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Elemental analysis by XRF and HE-PIXE on silver coins from the 16th - 17th centuries and on a gilded crucifix from the 12th century

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Abstract

Objects from the Dobrée Museum (Grand Patrimoine de Loire-Atlantique, conservation unit), silver coins minted in Nantes between the years 1561 and 1599 and a 12th-century fire-gilded crucifix were studied. The goal is to analyze trace elements in coins to determine silver sources and measure the thickness of the fire-gilding layer to provide information about the manufacturing technique of the crucifix. We focused on X-ray emission-based analysis, especially High Energy Particle Induced X-ray Emission (HE-PIXE) developed at ARRONAX cyclotron and handheld X-Ray Fluorescence (p-XRF) used at Arc'Antique laboratory. In this paper, four coins have been analyzed with HE-PIXE and p-XRF and three different locations on the crucifix. We detected indium and gold as silver markers in coins and we measured the thickness of the layer of gold on the crucifix. Those data are helpful to answer historical questions relative to the objects.

Keywords: Artefact, cultural heritage, X-ray spectroscopy, fire-gilding, raw materials, non-destructive techniques

1-Introduction:

The present study looks at two examples of metallic artefacts including silver coins minted in Nantes from 1561 to 1599 and a 12th century crucifix conserved in Dobrée Museum, Nantes. A study of the origin of the raw material used to mint those coins is crucial information to trace the silver supply in Nantes and understand the impact of geopolitical conflicts on trade. Based on previous works [1], [2] we decided to search for indium and gold trace elements in a silver matrix to follow ancient metal flux in Nantes monetary workshop. Regarding the crucifix, the remaining gilded areas on the J-C statuette and the cross are an essential aspect of the object. We want to characterize the manufacturing process by looking at the gold layer thickness and evaluate gilding homogeneity/heterogeneity.

For those purposes, we will use HE-PIXE and p-XRF techniques. The analysis is ongoing in Nantes with teams of ARRONAX Cyclotron, Subatech, IMN and Arc'Antique laboratories. Development of HE-PIXE

[3] shows that we can reach the tens ppm limit of detection for metallic elements using high energy beams, we will concentrate this work on indium and gold detection in silver matrix. The handheld device available at Arc'Antique could be used to detect gold in a larger amount of coins and so, we can concentrate HE-PIXE analysis to improve the indium detection limit. Gold quantification is made with HE-PIXE on a reference coin to calibrate p-XRF values. HE-PIXE could also be used to probe thick targets [4] thanks to the large particle range in the material and high K X-ray cross-section. We used K X-ray emitted by the crucifix's gold layer to measure its thickness. Because beam time is limited and HE-PIXE experiments imply object immobilization after irradiation, p-XRF analysis on the corpus studied is helpful to complete HE-PIXE analysis. Crucifix thickness measurements with HE-PIXE don't cover all the gilded area, p-XRF could be used to analyze other points of interest using HE-PIXE values as references. This work illustrates our analytical possibilities in Nantes to study cultural heritage objects with non-destructive methods like HE-PIXE and p-XRF.

In the next sections, we will detail the corpus studied in a historical context, explain the analytical setups and methodology and discuss the first results obtained for coins and crucifix analysis.

2-Corpus studied in historical context and the associated research problems

2.1-Silver coins

The Spanish crown has exploited a rich silver deposit in the city of Potosi since 1545. The supply of silver from Potosi rapidly exceeded Mexican production [5] and replaced the old silver stocks in Europe for the manufacture of coins. Spanish coins minted with Andean silver were then converted into French currency. Nantes occupied an important position on the Potosi money route.

The recycling of coins was a common practice, making it difficult if not impossible to determine if the Spanish or French coins were struck with pure silver coming directly from Potosi or if they were made from a mixture of silver from several sources, including Mexican or European ores and coinage [2]. Fortunately, Potosi silver deposits are *"characterized by measurable quantities of elements, which are quite rare, like indium. The presence of gold together with such element fingerprints the ore"* [2, p. 89]. As is the case for other trace elements such as palladium in Brazilian gold [5], indium is the tracer for Potosi silver, *"Bolivian silver with high indium contents also has a low concentration of gold"*. According to a previous study[2, p. 88], the arrival of Potosian silver in France was estimated to date back to 1575. We analyzed a coin from 1561 (Henri II-Teston) (see Figure 1 and Table 1) when Potosian silver had not arrived in France yet.



Figure 1 Coin minted in Nantes in 1561 head of Henri King of France

In France, ideological conflicts between Protestant and Catholic factions led to the War of the League (1588-1598), a civil conflict that was particularly intense in Britain until Henry IV signed the "Edit de Nantes" on April 30, 1598. The year 1598 is quite interesting to look at because Nantes was besieging under Charles X (king of the catholic league) and so it was no longer supplied in silver from common

trade routes. We analyzed two coins minted in Nantes in 1598, one during the siege (*Charles X*) and one just after the arrival of Henri IV in Nantes in 1598 (*see table 1 below*).

Table 1 Coins studied

Reign	Year	Monetary workshop	Denomination	Legal % Ag
Henri II	1561	Nantes	Teston	89.9
Charles X	1598	Nantes	¼ d'écu	91.7
Edict of Nantes 30th of April 1598 (peaceful act)				
Henri IV	1598	Nantes	¼ d'écu	91.7
Henri IV	1599	Nantes	¼ d'écu	91.7

The last coin we analyzed was minted in 1599 during a period of peace, more favorable to trade.

A set of 16th – 17th-century French silver coins were studied in [1]. *Table 2* quotes the ratios Au/Ag and In/Ag published for the coins minted in the Nantes workshop.

Table 2 Coins minted in Nantes were previously analysed [1]

Reign	Year	Monetary workshop	Denomination	% Ag	Au/Ag (ppm)	In/Ag (ppm)
Henri II	1554	Nantes	Teston	89.9	630	0.55
Henri II	1564	Nantes	Teston	89.9	750	0.05
Henri III	1576	Nantes	¼ d'écu	91,7	1310	1.48
Henri III	1582	Nantes	¼ d'écu	91.7	1300	0.38
Henri III	1589	Nantes	¼ d'écu	91.7	765	2.5
Henri IV	1599	Nantes	¼ d'écu	91.7	600	5.5

We chose to concentrate our work on the years 1598-1599 [6]. The previous data published did not focus on this period and, only a very few coins have been recovered among hundreds of thousands minted in 1598 (*Figure 2*).



Figure 2 ¼ d'écu minted in Nantes in 1598 - Henri IV [6], one of 6 found.

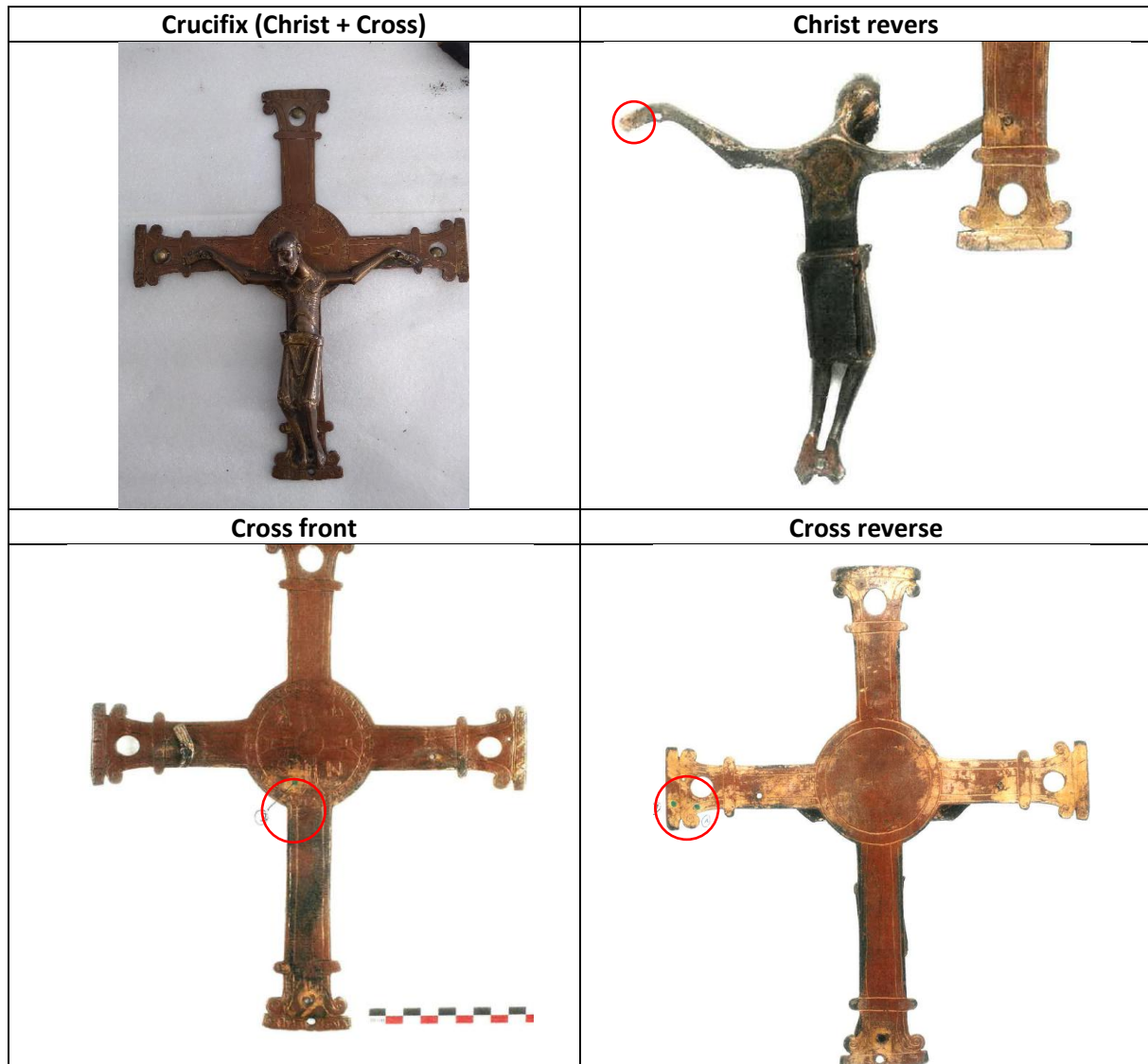
2.2 Fire-gilded crucifix

In 2019, the Dobrée Museum in Nantes acquired a precious crucifix [7]. This is a figure of Christ placed in the center of a cross, both elements have been gilded (*see Figure 3 below*). Despite the good general state of conservation, only a partial gilded layer remains. For historians, this type of

crucifix is reminiscent of other examples known in northwestern France, it can be dated from the first half of the 12th century [8].

In this work, several areas of analysis were selected for their good state of preservation based on visual observations, and for their sufficient size in comparison with the beam spot. (*circled areas in images shown in Figure 3*).

Figure 3 Analytical points with HE-PIXE on the crucifix



This kind of object was commonly gilded by a technique called “fire-gilding”. It was the predominant technique for the gilding of metalwork from 200 A.D. in Europe until the invention of electroplating in the 19th century” [9]. The progressive evolution from the ancient mechanical gold foil gilding to the chemical layer deposition by the mercury-gilding technique has been illustrated in [10]. Goldsmith techniques on copper-based alloys have been explained in detail in [11], and [12]. Fire-gilding consists of preparing a mixture of mercury and gold (amalgam process) applying this paste on a clean metal surface to be gilded, then heating the surface so that the gold binds the substrate and the mercury evaporates, and finally burnishing the surface to make it shine and soft. The mercury is never driven off completely by the heating process, the residual amount detected is between 8 and 25% [9, p. 58], [13]. The thickness of high-quality fire gilding was usually in the range of 2-10µm [9, p. 60]. Based on a quotation from the 12th-century metalworking manual of Theophilus [14], several

studies state that fire-gilding on cast copper alloy objects is difficult when alloying elements like tin, zinc, and particularly lead exceed a few per cent [12]. Metallurgical explanations are given in [9, p. 61-62]. Apparently, the purer the copper, the easier it is to apply mercury gilding. Otherwise, a thicker layer of gilding is required.

Several questions related to the manufacturing process of the crucifix are still under question. Both elements, the cross and the Christ seem to be made of the same metal and fixed one onto the other during the original assembly of the object. Alloy elemental analysis could reveal which kind of alloy has been used. This paper gives insight into the contribution of HE-PIXE to measure the gilding thickness and discuss the homogeneity of the coating surface. Further questions relating to the object manufacture will be asked in the discussion section.

3 Material and methods

3.1 High Energy PIXE analysis

The HE-PIXE experiments are performed at the cyclotron C70 in GIP ARRONAX. Thanks to in-air analysis, there are no restrictions on the size of the object.

A picture and schematic representation of the HE-PIXE experiment on coins are given below (*Figure 4*).

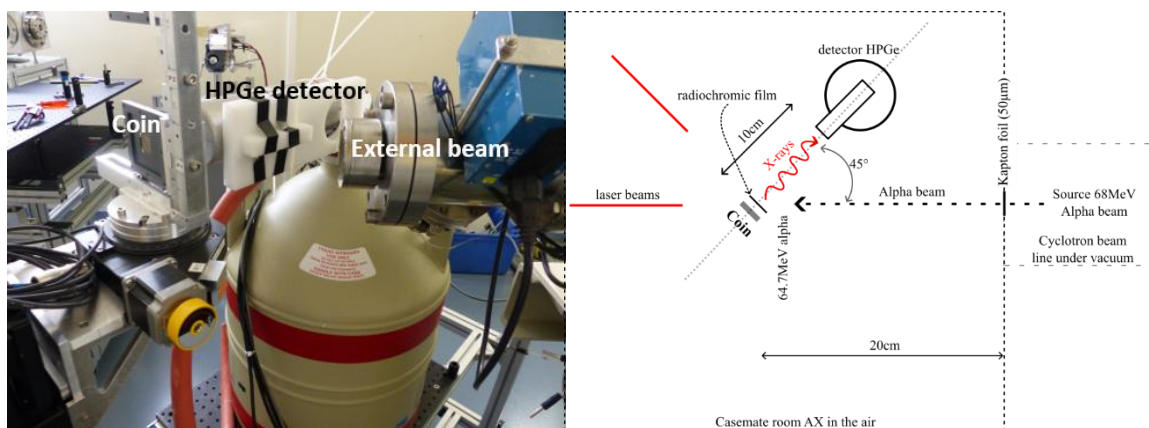


Figure 4 Picture and schematic representation of the HE-PIXE experiment on coins

We use sample holders (*see image on the in Figure 4*) to fix the coins in front of the beam and to choose an angle between the incident beam and detector axis. The analysis is made with an alpha beam of 68MeV. It reaches the target material (coin) with an energy of 64,7MeV (calculated with TRIM software [15]). Alpha beam range is about 600 μ m in silver alloy. The probing depth is limited to X-ray attenuation. Ag K lines are detected in the first 160 μ m, in this depth the beam energy stays high and the Ag X-ray production cross section barely decreases. The beam spot was 1cm diameter for coins (beam spot checked on a radiochromic film). We use a High Purity Germanium (HPGe) detector with a 50mm² active area and a 50 μ m thick beryllium window. It has a high efficiency for K lines of silver at 22keV and a good energy resolution (315eV at 22keV). The beam intensity for coins' analysis is lower than 0.1nA. We monitor the experiments using the count rate in the main peak (thousands of counts per second in the Ag K_{α} line) and maintaining a dead time of less than 15%. Acquisition time is typically 1h30 per coin. In our best setup conditions with optimal detector electronic parameters based on the analysis of several HE-PIXE spectra, we reached a signal-over-noise ratio of 300 in the indium region and a detection limit of 10ppm. Peak-to-background ratio is obtained by fitting the Ag K_{α} -line and evaluating an average background noise under the indium region.

A schematic representation for HE-PIXE in the geometry used for the crucifix analysis are given below (Figure 5).

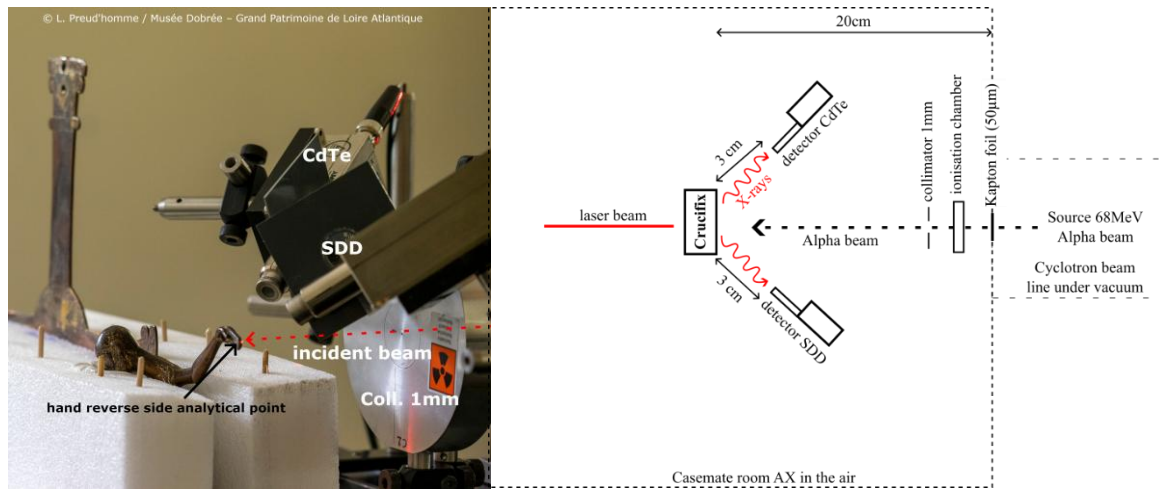


Figure 5 picture and schematic representation of the HE-PIXE experiment on the crucifix

The crucifix has been mounted on handmade support (see the image on the left in Figure 5) adapted to the chosen points (see Figure 3 in section 2.2). The analysis is made with an alpha beam of 68MeV alpha particles. HE-PIXE measurements of the layer of gold thickness have been done with Au K_{α} lines at 68,8keV. X-ray auto-attenuation in a gold layer of a few μm is negligible at high energy, so X-ray intensities are directly proportional to the total amount of gold in the gilded layer seen by the beam. We used standard Goodfellow gold foils of 2.3 μm , 10.7 μm and 14 μm thickness to calibrate the gilding measurements on the crucifix. On the object, we only estimate an average thickness value over the beam spot because the area irradiated is irregular. Differential attenuation of Cu K lines was used to evaluate the heterogeneity of the gilded surface compared to reference gold foils placed over a thick copper-based alloy substrate. The spatial resolution of HE-PIXE measurements depends on the beam shape, it was 4mm at the surface of the crucifix. Detecting setup for the crucifix required a compact system to analyze a complex shape object and to limit the irradiation time. We used a silicon drift detector (SDD) detector for its good efficiency and energy resolution for K X-rays of low elements. CdTe was used to detect energetic K lines of gold. Accumulated charge is measured with an ionization chamber for the crucifix to compare acquisitions with each other. Acquisition time is typically 15 to 30 minutes per point on the crucifix with low intensity (few pA) to reduce the activation level of the object.

3.2 p-XRF setup

The experimental set-up also involved a portable XRF device from Bruker, Germany, the commercial X-ray spectrometer TRACER III SD [16]. The main X-ray source is a 40 kV rhodium tube, with a current of 13 μA . The main excitation energy of the beam is given by the composition of the anode; Rh emitted K X-ray lines are around 20 keV. The samples were placed on the exit beryllium window and emitted X-rays were collected by a silicon drift detector (Figure 6).



Figure 6 p-XRF set up on coins

XRF spectra revealed the elemental composition of coins and crucifix. X-rays up to 40keV could be detected but the main excitation energy is the Rh K_{α} line at 20,2keV so elements with higher absorption edge are only excited by the Bremsstrahlung radiation. Trace element analysis on coins using this p-XRF is not adapted for indium detection because the In K edge is at 27,9 keV. The detector collimator also contains Palladium which generates X-rays overlap. However our p-XRF can be used for Au detection, L_{α} line is well defined in the spectra. We used a filter (Al/Ti/Cu) to reduce background noise in the energy region below 20 keV.

A standard silver matrix material (MBH-133X-AG1A) has been analyzed to measure the detection limit of our p-XRF set-up. Spectra have been proceeding using OriginPro software which allows accurate peak deconvolution and Gaussian fitting. Detection limits (DL) at a 95% confidence level, were determined according to the widely used formula

$$DL(ppm) = \frac{3C_i\sqrt{I_b}}{I_p}$$

Where C_i is the concentration of element i, in ppm: I_b is the background intensity below the corresponding peak and I_p is the net intensity of the corresponding peak (Table 3).

Table 3 Certified reference MBH-133X-AGA1-A – DL(ppm) obtained by p-XRF measurements

Elements	Certified concentration (%)	DL (ppm)
Ag K_{α}	77,37	85
Au L_{α}	1.48	53

4 Results

4.1 Historical silver coins

The HE-PIXE spectra in Figure 7 show the main elements present in the coins' alloy (silver and copper) easily distinguished by their K-lines. Gold and indium are also present among other prominent peaks. Figure 8 focuses on L_{α} and K_{α} lines of gold and indium respectively. XRF spectra focused on L_{α} lines obtained for the same coins are plotted in Figure 9.

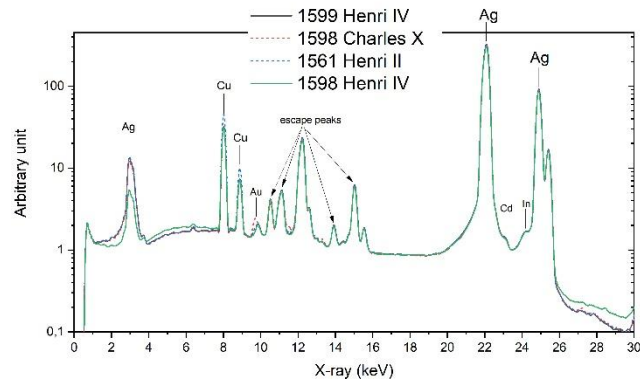


Figure 7 HE-PIXE spectra of five silver coins

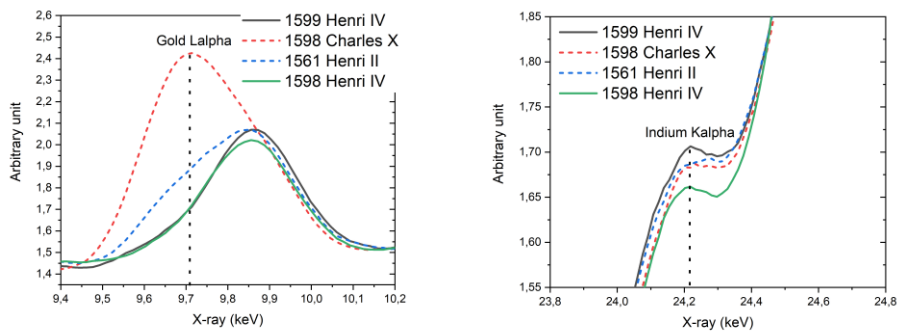


Figure 8 HEPIXE spectra - gold La lines and indium Kα line of silver coins

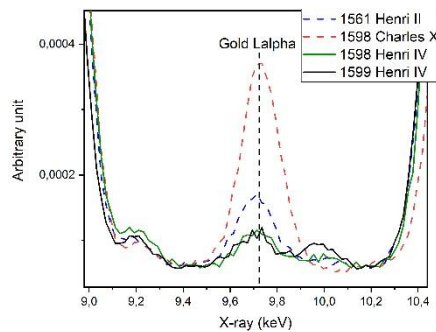


Figure 9 XRF spectra - gold La lines of silver coins

Indium was detected (>10ppm) with HE-PIXE in two coins minted after the Edict of Nantes (1598 and 1599 Henri IV). Figure 8 shows the characteristic peak at 24.2 keV. These two coins also have the lowest gold content (see Figures 8 and 9). The results for the four coins analysed are shown in Table 4. Gold quantities are expressed in ppm with an uncertainty $\leq 17\%$. The spectrum of the Charles X 1598 coin shows the highest gold peak. As indium levels are close to the detection limit, we have classified the coins according to whether indium is observable or not.

Table 4 First results obtained with HE-PIXE and p-XRF analyses on Nantes coins (Au/Ag (ppm) obtained by p-XRF and Indium detected by HE-PIXE)

Reign	Year	Monetary workshop	Denomination	% Ag	Au/Ag (ppm)	Indium detection
Henri II	1561	Nantes	Teston	89.9	623	< DL
Charles X	1598	Nantes	¼ d'écu	91.7	1850	< DL
Edict of Nantes 30th of April 1598						
Henri IV	1598	Nantes	¼ d'écu	91,7	293	Indium seen
Henri IV	1599	Nantes	¼ d'écu	91.7	296	Indium seen

4.2 Fire-gilded crucifix

The composition of the crucifix was obtained by HE-PIXE multi-elemental analysis (Figures 10 and 11). The statuette of Christ is made of brass (Cu, Zn, Sn) while the cross contains mainly copper. Other elements have been detected including Ti, Mn, Fe, Ni, Ag, Sb and traces of Pb. The layer of gold was applied by using fire-gilding, it was identified by Au and Hg.

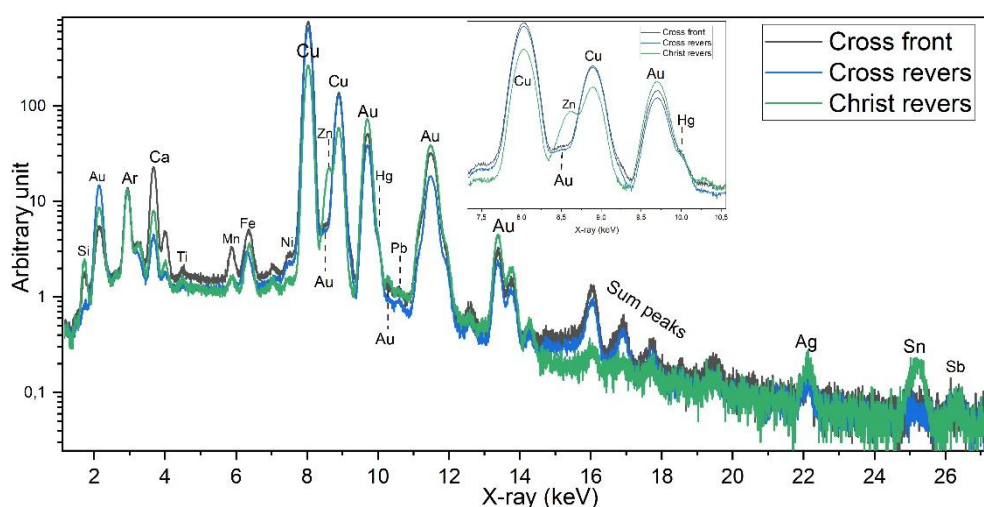


Figure 10 HE-PIXE SDD spectrum of the crucifix

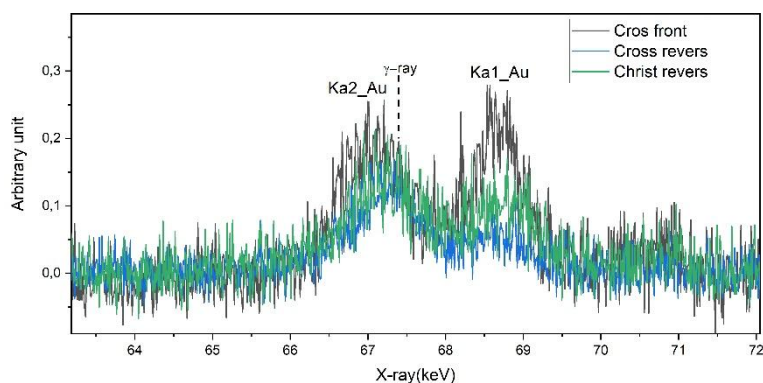


Figure 11 HE-PIXE CdTe spectrum of the crucifix

Figure 12 is our calibration curve obtained with reference gold foils. We plot experimental points on the object to find the corresponding thickness (Table 5).

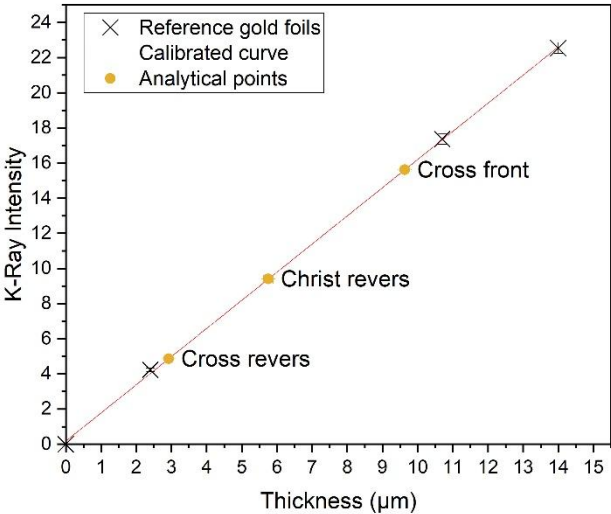


Figure 12 Gold layer thickness

Table 5 Measured thickness of the crucifix

Analytical points	Thickness
Christ revers	5.8±0.1µm
Cross revers	2.9±0.1µm
Cross front	9.6±0.2µm

Figure 13 shows the evolution of the Cu K lines ratio increasing gold layer thickness. Expected values for a homogeneous gold layer over copper substrate decrease exponentially. We plot the measured values of analytical points on the crucifix. Differences between expected and measured values are explained in section 5.

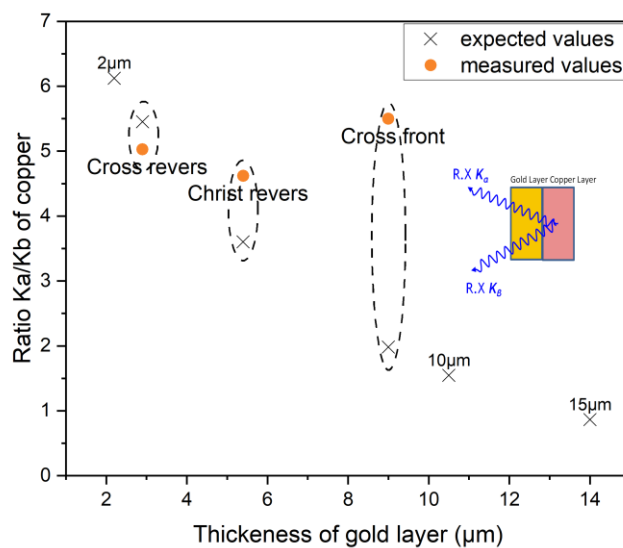


Figure 13 K lines copper ratio

5 Discussions

5.1 Coins analysis

The first results obtained for coins' analysis are in accordance with historical knowledge. As explained in *section 2*, the arrival of the Potosian silver in France is attested in 1575 so it is not surprising to not detect indium in our coin minted in 1561 (Henri II). In 1598, Nantes was besieging, so silver supply no longer came from common routes. In the coin minted before the Edict of Nantes (Charles X), we do not detect indium either (signal below the detection limit). However, for the two coins minted after the Edict of Nantes, Henri IV 1598 and 1599 Indium has been detected. This corresponds to the signature of the Edict of Nantes, symbolizing the return of peace to the kingdom. If we consider Au/Ag concentration in the same coins, we found a correlation between gold and indium. A high concentration of gold is characteristic of Mexican silver compared to Potosian one [5]. Coin from 1561 contains 623ppm of gold. The coins with the highest concentration of gold are from 1598 during the siege, Nantes workshop probably used old silver stocks to continue the coin production. A lower proportion of gold (290ppm) has been found in coins minted after the Edict of Nantes. The detection limit of 10ppm is not enough to find indium in a lower proportion but it is still possible to improve the HE-PIXE experimental setup and reach a lower limit. Despite a relative indium concentration of 5,5ppm in the only coins from 1599 minted in Nantes previously analyzed, we can clearly detect indium in coins from 1598 and 1599. We can expect to detect indium in more coins from the same period, this is necessary to act for a clear correlation between gold and indium and to show changes in the Nantes silver supply. In parallel with improving detection limits, experiments on silver standard materials containing indium traces will be done to confirm the HE-PIXE method and make the first quantification measurements.

There are other interesting facts to explore. [5] highlights that Mexican and Potosian silver ores can be distinguished with other trace elements than gold and indium, tin and antimony could be used. [2] explained that Potosian silver is not only characterized by high indium content but that germanium is also a good tracer. Elemental analysis of other traces may be done to better understand the sources of supply in silver coins minted in Nantes. Furthermore, [2] explained that *"the arrival of Potosian silver certainly correspond with the introduction in Potosi mine of the more productive silver*

extraction method by mercury amalgamation in 1572". The arrival of Potosi silver in Nantes around 1570 should be explored. In 1618, the 30 years' war began and put an end to trade between France and Spain. Spanish- American silver was no longer imported, leading to the liquidation of Andean stocks until 1626. A larger project will focus on the production of the Nantes mint until 1626 with much more coins of distinct years to confirm first observations and cover another aspect of Nantes's history.

5.2 Crucifix analysis

The HE-PIXE thickness measured on the crucifix is in accordance with the values given in the literature regarding fire-gilding on copper-based alloys (2 μ m to 10 μ m) [9]. However, calculated values correspond to the average thickness over the beam spot. $K_{\alpha 1}(Au)$ line intensity is proportional to the total amount of gold present at the surface. Differential X-ray attenuation of the underlying copper depends on the thickness of the gilding. Assuming a surface of heterogeneous thickness under the beam, the intensity of the copper X-rays detected may be higher for the same thickness value if the gilding is not distributed over the entire area analyzed, and there are un-gilded spaces. *Figure 9* shows that cross revers analytical point has a quite homogeny surface while other points are rather uneven. Near-surface characterization could be done using low-energy X-rays like L and M lines of gold, work is in progress on this point.

First HE-PIXE results are not enough to say if J-C and cross were made with the same thickness of gold. As we have seen, historical fire-gilded objects are usually made with pure copper or copper enriched surface. We were limited with the number of points to be analyzed because the object could not stay at cyclotron ARRONAX very long. That is the reason why we planned to do p-XRF analysis on other points. To conclude on a probable correlation between the gold thickness and the substrate material composition we need to gather enough data on the object and compare experimental results with visual observation of a good conservation state in the area of interest. Other methods such as RBS [10], [17], [18] or differential PIXE [19], [20] can be used on this type of object to characterize the interfaces between the gilding and the substrate, and to study the diffusion of gold into the copper as well as the oxidation of the substrate. HE-PIXE is not dedicated to analyzing the inter-diffusion effect at the film-substrate boundary and does not evaluate the Hg concentration profile in Au [29]. These questions are outside the scope of this study.

6 Conclusion

This work features the first application of the high-energy PIXE technique for non-destructive analysis of cultural heritage objects at cyclotron ARRONAX. Two case studies were detailed, detecting trace elements in silver coins, and characterizing the thickness of fire-gilding on a handcrafted copper alloy crucifix. Regarding coin analysis, our preliminary results are in concordance with historical knowledge. Indeed, religious conflicts probably had a major impact on South American silver imports, and the resumption of minting activity in the city of Nantes coincided with the ratification of the peace treaty in Brittany in 1598. Concerning the crucifix, conservators wanted to find out more about the gilding of the object to situate this specific object among other similar works and compare technical characteristics within a historical investigative framework. The gilding thickness measured on the Christ and his cross was shown to corroborate the extant body of literature i.e., that fire-gilding on brass is between 2 μ m and 10 μ m thick. Those results need to be completed by analysis of more coins and further analysis on additional points on the crucifix.

7 Acknowledgment

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8 Data availability statement

The datasets generated and analysed during the current study are available from the corresponding author upon request.

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