

Article

A Multi-Technique Study of 49 Gold *Solidi* from the Late Antique Period (Late 4th–Mid 6th Century AD)

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Abstract

This study investigates 49 gold *solidi* issued between the 4th and 5th century AD to determine their chemical composition. The coins were first catalogued by recording mass, diameter, and thickness. All specimens underwent non-destructive μ -EDXRF analysis to identify main elements, followed by semi-quantitative fineness evaluation. To validate these results, six coins were randomly micro-sampled: material was dissolved in aqua regia and analysed by ICP-AES for gold quantification and ICP-MS for high precision trace element determination. The non-destructive analyses showed consistently high gold percentages, confirming authenticity and the extensive use of this noble metal during the studied period. Two distinct groups were identified based on the XRF Pt/Pd ratio, suggesting the use of gold from different sources. Comparison of μ -EDXRF and ICP-AES gold contents shows no statistically significant differences; however, this apparent agreement should be interpreted cautiously, as it mainly reflects the limited resolving power of ICP-AES at very high gold concentrations rather than definitive evidence for the absence of surface-related effects. Trace elements analysis detected low concentrations of Cu, Sn, and Pb suggesting the use of alluvial gold for minting. The presence and correlation of terrigenous elements (Al, Ca, Ti, Cr, Mn, Fe, Ni, Zn, Sr) indicate soil as the burial site.

Keywords: gold coins; numismatics; metals; micro-EDXRF; ICP-AES; ICP-MS



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1. Introduction

Gold (Au) has been one of the earliest metals intentionally exploited by human societies, due to its natural occurrence in native form, its chemical stability and its ductility. The earliest known crafted gold artefacts—most famously those from the Varna I cemetery in Bulgaria—date to the mid-5th millennium BC and bear witness to a sophisticated early metallurgy in the Chalcolithic Balkans [1]. From antiquity onwards, gold circulated widely as a prestige material and, later, as a monetary standard that shaped political and economic systems across the Mediterranean [2].

From the first appearance of coinage in the late 7th century BC, the challenges associated with separating gold from silver (Ag) led to widespread use of electrum [3,4]. Advances in refining technologies, however, enabled the production of high-purity gold coinage already by the 6th century BC, as shown by the analyses of the Sardis finds [2]. In

the Late Roman and Early Byzantine periods, the *solidus* became the Empire's foundational gold denomination. Introduced by Constantine around AD 310 and struck at 1/72 of the Roman pound (i.e., an individual weight of about 4.55 g), the *solidus* maintained remarkable stability in weight and appearance, although variations in purity and minor-element content reflect administrative changes and economic fluctuations [5,6].

Scientific analysis of ancient coins plays a fundamental role in numismatic studies, because it allows the reconstruction of minting practices, alloy composition, circulation, debasement episodes and—potentially—the provenance of the metal (ore source) used. Chemical analyses carried out over the past decades demonstrate that Late Antique gold coins usually contain very high gold percentages, but their silver, copper (Cu) and platinum-group element (PGE) contents can vary significantly [7,8]. These minor and trace elements are crucial indicators of both the refining technology and the geological origin of the metal. Platinum (Pt) and palladium (Pd) are generally more stable than other PGEs during ancient gold refining processes, particularly during cementation and cupellation. Although experimental studies indicate that slight depletion of Pt and Pd may occur under specific cementation conditions, their concentrations are typically less affected than those of other trace elements, making them informative indicators of refining processes and, to some extent, of the original metal source [9–12].

The archaeometric study of gold coinage has increasingly relied on multi-technique approaches capable of assessing both surface and bulk compositions [13]. While bronze [14] and silver-copper alloy coins [15] commonly undergo surface enrichment or depletion—often caused by soil encrustations, superficial contaminants, or localized chemical alterations—gold artefacts generally exhibit negligible corrosion and thus much more limited surface modification. Recent large-scale studies on Roman gold coinage, notably those conducted within the *Gold Coinage in the Roman World Project*, have demonstrated that for well-preserved gold coins the compositional differences between surface and bulk are generally negligible. For these reasons, the integration of non-destructive techniques (e.g., X-Ray Fluorescence, XRF) with micro-destructive techniques can maximize the information extracted from precious, archaeologically valuable specimens while minimizing damages [16–18]. The combined use of XRF, LA-ICP-MS and muonic X-ray emission spectroscopy has shown a strong agreement between surface-sensitive and sub-surface analyses for Roman *aurei* and *solidi*, in contrast to what is commonly observed for silver coinages, where intentional surface enrichment has been clearly documented [19,20]. In particular, depth-profiling investigations using negative muons revealed surface-enriched layers extending up to several hundred micrometres in silver coins, whereas no comparable compositional gradients were detected in Roman gold coinage [21].

This study examines a group of 49 Late Antique gold coins—47 *solidi* and 2 *tremisses*—issued in the mints of Constantinople, Thessaloniki, and Ravenna (Table 1). The coins were provided to the authors without any accompanying archaeological documentation; according to the information received, they reportedly originated from a hoard in the Balkan region, although the exact discovery context remains unknown. Spanning from the reign of Gratian (AD 367–383) to that of Justinian I (AD 527–565), this coherent assemblage offers a valuable opportunity to reconsider the fineness, metallurgical variability, and trace elements signatures of gold coinage in Late Antiquity.

The aims of this research are therefore:

1. to quantify major, minor and trace elements using combined XRF and Inductively Coupled Plasma (ICP) approach;
2. to investigate the presence of PGEs (Pt, Pd) as potential indicators of ore sources and refining practices;

3. to assess the consistency between surface and bulk compositional information obtained by different analytical techniques.

Through this integrated analytical strategy, the study contributes new insights into minting procedures, metallurgical choices, and the circulation of gold in the eastern Mediterranean between late 4th to mid 6th century AD.

Table 1. List of coins under study. Each coin has been assigned a sequential number from 1 to 49. Asterisks (*) indicate coins subjected to micro-sampling.

Emperor	Period of Issue (AD)	Number of Samples	Sample Code
Gratian	367–383	1	11
Valentinian II	375–378	1	33
Theodosius I	379–395	2	15; 20
Arcadius	395–408	6	1 *; 4; 8; 12 *; 16; 24
Arcadius for Aelia Eudoxia	400–404	1	2
Honorius	395–423	10	6; 7; 9; 10; 13; 14; 18; 22; 23; 30
Theodosius II	408–450	14	3; 5 *; 17; 19; 21; 26; 28; 34; 39; 42 *; 45 *; 46; 47; 48
Theodosius II for Aelia Pulcheria	414–453	2	27; 38
Valentinian III	425–455	9	29; 31; 35; 36 *; 37; 40; 41; 43; 44
Anastasius I	491–518	1	32
Justin I	518–527	1	25
Justinian I	527–565	1	49

2. Materials and Methods

2.1. Chemicals and Apparatuses

All chemicals used were of analytical quality. Nitric acid (67–69% *v/v*) and hydrochloric acid (30% *v/v*) were sourced from VWR (Milan, Italy). Water conforming to reagent grade standards was generated using a Millipore purification pack system (MilliQ water from Millipore, Burlington, MA, USA).

All 49 coins were catalogued with a sequential number and photographed. The average mass ($N = 3$) was determined by using an analytical weigh scale (Sartorius Series CPA225D) with a capacity of 220 g, a readability of 0.01 mg, linearity ≤ 0.03 mg, standard deviation ≤ 0.02 mg, and a stabilisation time of ≤ 6 s. Furthermore, with the assistance of Vernier callipers, the diameter and thickness of each coin were measured at three different points.

A 99.9% Au reference sample ($4.0 \times 4.0 \times 0.52$ mm, 0.2 g), satin-finishing and pickled, was produced by a professional goldsmith to support semi-quantitative analysis.

2.2. μ -EDXRF

Surface compositions were obtained using an ARTAX 200 micro-XRF spectrometer (provided by Bruker Nano GmbH in Berlin, Germany). This instrument is equipped with

an air-cooled Mo X-ray fine focus tube (maximum 50 kV, 1 mA, 40 W), which is controlled by a compact high-voltage generator unit and features a 650 μm collimator.

Additionally, it has a Peltier-cooled XFlash[®] silicon drift detector with 10 mm² of active area and an energy resolution of <150 eV for Mn-K α at 100 kcps. A CCD camera with 500 $\times$ 582 pixels is integrated for sample positioning. The instrument's focal spot measures 1.2 $\times$ 0.1 mm², offering a lateral resolution of 0.2 mm, and it includes a 100 μm beryllium window.

We utilised the ARTAX control semi-quantitative XRF software (version 5.3.14.0, licensed by Bruker AXS Microanalysis GmbH, Berlin, Germany) for both hardware control and the evaluation of analytical data. Data were represented in the form of counts per second (cps) versus energy (keV). The instrumental settings were configured as follows: X-ray tube = 30 W, Mo target voltage $U = 50$ kV, current $I = 700$ μA , and an acquisition time of 60 s (live time). The collimator was set at 650 μm in an air environment.

The elements examined included gold (Au) L α 1 9.71 keV, silver (Ag) K α 1 22.16 keV, copper (Cu) K α 1 8.05 keV, palladium (Pd) K α 1 21.18 keV, platinum (Pt) L γ 1 12.93 keV, iron (Fe) K α 1 6.40 keV, nickel (Ni) K α 1 7.48 keV, strontium (Sr) K α 1 14.16 keV, calcium (Ca) K α 1 3.69 keV, potassium (K) K α 1 3.31 keV, manganese (Mn) K α 1 5.89 keV, titanium (Ti) K α 1 4.51 keV, vanadium (V) K α 1 4.51 keV, and zinc (Zn) K α 1 8.64 keV.

Four spectra were acquired for each coin, consisting of two on the obverse (recto) and two on the reverse (verso).

Attempts were made to avoid encrusted or corroded micro-areas, some soil-derived inclusions were unavoidable due to the long-term burial environment, the fragility of the patinas, and the decision to avoid mechanical or chemical cleaning that could alter the surface composition. This constraint is well recognised in studies of buried gold artefacts. While different instruments and specific settings were used, our approach is broadly consistent with established μ -EDXRF procedures for the analysis of ancient coinages, as reported in Green et al. [19], Bayazit and Seker [22], Buccolieri et al. [23], and Marussi et al. [17].

2.3. Sample Preparation for ICP Analyses

Since Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) require solution-based analysis, sampling is necessary. Micro-destructive sampling was carried out on six coins (Table 2) using a professional cutter to extract small flakes from the coin edges to avoid affecting iconography or legends [16,17]. The coins were selected randomly, based solely on analytical and conservation criteria (variation in thickness, preservation state, and inclusion of one *tremissis*), as no contextual or numismatic information was available at the time of analysis. The collected material was weighed using an analytical weigh scale (Sartorius Series CPA225D). The obtained flakes (about 7 mg) were dissolved in aqua regia (3:1 HCl:HNO₃), and heated overnight to promote the dissolution. The solutions were then appropriately diluted in a 100 mL volumetric flask (class A) with MilliQ water for subsequent analyses.

The thickness of the collected flakes, corresponding to several tenths of a millimetre, ensures that the subsequent analyses probe a greater depth of the metal than the surface-sensitive XRF measurements employed in this study or typical LA-ICP-MS analyses, providing complementary information on the coin's internal composition.

Table 2. The six coins micro-sampled with their respective codes and issuing emperors (1–10 scale).

					
<i>Solidus</i> no. 1, Arcadius (AD 395–408)	<i>Solidus</i> no. 5, Theodosius II (AD 408–450)	<i>Solidus</i> no. 12, Arcadius (AD 395–408)			
					
<i>Solidus</i> no. 36, Valentinian III (AD 425–455)	<i>Tremisses</i> no. 42, Theodosius II (AD 408–450)	<i>Solidus</i> no. 45, Theodosius II (AD 408–450)			

2.4. ICP-AES

Gold was quantified using an ICP-AES spectrometer (PerkinElmer® Optima™ 8000, Waltham, MA, USA).

Calibration, which was linear within the concentration range of 0.1–10 mg L^{−1}, was conducted following the dilution of a multi-standard solution with an initial concentration of 10 mg L^{−1} for ICP analysis (Periodic Table Mix 2 for ICP TraceCERT®, Sigma-Aldrich, St. Louis, MO, USA). The limit of detection (LOD) for the solution samples at the operating wavelength (242.795 nm) was 0.02 mg L^{−1}. The coefficients of variation for repeatability (RSD %) were determined to be less than 5%.

The accuracy of the analysis and the matrix effect were evaluated by means of laboratory-fortified samples prepared by spiking a standard solution different from that employed for instrument calibration into actual samples.

2.5. ICP-MS

Trace metal concentrations were determined using an ICP-MS NexION 350x Spectrometer from PerkinElmer (Waltham, MA, USA) equipped with an ESI SC autosampler. The quantified elements were: silver (Ag), copper (Cu), platinum (Pt), palladium (Pd), tin (Sn), lead (Pb), mercury (Hg), aluminium (Al), calcium (Ca), iron (Fe), titanium (Ti), strontium (Sr), chromium (Cr), manganese (Mn), nickel (Ni), and zinc (Zn). Particular attention was given to PGEs (Pt, Pd), as they are robust indicators of ore sources. The analysis was conducted in KED mode (Kinetic Energy Discrimination), with ultra-high purity helium (at a flow rate of 4.8 mL min^{−1}) used to prevent interference caused by cell-formed polyatomic ions.

Calibration of the instrument, which was linear within the concentration range of 0.5–100 µg L^{−1}, was carried out following the dilution of multi-standard solutions initially at a concentration of 10 mg L^{−1} for ICP analysis (Periodic Table Mix 1 for ICP TraceCERT® and Periodic Table Mix 2 for ICP TraceCERT®, Sigma-Aldrich, St. Louis, MO, USA). The composition of the samples was determined using the calibration curve method obtained by analysing standard solutions. The LOD for each element were as follows: Ag 0.02 µg L^{−1}, Cu 0.20 µg L^{−1}, Pt 0.005 µg L^{−1}, Pd 0.005 µg L^{−1}, Sn 0.07 µg L^{−1}, Pb 0.06 µg L^{−1}, Hg 0.01 µg L^{−1}, Al 0.10 µg L^{−1}, Ca 1.2 µg L^{−1}, Fe 1.5 µg L^{−1}, Ti 0.05 µg L^{−1}, Sr 0.05 µg L^{−1}, Cr 0.10 µg L^{−1}, Mn 0.03 µg L^{−1}, Ni 0.20 µg L^{−1}, and Zn 0.09 µg L^{−1}.

2.6. Data Analysis

Consistency between surface (μ -EDXRF) and near-bulk (ICP-AES) results was assessed using a paired *t*-test for repeated measurements and Bland–Altman analysis. All analyses were performed within the R software environment for statistical computing and graphics (R version 4.1.2 “Bird Hippie”), on a commercially available workstation (x86_64-apple-darwin17.0 64-bit).

3. Results

3.1. Preliminary Non-Invasive Investigation by μ -EDXRF

The measurement of the physical characteristics showed good uniformity and conservation of the samples. The measured masses ranged from 4.22 to 4.54 g, with an average of 4.39 g, which is very close to the theoretical value of 4.50 g [5]. The two tremisses also had an average mass of 1.49 g and 1.50 g, matching the one-third ratio [24].

Each *solidus* was analysed by μ -EDXRF spectroscopy at four points (two on the recto, presenting the emperor’s face, and two on the verso). Spectra were highly consistent, except in the presence of visible surface concretions. These produced a distinct Ca $K\alpha$ peak (3.69 keV) and attenuated Au lines. Other elements (K, Mn, Ti, V, and Zn), probably related to the burial site, were identified in some coins [18].

A semi-quantitative estimate of the gold content in the coins was obtained by normalizing the area of the Au $L\alpha$ peak (9.67 keV) to the sum of the peak areas of the major elements (Au, Ag, Cu, Pt, and Pd) (Figure 1). The *solidi* are grouped according to the authority. A 99.9% gold standard, treated with satin-finishing and pickling processes, was used to validate the calculation procedure. As these gold coins are well-preserved, it could be reasonably assumed that the surface is representative of the entire sample [25]. The coins show uniformly high gold content (>97%), in agreement with previous work indicating that the Constantinopolitan gold coinage remained essentially unalloyed until the end of the 9th century [26].

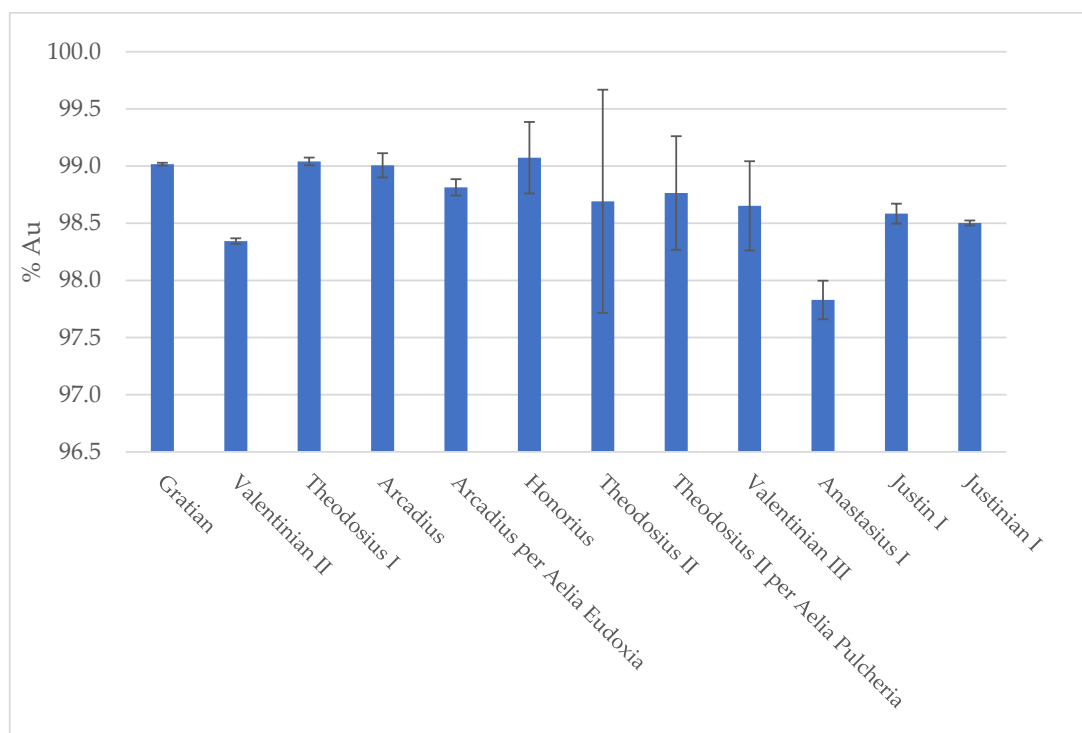


Figure 1. The gold content obtained from the ratio of the Au $L\alpha$ peaks and the sum of the peak areas of the major elements (Au, Ag, Cu, Pt, and Pd). Error bars express the standard deviation.

The ratios between Cu, Ag, Pt, and Pd were also calculated. Two discrete compositional groups emerged when considering the Pt/Pd ratio: Group A (37 coins) with an average ratio of 3.1 ± 0.4 and Group B (9 coins) with an average Pt/Pd ratio of 7.5 ± 0.5 (Table S1). Three coins (No. 13, 36 and 46) were not considered because their Pd peaks were at the background level of the instrument. The existence of two coherent Pt/Pd clusters (Figure 2) suggests that the coins—although recovered together—may tentatively reflect two geologically distinct gold sources or the incorporation of recycled metal circulating through different supply networks.

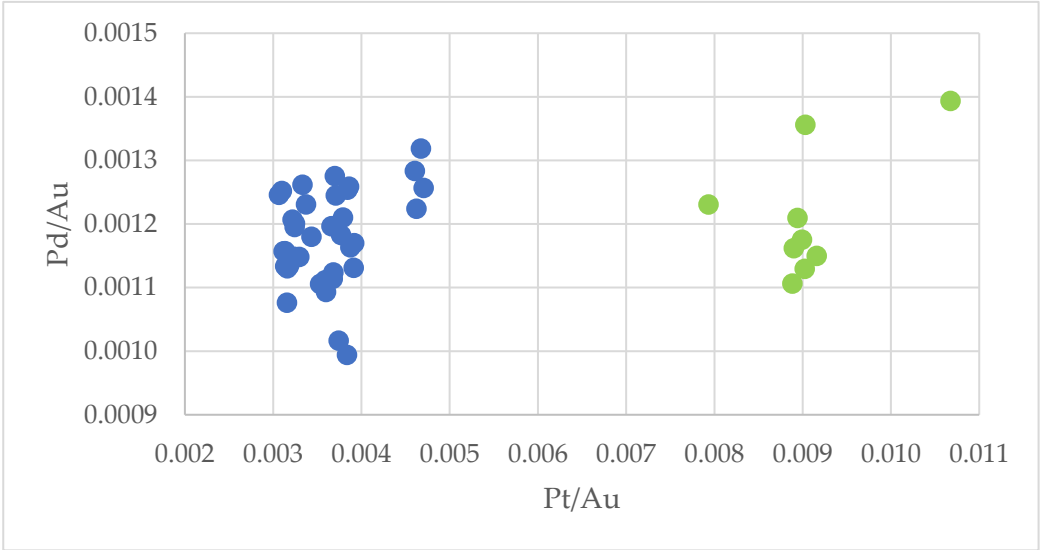


Figure 2. Platinum and palladium contents normalised to gold for all the 49 coins under study. In blue are highlighted the *solidi* with an average Pt/Pd ratio of 7.5, whereas in green are those with an average ratio between the two elements of 3.1.

3.2. Determination of Trace Elements by ICP-MS

The ICP-MS results, expressed in mg kg^{-1} (Table 3), support the interpretation that the analysed coins were produced from alluvial gold containing naturally occurring impurities, with minimal intentional alloying. Copper contents are consistently below 2 wt%, while Sn and Pb are present only at trace levels. The low Sn concentrations likely reflect incidental cassiterite inclusions, a recognised feature of placer gold deposits, rather than metallurgical additions.

Table 3. Average content of trace metals expressed in mg kg^{-1} for the six coins selected for the ICP-MS analysis. Concentrations are reported concerning the mass of material sampled and dissolved.

Coin Number	Emperor	Ag	Cu	Pt	Pd	Hg	Pb	Sn	Ni	Al	Ca	Ti	Cr	Mn	Fe	Zn	Sr	Total
1	Arcadius	1162	99.1	39.4	2.53	60.0	3.94	137	276	4.16	54.0	2.50	471	39.6	2539	1.44	<0.64	4892
12	Arcadius	1627	134	449	14.4	1.06	30.8	50.8	23.0	4.26	35.3	2.44	<1.24	2.58	266	3.65	<0.64	2644
5	Theodosius II	11,514	2219	151	23.1	5.30	81.3	19.7	47.4	61.2	1854	3.07	30.5	12.6	879	50.2	11.2	16,963
42	Theodosius II	2077	514	261	8.32	0.61	153	35.0	10.6	2.87	32.7	2.22	<1.24	13.9	1734	15.1	<0.64	4860
45	Theodosius II	5479	422	384	21.2	4.78	31.6	41.8	20.8	54.3	2104	2.42	24.6	21.5	1589	32.3	12.8	10,246
36	Valentinian III	2235	1190	248	28.9	1.18	25.3	10.1	1298	<1.72	77.6	1.07	1822	144	9660	4.28	0.99	16,747

Coin No. 1 displays detectable Hg amounts (around 60 mg kg^{-1}). Despite this, its mass and Au content rule out the possibility of surface gilding or counterfeiting, and the mercury is likely residual from geological or metallurgical processes [27,28].

Although μ -EDXRF analysis identified two Pt/Pd groups, the limited number of ICP-MS samples, combined with the bulk nature of the micro-destructive analyses, prevented

a robust validation of this surface-based pattern. Nevertheless, all micro-sampled coins show Pt content higher than Pd content.

A bivariate analysis based on a correlation matrix of characteristic soil elements (Al, Ca, Ti, Cr, Mn, Fe, Ni, Zn, and Sr) was performed to investigate the nature of surface encrustations (Table 4). Strong positive correlations among these elements indicate a shared geochemical signature typical of continental (terrigenous) soils, distinguishing them from anthropogenic or alluvial sources. In fact, the correlations observed between Cr, Mn, Fe, and Ni confirm that iron and nickel have a terrigenous origin, as well as Zn, which positively correlates with Ca, Al, and Sr, supporting their interpretation as soil-derived contaminants rather than alloy components.

Table 4. Correlation matrix for the bulk data set (bivariate analysis) for the terrigenous elements. Values greater than 0.5 or lower than −0.5 are in bold.

	Ni	Al	Ca	Ti	Cr	Mn	Fe	Zn	Sr
Ni	1.000								
Al	−0.415	1.000							
Ca	−0.359	0.986	1.000						
Ti	−0.879	0.597	0.498	1.000					
Cr	0.998	−0.431	−0.374	−0.873	1.000				
Mn	0.993	−0.371	−0.302	−0.885	0.993	1.000			
Fe	0.986	−0.397	−0.325	−0.909	0.985	0.996	1.000		
Zn	−0.413	0.943	0.898	0.587	−0.438	−0.377	−0.382	1.000	
Sr	−0.335	0.983	1.000	0.476	−0.350	−0.277	−0.301	0.894	1.000

3.3. Inter-Technique Comparison of Gold Fineness Estimates

Micro-sampling of six coins (five *solidi* and one *tremissis*) allowed a limited assessment of gold fineness using ICP-AES, providing an independent check on the high Au contents inferred from μ -EDXRF analyses. The dissolved fragments yielded Au concentrations consistent with very fine gold alloys (Table S2), in agreement with the presence of the “OB” inscription on the reverse, traditionally interpreted as an indication of refined gold (*obryzum*) rather than a guarantee of absolute chemical purity [29].

It must be stressed, however, that the primary objective of the ICP-AES measurements was not to resolve subtle surface–bulk compositional gradients, but rather to provide a semi-quantitative estimate of near-bulk fineness while preserving the integrity of the coins. In gold alloys with Au contents exceeding ~95–98%, the analytical uncertainties associated with ICP-AES become large relative to the magnitude of any expected surface enrichment effects, limiting the method’s sensitivity to small compositional differences.

For this reason, the investigation of potential surface alteration phenomena relies mainly on the comparison between surface-sensitive μ -EDXRF and high-precision ICP-MS data. While μ -EDXRF probes only the outermost layers of the coins (with a penetration depth of approximately 8–60 μ m [30]), ICP-MS provides more precise quantitative information on trace elements and bulk-related elemental ratios.

A comparison between μ -EDXRF and ICP-AES Au gold contents for the six micro-sampled coins is reported in the Supplementary Materials (Figure S1). Statistical testing (paired *t*-test and Bland–Altman analysis) indicates that the observed offsets are not statistically significant. This apparent agreement should be interpreted cautiously, as it primarily reflects the limited resolving power of ICP-AES at very high gold concentrations rather than conclusive evidence for the absence of surface enrichment.

Overall, the combined μ -EDXRF and ICP-MS results—supported by comparison with published bulk analyses—indicate that surface effects, if present, are minor and do not substantially bias the compositional assessment of Late Antique gold coinage.

4. Discussion

The multi-analytical approach confirms that the coins under study were manufactured from exceptionally pure gold, in keeping with the long-recognized stability of Late Roman and Early Byzantine gold objects [6,7]. While an indirect estimate of gold content can be obtained by subtracting the sum of trace elements measured by ICP-MS from 100%, this approach does not account for light elements (C, O, N, S) or other minor constituents. Gold fineness was primarily evaluated through the use of μ -EDXRF and ICP-MS, which indicate high Au contents that fall within the range reported for contemporary issues from other hoards and museum collections [13,31,32].

Comparative data from the literature further support our results. A *solidus* of Julian II has been reported with a gold content of about 95.2% [19]. For Theodosius II, both bulk and surface analyses conducted on museum collections consistently indicate high fineness. In particular, XRF and LA-ICP-MS measurements on coins from the Ashmolean Museum generally report gold contents between approximately 98.6% and 99.7% [33]. Comparable values have been obtained through Proton Activation Analyses (PAA) carried out by Morrisson et al. [34], which typically range from about 98.65% to 99.43%. Similarly, Biborski and Biborski reported gold contents of around 99.2% for a *solidus* of Theodosius II from Prehuki, Sanok County [35]. These independent datasets are fully consistent with the low Ag and Cu concentrations measured by ICP-MS in our Theodosian issues, which imply gold purities close to 99%. Later issues of Valentinian III are reported to contain slightly lower gold contents, just above 96% [36], suggesting that some of the coins analysed here may belong to the earlier phases of his coinage.

As an additional check, gold content was also measured directly using ICP-AES on micro-sampled fragments. While this provided an independent estimate of fineness, the method's limited precision at very high Au concentrations means that these results should be regarded as indicative only and do not provide definitive information on potential surface-related effects.

The consistently low concentrations of Cu, Ag, Pb, and Sn measured in bulk samples are compatible with the exploitation of natural alluvial placers, characterized by minimal alloying and limited geochemical impurities [37]. Similar trace-element signatures have been reported for Late Antique and Byzantine coinage, where alluvial gold was often minimally processed aside from cupellation and salt cementation [9,11,27]. The sporadic detection of Sn and Pb agrees with previous observations that minor inclusions—often inherited from cassiterite (SnO_2) or galena (PbS) present in alluvial deposits—may occasionally survive metallurgical refining [38–41]. The available data do not allow attribution to specific mining regions or geological contexts. Provenance considerations should therefore be regarded as indicative and exploratory, rather than conclusive.

A particularly noteworthy outcome of the non-destructive screening is the identification of two distinct Pt/Pd ratios. Platinum-group elements have emerged as tracers for reconstructing geological sources and bullion circulation pathways in ancient gold [10,12]. The separation between the two Pt/Pd groups in our dataset is evident at the surface-analysis level. However, this distinction is not reproduced by the micro-destructive analyses, most likely due to the very limited number of coins subjected to ICP-based techniques (6 out of 49). Such a small subset is unlikely to capture the full compositional variability highlighted by the XRF results across the entire assemblage. Consequently, the lack of full agreement between μ -EDXRF and ICP-MS for Pt/Au and Pd/Au ratios reflect limitations in sample representativity and trace-level sensitivity, rather than invalidating the analytical approach.

A comparison between μ -EDXRF and ICP-AES Au contents for these six coins is reported in the Supplementary Material (Figure S1). Statistical testing indicates that the

observed offsets are not statistically significant. However, this apparent agreement should be interpreted cautiously, as it primarily reflects the limited resolving power of ICP-AES at very high gold concentrations rather than conclusive evidence for the absence of minor surface effects. Overall, the combined μ -EDXRF and ICP-MS results indicate that surface effects, if present, are minor and do not substantially bias the compositional assessment of these coins.

The metallurgical and compositional homogeneity observed across most specimens is in accord with historical reconstructions of Late Antique minting policies, which emphasized strict control over gold purity [3,5,29]. Slight deviations among specimens attributed to different mints likely reflect subtle differences in refining efficiency or bullion procurement, rather than intentional debasement. The presence of two Pt/Pd groups within a single hoard may reflect the circulation of gold from different geological provinces within the Eastern Mediterranean. In this region, multiple mining districts—particularly in Anatolia—are known to have been exploited during the Roman and Byzantine periods, suggesting a potentially diverse metal supply network in Late Antiquity [40].

On the whole, the combined use of surface-sensitive and bulk analytical methods provides a useful framework for discussing the metallurgical characteristics of these coins within the broader context of Late Antiquity. While the results are consistent with the generally high purity documented for imperial gold coinage, they also point to subtle compositional and technological features that may reflect the complexity of metal circulation and refining practices during this period.

5. Conclusions

Thanks to the availability of a gold standard, it was possible to semi-quantitatively determine the gold content in all 49 Late Antique gold coins. The results obtained from non-invasive analysis with μ -EDXRF showed that no minting debasement occurred during the period when the coins under study were issued (AD 367–565). Furthermore, no forgeries were identified, confirming that in the 4th–mid 6th centuries, the Roman and Byzantine Empires had a high availability of gold for coin production. The Pt/Pd ratio is indicative of potential information about the origin of gold, as these two elements are not significantly affected by metallurgical refining processes. By comparing the areas of the non-interfering peaks $L\gamma_1$ of Pt and $K\alpha_1$ of Pd, two compositional groups were distinguished, consisting of 37 and 9 coins, respectively. Out of the total of 49 *solidi*, three coins did not show the characteristic palladium peaks.

The specimens investigated in this study hold high historical value, which is why micro-destructive analyses were performed on only six coins, selected using a blind method to avoid experimenter's bias. A few milligrams of samples were collected from the edges of the coins. Although the sampling method used had some limitations due to the scarcity of material obtained, it provided representative samples of the gold *solidi* under study for the purpose of quantifying the principal metal and trace elements.

Direct gold determination by ICP-AES provided an independent estimate of fineness; however, the limited precision of this technique at very high gold concentrations restricts its resolving power for assessing subtle surface-related effects.

Regarding trace elements, quantified by ICP-MS, the presence of tin and the low concentrations of copper and lead suggest that the gold used to produce the six analysed coins had alluvial origin. However, any provenance-related interpretation remains tentative and represents a perspective for future research based on larger datasets and comparative reference materials. The Pt/Pd ratios obtained by the micro-destructive technique did not show any particular trend, perhaps due to the limited number of samples chosen for sampling. The gold content estimated indirectly by subtracting trace-element percentages

from 100% was consistent with published values for contemporary *solidi*, supporting the reliability of our approach. Finally, the analysis and quantification of the main terrigenous elements showed positive correlations between Cr, Mn, Fe, and Ni, and between Ca, Al, and Sr, leading to the conclusion that the burial site of the coins was the soil.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/heritage9010038/s1>. Table S1: Pd/Au, Pt/Au and Pt/Pd ratios of the 49 gold coins. Three coins (No. 13, 36 and 46) exhibited comparable Pd peaks within the background noise of the instrument, so the calculation of Pt/Pd ratio was not possible; Table S2: Average content of trace metals expressed in mg kg^{−1} for the six coins selected for the ICP-MS analysis. Concentrations are reported concerning the mass of material sampled and dissolved. Figure S1: Average gold percentage obtained by μ -EDXRF in blue and by ICP-AES in orange. Error bars express standard deviations.

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Abbreviations

The following abbreviations are used in this manuscript:

AD	Anno Domini
BC	Before Christ
μ -EDXRF	micro-Energy Dispersive X-Ray Fluorescence
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
LOD	Limit of Detection
PAA	Proton Activation Analysis

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