COMPOSITIONAL STUDY OF ANCIENT COINS FOUND IN DURRËS USING DIFFERENT ANALYSIS METHODS

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Abstract

Archaeological investigation is challenging, especially in coins' cases, because of the sampling difficulties, at the same time, very important to understand the political and economic developments of a certain region and period. In this paper we studied seven coins excavated in a monument in the center of Durrës (ancient city of Epidamnos, Dyrrah), Albania. The study of these coins is done in collaboration with the archaeologists of the Archaeological Museum Durrës, although they were already damaged. The aim of this study is to investigate the alloy composition used in the cases of these coins, all excavated among other metallic objects in Durrës. Laser-induced breakdown spectroscopy (LIBS) and X ray fluorescence (XRF) were used to qualitatively determine the composition of the coins. All the objects of this study had a variety of compositions from pure Cu to Cu-Sn-Pb-Fe alloys. The elemental composition of the coins was compared with what was previously determined with μ - X ray fluorescence (μ-XRF). Qualitative results of the two methods were on average significantly similar, as affirmed by values of Jaccard Similarity coefficients calculated. These average values were 0.52 for μ-XRF - XRF of the UI, 0.65 for LIBS - XRF of the UI and 0.67 for LIBS - μ-XRF. LIBS qualitative composition of studied coins was also compared by means of respective Jaccard Similarity coefficients for each pair of coins. Results show significant similarity among coins. Coins with file no 8414, 8378, 8321, 8408 and 8342 show the highest average similarity with others, while the ones with file no 8382 and 8425 present the lowest.

Key words: *coins, Albania, LIBS, XRF, elemental composition, Jaccard Similarity coefficients.*

Përmbledhje

Studimi arkeologjik është sfidues, sidomos në rastet e monedhave, për shkak të vështirësive të marrjes së kampionëve, në të njëjtën kohë, shumë i rëndësishëm për të kuptuar zhvillimet politike dhe ekonomike të një rajoni dhe periudhe të caktuar. Në këtë artikull kemi studiuar shtatë monedha të zbuluara në një monument në qendër të Durrësit (qyteti antik i Epidamnos, Dyrrah), Shqipëri. Studimi i këtyre monedhave u krye me bashkëpunimin e arkeologëve të Muzeut Arkeologjik Durrës, edhe pse ato tashmë ishin dëmtuar. Qëllimi i këtij studimi është të hetojmë përbërjen e përlidhjeve të përdorura në rastet e këtyre monedhave, të gjitha të zbuluara mes objekteve të tjera metalike në Durrës. Spektroskopia LIBS dhe fluoreshenca me rreze X (XRF) u përdorën për të përcaktuar në mënyrë cilësore përbërjen elementore të monedhave. Të gjitha objektet e këtij studimi kishin një shumëllojshmëri kompozimesh nga Cu i pastër deri te përlidhjet Cu-Sn-Pb-Fe. Përbërja elementore e monedhave u krahasua me atë që ishte përcaktuar më parë me μ - fluoreshencë me rreze X (μ-XRF). Rezultatet cilësore të dy metodave ishin mesatarisht shumë të ngjashme, siç afirmohen nga vlerat e koeficientëve të ngjashmërisë Jaccard, që janë llogaritur. Këto vlera mesatare ishin 0.52 për μ-XRF - XRF të UI, 0.65 për LIBS - XRF të UI dhe 0.67 për LIBS - μ-XRF. Përbërja cilësore e përftuar me LIBS e monedhave të studiuara u krahasua gjithashtu me anë të koeficientëve përkatës të ngjashmërisë së Jaccard për çdo çift monedhash. Rezultatet tregojnë ngjashmëri të konsiderueshme midis monedhave. Monedhat me nr. kartele 8414, 8378, 8321, 8408 dhe 8342 rezultuan të kenë ngjashmërinë mesatare më të lartë, ndërsa ato me nr. kartele 8382 dhe 8425 paraqitën më të ultën.

Fjalë kyçe: *monedha, Shqipëri, LIBS, XRF, përbërje elementore, koeficientët e ngjashmërisë Jaccard.*

Introduction

Epidamnos or Dyrrah (Durrës) was among the largest cities of the ancient and medieval Mediterranean region. According to (Çakaj et al, 2023), the city of Dyrrah was built by the Illyrian tribe of Taulants, in the XIII-XI centuries B.C. The Pelasgians are considered as the first inhabitants of Dyrrah before the Illyrians. They built the first prehistoric settlements in the surroundings of the city, as the Erzen River shore was suitable for living, as well as the lowlands around and further west. This took place because of appropriate and favorable Mediterranean climate conditions.

The first port named Dyrrah was established where today is the actual port of Durrës. Two kings of Illyrian origin, Dyrrah and Epidamn, founded this ancient city. (Bowes et al, 2009) write that Durres was the principal city of Epirus Vetus and the land terminus of the Via Egnatia, the road that throughout late antiquity and the Byzantine period linked Rome to Constantinople. Durrës also sat on a major Adriatic trade route linking the northern Greek Islands to Dalmatia and northern Italy. Thus, like Marseilles or Thessaloniki, Durrës was a place where road met sea and the cultural currents of east and west mingled.

During the Iron Age, production of the first coins began, such as the Greek silver ones (year 580 B.C.), the gold coins from Lydia, west of Turkey (year 550 B.C.) and those of King Philip of Macedonia (year 350 B.C.). Alloys of gold and silver with copper began to be produced, so coins would become harder, cheaper and last longer. The main production process of coins was stamping (Çakaj et al, 2023).

Coins of the 4th century BC were mostly spread on the coastal area of the Adriatic Sea, which evidences maritime trade, and also in Sicily, which is the result of military campaigns. In the 3rd century BC, coins of Dyrrah appear in the territory of modern Romania and Bulgaria, or in coastal cities, witnessing the development of land and sea trade routes. Colonists from Corinth brought also new technologies and arts, and metal money as their means of trade. Later, the citizens of Dyrrah learned to produce their own coins, which is where the history of the development of the coin business of this city begins. Their own coinage, largely similar to that minted at Corinth, showed some differences. In particular, an image of a cow feeding a calf was placed on the obverse, and a square with a characteristic star pattern was depicted on the reverse. From the 4th century BC, bronze coins were minted in Dyrrah, with an exchange value lower than that of silver coins and many times higher a variety (Kasa, 2024).

The raw material used for the production of an object gives important information about it and its origin as well. The characterization of archaeological artefacts is interesting and challenging from the historical, conservation and restoration points of view to shed light on the environmental conditions, habits, economy, raw materials resources and the technology level of ancient societies. The composition of the archaeological artefacts and damage diagnosing are very helpful for the conservation and restoration process, as well as the authentication of objects (Arafat et al, 2013).

The use of proper analytical methods to determine the chemical constituents of examined objects has become a necessary component of the systematic analysis of cultural heritage objects. Objects made of metal or metal alloys have been widely used since metallurgy was invented. The main materials used include copper and bronze (copper-tin alloys in the Bronze Age), and later iron. Other metals used include lead and tin. Also, metal alloys have been extensively used in coinage (Anglos et al, 2014). Copper forms alloys with tin to reduce the melting temperature, increase the hardness and resistance from corrosion, also lowering brittleness. Lead added in bronzes precipitates along grain boundaries because it is not soluble in copper. Lead also lowers the melting temperature, increases the fluidity of metal during casting and the object surface quality, as well as reduces the cost of production (Scott, 1991; Scott, 2012).

Cultural heritage diagnostics and composition determination deals with the complexity and diversity of materials and also with limitations imposed by non-sampling policies. Transportation of these objects in laboratories often requires complicated and long bureaucratic procedures. The potential of LIBS with this regard has been shown by several research papers that have appeared in the last few years.

Laser Induced Breakdown Spectroscopy (LIBS) is a type of atomic emission spectroscopy which uses a highly energetic laser pulse as the excitation source. The laser is focused to form plasma, which atomizes and excites samples. In recent years, several groups have proposed the use of LIBS as capable of giving information on the sample compositions with minimal damage to the artwork, being minimally invasive, even though not a strictly non-destructive technique. It allows determination of all elements with a single measurement in a few seconds. In LIBS measurements, samples do not need chemical treatment and so the risk of their contamination is minimized (Melessanaki et al, 2002; Tzortzakis et al, 2006; Gaona et al, 2013).

Materials and methods

LIBS method consists in the use of an intense laser pulse focalized on the sample surface, which causes evaporation, atomization and ionization of the material. This produces plasma, which expands and cools very rapidly. It emits fluorescence characteristic radiation of the neutral or ionized atoms in the plume, which represent the elemental content of the solid surface probed. LIBS spectrum proper interpretation yields the compositional information of the material examined by the characteristic, sharp atomic emission peaks in the spectrum, reflecting the local elemental composition of the sample. Delivering a certain number of laser pulses on the same spot, one can monitor the elemental content of successive layers. The technique offers unparalleled speed and a nearly microscopic spatial resolution (Anglos et al, 2014; Cristoforetti et al, 2006; Harith, 2013). However, one of the most stringent constraints to the application of LIBS technique to cultural heritage studies is the use of reference calibration standards, because of the matrix effect (Melessanaki et al, 2002).

XRF is the emission of characteristic secondary X-rays from a material that has been excited by being bombarded with high-energy X-rays or gamma rays. Ionization of the component atoms takes place and may occur if the atom is exposed to radiation with an energy greater than its ionization energy. Energetic enough x-rays expel tightly held electrons from the inner orbitals making the electronic structure of the atom unstable, with electrons in higher orbitals “falling” into the lowers, releasing an energy photon characteristic of the atoms present, thus determining and quantifying the chemical composition of various materials (Salimbeni and Pezzati, 2005; Potts and West, 2008).

The radiation source for the LIBS configuration used is a 30fs laser system, with 0.39 mJ/pulse (DUO Legend Elite) power, wavelength 800 nm and with 10 Hz frequency. Femtosecond laser pulse (Ti: Sapphire Femtosecond laser) focuses on the surface of the sample and the light emitted by the plasma is collected by means of an optical fiber, located near the plasma plume and inserted into a spectrograph, and the light is collected by the electrons; the size and array of which determine spectral resolution. The laser beam has an initial diameter of 1cm and focuses using a convex lens with a focal distance of 23 cm. Control over peak intensity is achieved using several filters with neutral density in a high degree. Radiation emitted by laser-induced plasma is collected by a collimator (Andor ME-OPT-0007) and then analyzed using a closed spectrograph (Andor iStar). To be able to simultaneously study a wide part of the emitted spectrum (200-60 nm) a 150 line/mm grid is used. This also guarantees better light collection efficiency for the iCCD closed camera.

For the XRF analysis, Bruker M6 JETSTREAM XRF scanner was used. The technical characteristics are as follow: X-ray tube with micro-focusing; working voltage 50 kV; Rh anode with 600µA current; polycarpellary lens; analysis area (spot) adjustable from 100 µm to 600 µm (spot diameter); dual 60 mm^2 SDD detector; the range of detectable elements from Na to U; the image of the sample in real time is obtained with two colour cameras, which capture images with dimensions of 30 by 22 mm^2 and 11 by 8 mm^2, respectively; high zoom camera allows changing the focal length to adjust the working distance. The main advantage of this device is the scanning of the sample and the acquirement of elements distribution maps (elements mapping). The scanned area is 800 (width) x 600 (height) mm^2, minimum step size 10 µm and maximum scan speed 100 mm/s. The device is accompanied by the software for mechanical control and spectrum analysis.

LIBS and XRF analysis of seven coins (Fig. 1) were carried out in the Department of Physics, at the University of Ioannina.

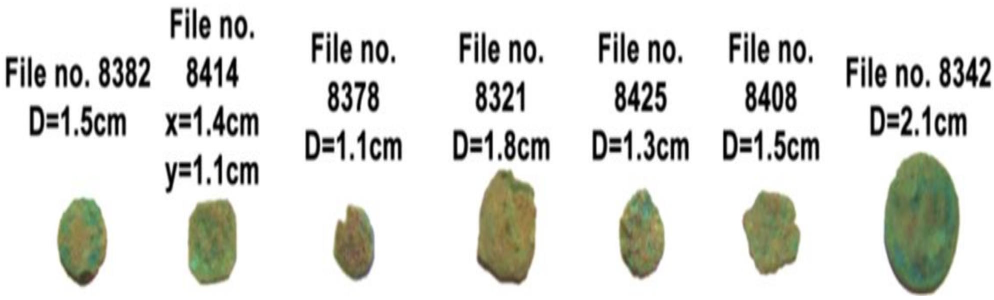


Figure 1. The seven coins at the center of this study (D - diameter, x - width, y - length) (Çakaj et al, 2023).

The studied coins were found in a macellum monument in the centre of Durrës among ceramics and other metallic objects. The monument of Macellum-Forum in the centre of Durrës (Fig. 2) was discovered in 1986 and the excavations of the year 2000 brought to light many ceramics and metallic objects. The monument was built around 500 A.D. in honour of Anastasius emperor and the influence of the architecture came from the Roman Empire (Çakaj et al, 2023).

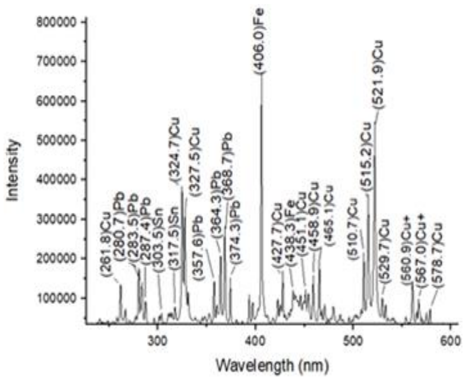
Excavations revealed an extensive complex of concentric structures of the Late Roman and Early Byzantine eras. Initially, it was identified as a market complex (*macellum*) of a type known in numerous Roman cities. The circular paved area of a diameter of 40m within a colonnade at the centre represented a space intended for more formal activities, a Forum comparable with the Curved Forum at Constantinople. A central focus of the area was a rotunda of 5.75 m diameter that may have supported monumental statuary or possible a column. The dating evidence recovered from beneath the level of the Forum paving indicated a construction date around the end of the sixth century (Hoti et al, 2011).

Figure 2: The Macellum Forum in the center of Durrës

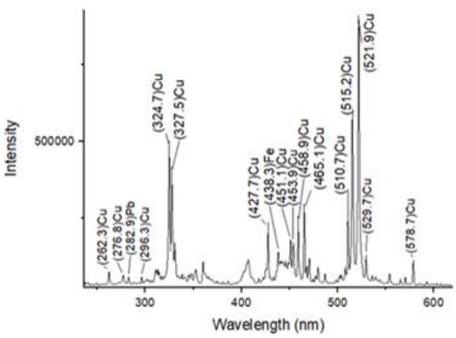
Results and discussions

Respective spectra for the seven coins are presented in Figure 3 and qualitative results are summarized as part of Table 1. All analyzed coins are copper alloys, as expected. From the LIBS results, coins with file no 8414, 8378, 8321, 8408 and 8342 consist of a Cu-Pb-Fe alloys, while coins with file no 8382 and 8425 contain Cu, Pb, Sn, Fe. Cooper and bronze were used during the Bronze Age, while iron was an element that was added in a later period to metal objects in general, and coins in particular. So, one could hypothesize that these coins might belong to a later period than the Bronze Age.

Lead added to bonzes, as it is not soluble in cooper, increases the fluidity of the metal, making it easier to work with, resulting in a better surface quality and lower production cost, as one could suggest for the coins of this study.



a)



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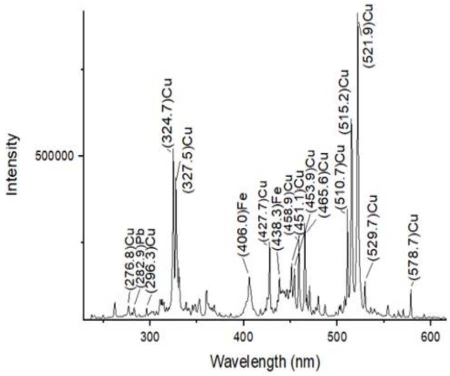

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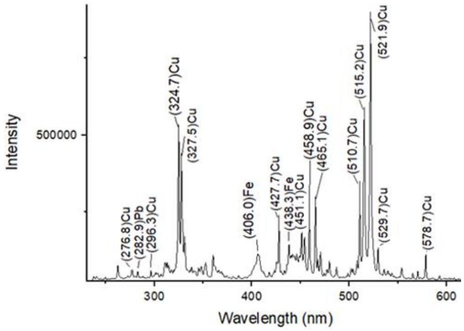

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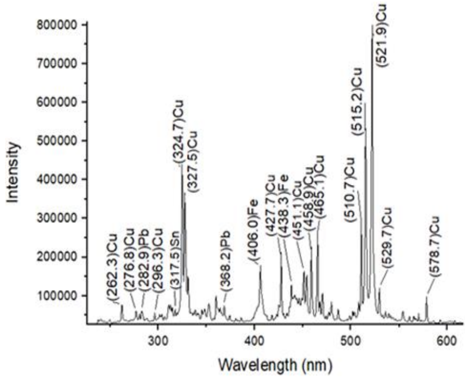
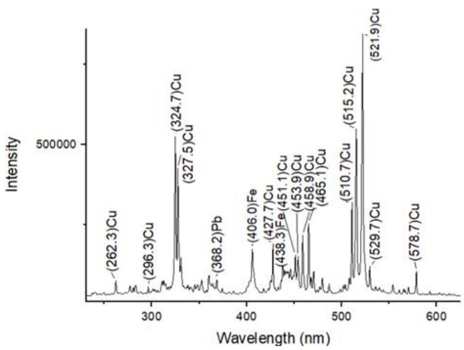
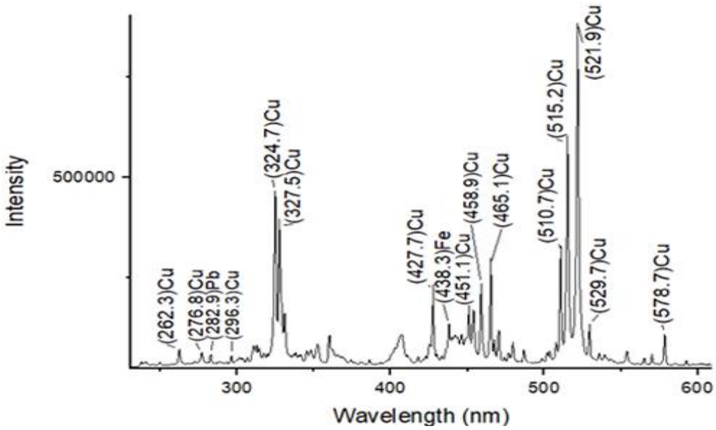


e)



f)



g)

Figure 3. The LIBS spectra for the seven coins with file no.: a) 8382, b) 8414, c) 8378, d) 8321, e) 8425, f) 8408, g) 8342.

The seven coins of this study have been also analyzed with XRF at the Department of Material Sciences at the University of Ioannina and previously analyzed by means of μ-XRF according to Çakaj et al, 2023. We considered the comparison of the results of the two different methods, as being interesting, despite the fact that our LIBS study provided only a qualitative evaluation of the composition elements of these coins.

(Wallace et al, 2020) affirm that LIBS is a micro-destructive and corrosion-penetrating method, while XRF has a very limited penetration. There are studies showing that mechanical cleaning before XRF (often not permitted in museums) can spare intragranular corrosion rather than giving results truly representative of the bulk (core) metal. Thus, destructive abrasive cleaning of the type used in some studies is unlikely to be consistently reliable.

The potential ability of LIBS to burn down to the original metal surface through corrosion in a small area is attractive. Other factors influencing differences between results of the two methods include whether the objects are precisely measured under the same conditions, or whether they are homogeneous or not. Corrosion structure might have minor distorting effects on XRF measurements or LIBS could fail to penetrate fully through corrosion or its results could be influenced by plasma geometry (Wallace et al, 2020).

Table 1 summarizes elements detected in respective coins.

Table 1. Elements detected in the seven coins and respective analysis.

Coin with file no	**Elements**					**Analysis**
8382	Cu	Pb				XRF Çakaj et al, 2023
	Cu	Pb	Sn			XRF UI
	Cu	Pb	Sn	Fe		LIBS UI
8414	Cu	Pb	Fe	Sn	Cr	XRF Çakaj et al, 2023

	Cu					XRF UI
	Cu	Pb	Fe			LIBS UI
8378	Cu	Pb	Sn			XRF Çakaj et al, 2023
	Cu	Pb				XRF UI
	Cu	Pb	Fe			LIBS UI
8321	Cu	Pb	Fe			XRF Çakaj et al, 2023
	Cu	Pb				XRF UI
	Cu	Pb	Fe			LIBS UI
8425	Cu	Pb	Fe			XRF Çakaj et al, 2023
	Cu	Pb	Sn			XRF UI
	Cu	Pb	Sn	Fe		LIBS UI
8408	Cu	Pb	Fe	Cr		XRF Çakaj et al, 2023
	Cu	Pb				XRF UI
	Cu	Pb	Fe			LIBS UI
8342	Cu	Pb	Fe	Cr	Ni	XRF Çakaj et al, 2023
	Cu	Pb				XRF UI
	Cu	Pb	Fe			LIBS UI

To make a comparison between sets of our qualitative data, we decided to use the Jaccard Similarity coefficient, based on the presence or absence of specific elements (Niwattanakul et al, 2023, Butcher, 2018). The Jaccard Similarity coefficient measures the similarity between two data sets as follows:

$$\text{Jaccard Similarity} = \frac{\text{Number of common elements}}{\text{Total number of distinct elements}}$$

We calculated respective Jaccard Similarity coefficients for each pair of coins and for each pair of analysis. Results are presented in Table 2 and Table 3.

Table 2. Jaccard Similarity coefficients for each pair of studied coins. LIBS results. (Av.J.S.=Average Jaccard Similarity)

Coin with file no.	8382	8414	8378	8321	8425	8408	8342
8382	1	0.75	0.75	0.75	1	0.75	0.75
8414	0.75	1	1	1	0.75	1	1
8378	0.75	1	1	1	0.75	1	1
8321	0.75	1	1	1	0.75	1	1
8425	1	0.75	0.75	0.75	1	0.75	0.75
8408	0.75	1	1	1	0.75	1	1
8342	0.75	1	1	1	0.75	1	1
Av. J. S.	**0.82**	**0.93**	**0.93**	**0.93**	**0.82**	**0.93**	**0.93**

Table 3. Jaccard Similarity coefficients for each pair of analysis (University of Ioannina - UI). (Av.J.S.=Average Jaccard Similarity)

Coin with file no.	Çakaj et al 2023 - µ-XRF / UI - XRF	UI - XRF / UI -LIBS	UI - LIBS / Çakaj et al 2023 - µ-XRF
8382	0.67	0.75	0.5
8414	0.2	0.33	0.6
8378	0.67	0.67	0.5
8321	0.67	0.67	1
8425	0.5	0.75	0.75
8408	0.5	0.67	0.75

8342	0.4	0.67	0.6
Av. J. S.	**0.52**	**0.65**	**0.67**

One can see (Table 2) that coins with file no 8414, 8378, 8321, 8408 and 8342 show the highest average similarity with others, while the ones with file no 8382 and 8425 are the least similar with the studied coins. Average Jaccard Similarity coefficients take values in the interval [0.82, 0.93], so we might consider a high similarity among coins. Note that the values of Jaccard Similarity coefficients lie in the interval [0, 1]. Cu is the element found in every coin, followed by Pb, Fe and Sn in most of the cases.

Table 3 shows that the average Jaccard Similarity coefficient for the two XRF analysis is 0.52 while the one for XRF versus LIBS, analysis performed at the University of Ioannina, is 0.65. The low average Jaccard Similarity coefficient for the two XRF methods might be explained with the different analyzing conditions. The highest average Jaccard Similarity coefficient of 0.67 belongs to LIBS versus µ-XRF Çakaj et al 2023. More accurate statistical comparisons will need a larger number of analytical results.

Conclusions

Based on the results showing the elemental composition using µ-XRF (Çakaj et al, 2023), XRF and LIBS (University of Ioannina), we can make some qualitative inferences about the potential production technique of the coins. However, it is important to note that a definitive determination of the production technique would require additional information and potentially more advanced analysis techniques.

- The presence of consistent elements (e.g. Cu, Pb, Fe, Sn) across most coins suggests a consistent base composition of the coins, which could indicate a standardized production process.
- The presence of specific elements like Cr and Ni could suggest intentional alloying for certain properties or purposes such as enhancing durability or appearance.
- The variations in detected elements between XRF and LIBS may imply differences in the sensitivity or specificity of the techniques or variations in the surface composition versus bulk (core) metal composition.

- Coins with high Jaccard Similarity, especially in major elements, could suggest a similar alloy composition and potentially a standardized production method.
- If certain coins have consistently additional elements in one technique not the other, it may suggest differences in the production process or post production treatments.

It is important to consider that analyzing the production technique of the coins requires a holistic understanding considering historical, archaeological, metallurgical and contextual information.

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