit distinct physical features compared to those from Lisbon. These differences are linked to the manual striking process, where mintmarks were engraved by applying a hammer to the upper die. As described by Neiva et al. (2005), the senior minter held responsibilities such as aligning mint markers and ensuring quality control, which could introduce subtle but consistent variations between mints.

Therefore, the PCA analysis not only highlights chemical distinctions in alloy composition but also uncovers physical minting signatures, reinforcing the idea that regional minting practices left measurable imprints on the coins.

Conclusions

The Portable X-Ray Fluorescence (pXRF) technique proves to be a highly valuable tool for the analysis of coins considered historical heritage. Its non-destructive and portable nature allows researchers to examine artifacts in situ, preserving their integrity and enabling studies within museum environments where removal is not permitted.

Through pXRF, the elemental composition of the metal alloys used in the minting of Portuguese coins was successfully quantified. When combined with Principal Component Analysis (PCA), the data enabled a robust classification of the coins according to the city of origin, distinguishing those minted in Lisbon from those minted in Porto.

This integrated approach not only enhances our understanding of historical minting practices but also demonstrates the power of analytical chemistry and statistical modeling in uncovering cultural and technological insights from heritage materials.

The results presented in this study reinforce historical accounts and previously published research indicating that the intense military activity during the reign of King João I had a direct economic impact, particularly on the minting of coins. This period of conflict led to a reduction in the availability of precious metals, notably silver (Ag), used in coin production.

A significant number of coins analyzed contained no detectable silver, while those that did exhibited Ag concentrations below the legally established threshold of 2.78%. Only one coin exceeded this legal standard, and another met it precisely, highlighting the inconsistency in alloy composition during this economically strained era.

These findings underscore the economic pressures faced during King João I's reign and provide material evidence of how wartime conditions influenced monetary practices, aligning with documented historical narratives.

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Author Contributions

G. A. L. Nogueira: conceptualization, data curation, formal analysis, investigation, writing - original draft, supervision, validation, visualization, writing - review and editing. **P. S. Parreira**: conceptualization, data curation, formal analysis, investigation, methodology, writing - original draft, supervision, validation, visualization, writing - review and editing. **R. B. Scorzelli**: data curation, funding acquisition, supervision, validation, visualization, writing - review. **C. R. Appoloni**: conceptualization, data curation, formal analysis, investigation, supervision, validation, visualization, writing - review and editing.

Conflicts of Interest

The authors declare no conflict of interest.

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