

Metallurgic Analysis of Tetrachic Folles

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Abstract

Tetrarchic folles have long been considered a well-studied piece in Roman Imperial numismatic archaeology, especially regarding the presence of its silver wash. Through the employment of various spectrographic techniques, most notably Raman and X-Ray Fluorescence, this paper investigated the metallurgic composition of these folles, with a particular emphasis on their silver content. Although expected to be significantly eroded and hence, maintaining little of their initial silvering, this investigation revealed various surprising results, ranging from high silver concentrations to the presence of unexpected contaminating agents. Therefore, this question added to the archaeological debate regarding the durability of this patina, its true nature and hence, its means of application.

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1. Description of Assigned Artefacts

The artefacts represent a small sample of Tetrarchic folles which vary significantly in typology and provenance. All coins are identified as per Roman Imperial Coinage VI, accessed from Wildwind's Coins (Wildwinds, n.d.). Figure 1.1 below correlates each coin, as per Appendix A, to its typology, inscriptions, mint marks and mints.

Coin	Type	Reverse Inscription	Obverse Inscription	Emperor	Mint Mark	Mint
A	RIC VI 108b	“GENIO POPVLI ROMANI”	“IMP MAXIMIANVS P F AVG”	Maximian	SIS	Siscia
B	RIC VI 134b, A	“SACRA MONETA AVGG ET CAES NOSTR. “	“IMP MAXIMIANVS P F AVG”	Diocletian	SIS	Siscia
C	RIC VI 25a	“GENIO POPVLI ROMANI.”	“IMP CC VAL DIOCLETIANVS PF AVG “	Diocletian	TH	Thessalonica
D	RIC VI 25b, P	“GENIO POPVLI ROMANI.”	“IMP MAXIMIANVS PF AVG”	Maximian	AQS	Aquilae
E	RIC VI 28a	“GENIO POPVLI ROMANI.”	“IMP DIOCLETIANVS AVG”	Diocletian	None	London
F	RIC VI 11b, A	“GENIO AVGG ET- CAESARVM NN “	“GAL VAL MAXIMIANVS NOB CAES”	Galerius	KA	Cyzicus
G	RIC VI 105a	“FORTVNAE REDVCI CAESS NN”	“IMP C DIOCLETIANVS PF AVG “	Diocletian	~RP	Rome

Figure 1.1 (Above): Table correlating coins to their typologies and mints.

This set of 7 coins effectively demonstrates the degree of variation and ubiquity of the folles across the empire, in their sheer variety in mint location and style of design. All coins but coins B and G featured a depiction of Genius, with a cornucopia in his left and paterna in his right, clothed only in chlamys on the left shoulder and modius on the head. Amongst this basic motif, there was significant variation in the proportionality of figures and the depictions of the cornucopia, most notably seen in the contrast between coins E and A. Similarly, coins B and G, which both depict Moneta with scales and a cornucopia, have a high degree of contrast in their styles. Regarding obverses, each coin followed the motif established in depicting emperors on their reverses. Notably, Maximian and Diocletian occurred most frequently, on three coins each, followed by Galerius on Coin F. Constantinus was not depicted in this set of folles.

The key consideration regarding the appearance of folles are their visual silvering. In this set of coins, coins C, D and E appeared to be the least eroded and presented the highest visual degree of silvering, while coins A and F appeared to be the most heavily oxidised.

2. Historical Context of Artefacts

The series of Tetrarchic folles represent the consequence of what Cope (COPE, 1996) determines to be “one of the greatest landmarks in Roman Imperial coinage” under Diocletian’s reforms of 294 CE, which proved a great overhaul from the repeatedly debased antoninianus of previous emperors. Diocletian’s reforms, primarily, were a response to the hyperinflation caused by this debasement of previous currencies, which was only exacerbated by significant individual

debasement using non-silver alloying agents. Although these reforms never solved the economic issue, they did help in slowing the rates of inflation, allowing for later economic success.

As argued by Ross in “Diocletian and the Tetrarchy” (Ross, 2004), Diocletian sought increased order and centralisation in the minting and distribution of coins, including the augmented use of provincial capitals, standardised and mandated mint marking and the introduction of new currency. This new currency included new *aureus*, *argenteus*, and the *folles*, which formalised coin washing as a technique to establish the copper coin as part of the silver coin set. Hence, the *folles* became a symbol of the new stability introduced by the Tetrarchy, until the retirement of Diocletian and Maximian.

3. Scientific Context; Spectroscopic Techniques

4.1. X-Ray Fluorescence

The primary means of metallurgic investigation for the *folles* will be with the use of point-based and mapping X-Ray Fluorescence (XRF). XRF manipulates the particular behaviour of substances when exposed to specific frequencies of X-Rays, such that photons are absorbed by atomic electrons, which forces them into an excited state. When released from this excited state, in a return to their initial energy level, energy is released at a frequency lower than that of the initial photon, known as a spectrum. These spectra differ by element and hence, with a knowledge of known spectra by element, they can be used to determine elemental composition. Notably, XRF forms an ideal analysis technique for this project due to its low information depth and non-destructive nature, allowing for a determination of surface percentage composition data for each coin. Both XRF mapping and point-based XRF were utilised for this project as, upon visual analysis, silvering differed dramatically even on the surface of an individual sample.

4.2 Raman Spectroscopy

Raman spectroscopy will form a supplementary analytical technique for this investigation due to its ability to accurately determine the identity of specific bonds, allowing for assertions to be made specifically about oxidation of particular metals. In Raman spectroscopy, a sample is exposed to monochromatic light of a known frequency, which hence scatters elastically, or without losing energy, known as Rayleigh scattering. However, a slight proportion of this light is scattered with a small loss or gain of energy, known as Raman scattering. A Raman spectrometer utilises this scattering to determine absorbance spectra for a given substance, which can be used to determine bonding and hence, material identities when compared to known spectra of specific bonds. Significantly, like XRF, Raman spectroscopy is also non-destructive and is hence, very useful in determining the presence of metal oxides and organic compounds.

4. Enquiry Questions and Hypothesis

The investigation was centred on five primary data-focused enquiry questions that are as follows:

1. To what extent is the silver patina still present after erosion?
2. Following this erosion, to what extent has the now exposed copper oxidised?
3. What alloying agents were used in the formation? How did this differ by mint?
4. How does percentage composition differ by mint?
5. How was this silver wash likely applied?

It is currently believed that these Tetrarchic folles will have experienced a high degree of erosion since the 3rd Century and hence, will exhibit little to no remaining patina and as per (COPE, 1996), will have significant portions of alloying agents such as tin (Sn) and lead (Pb). It is also highly likely, due to the nature of local production throughout the Roman Empire, that there will be minor differences by mint in metallurgical composition and degree of erosion.

5. Instrumentation

5.1 Point Based XRF

A Bruker Tracer 5i XRF Spectrometer was employed to collect initial spectra for each coin, with various scans taken on either obverse or reverse, as indicated by Figure 5.1.1. Notably, each coin was scanned on a point detailed with the most visual silvering so as to ascertain the most accurate percentage composition data for the coin as it initially was. Under analysis from Sydney Analytical (University of Sydney), this data was adjusted as per copper calibrations which were ideal for representing both Cu and Ag and represented both as percentage composition data and as individual spectra.

Coin	Face Scanned
A	Reverse
B	Obverse
C	Obverse
D	Reverse
E	Reverse
F	Obverse
G	Obverse

Figure 5.1.1 (Above): Table depicting the face scanned with point-based XRF by coin.

5.2. XRF Mapping

A Bruker ARTAX800 μ -XRF Spectrometer was used by Sydney Analytical to analyse Coin A (As per Appendix B). This spectrometer utilised a “box-shaped” of repeated linear scans across an area on the obverse of the coins in order to track how composition changed throughout the coin, compared to the initial point. This model also had a significantly lower information depth than the portable version used for point-scanning, hence the overall increase in Ag peaks. Figure 6.2.1 shows the point based and mapping data for Coin A. (To be attached when I figure mapping out)

5.3 RAMAN Data

The Bruker BRAVO Handheld Raman Spectrometer was employed on the obverse of Coin A and the reverse of Coin E to determine how the presence of copper (I and II) oxide differed between a heavily eroded and a significantly silvered coin respectively. Both samples were prepared and underwent one scan from the BRAVO Raman Spectrometer each, which produced readable spectra when observed using Opus Viewer.

6. Results and Discussion

6.1 X-Ray Fluorescence

The XRF Data proved to be central in illustrating the difference in percentage composition of metals in each coin. The tabulation spectra using copper calibrations into percentage compositions created inaccuracies regarding very low peak heights and potential overlap between Sn and Ag peaks, represented by negative percentages and a percentage sum greater than 100, respectively. However, despite these inaccuracies, XRF data proved to be critical to ascertaining the degree of erosion specifically and across all samples.

Spectra	A	B	C	D	E	F	G	\bar{x}	σ
Manganese (Mn)	0.010	-0.009	0.025	0.008	0.027	0.017	-0.002	0.011	0.013
Iron (Fe)	0.032	0.071	0.342	0.059	0.230	0.065	0.131	0.133	0.113
Cobalt (Co)	0.000	-0.015	-0.019	-0.013	-0.022	-0.014	-0.003	-0.012	0.008
Nickle (Ni)	0.005	-0.009	-0.019	-0.015	-0.013	0.008	0.003	-0.006	0.011
Copper (Cu)	91.357	88.378	88.372	90.463	85.467	86.723	89.331	88.584	2.043
Zinc (Zn)	0.285	0.261	0.152	0.143	0.644	0.226	0.279	0.284	0.169
Arsenic (As)	0.026	0.210	0.184	0.215	0.420	0.130	0.133	0.188	0.121
Lead (Pb)	3.821	2.575	2.412	1.965	3.470	2.873	3.750	2.981	0.715
Bismuth (Bi)	-0.022	-0.004	0.028	0.006	0.020	-0.029	-0.024	-0.004	0.023
Zirconium (Zr)	0.014	0.002	0.021	0.000	0.023	0.011	0.012	0.012	0.009
Niobium (Nb)	-0.337	-1.009	-1.230	-0.934	-0.690	-1.549	-0.629	-0.911	0.403
Silver (Ag)	1.647	5.306	6.133	5.347	2.706	7.419	3.068	4.518	2.080
Tin (Sn)	3.379	3.205	2.280	2.106	6.223	3.128	3.355	3.382	1.355
Antimony (Sb)	0.133	0.165	0.131	0.058	0.124	0.176	0.057	0.121	0.047

Figure 6.1.1 (above): Percentage composition data by element and sample, with mean and standard deviation.

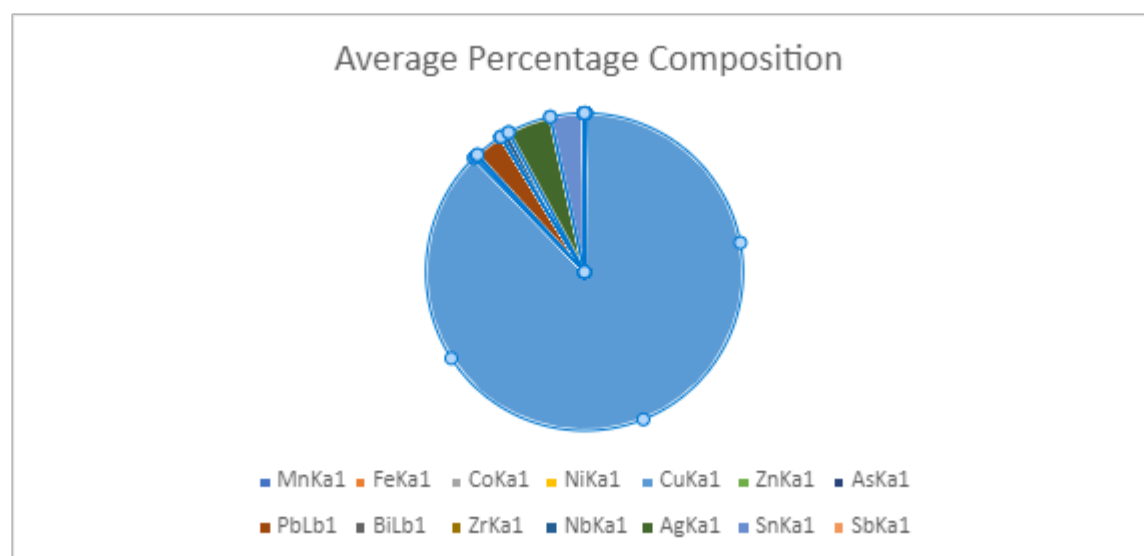


Figure 6.1.2 (above): Pie chart of the average percentage composition of the set of folles.

As per Figure 6.1.2, on average, concentrations of copper and silver varied significantly from the figures presented by Cope, such that copper concentrations were much lower, 88.58% on average, while silver concentrations were overall much higher, 4.52% on average compared to approximately 2% from Cope's research, which is likely higher than the presented figure due to the overlap between Ag and Sn. This indicates an overall much higher retention of the initial patina than expected, illustrating the extent of erosion was much lower than originally anticipated.

However, the standard deviation in silver indicated by Figure 6.2.1. is very significant in illustrating an average of 46% variation from the mean. This demonstrates that each sample varied significantly in their degree of erosion, as expected, where coins C and F appeared to have maintained the heaviest patina, at 6.13% and 7.14% respectively, while coins A and E appear to be the most eroded, with 1.64% and 2.7%. Coin E is particularly significant, as there was visible silvering on the obverse of the coins and that Cope specifically details the average fineness of London-minted coins as 1.9% on average. However, this may be due to the significant overlap between Sn and Ag in this XRF data, as the percentage Sn for sample E was also proportionately high at 6%. Figure 6.1.3. below reveals the individual spectra for each of these coins with their photographs.

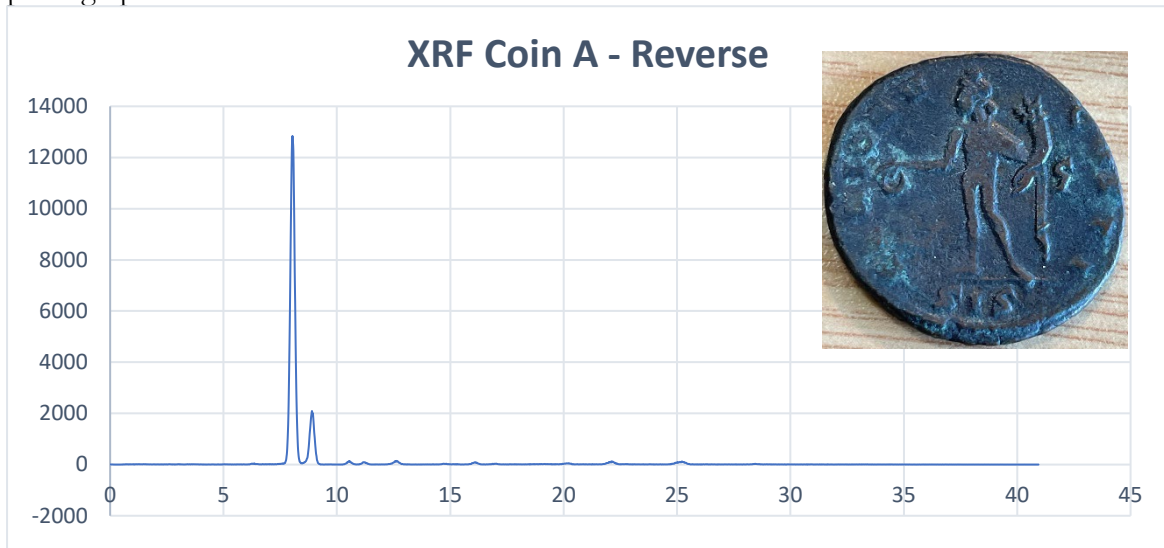


Figure 6.1.3 (above): XRF spectrum of the reverse of Coin A with its photograph.

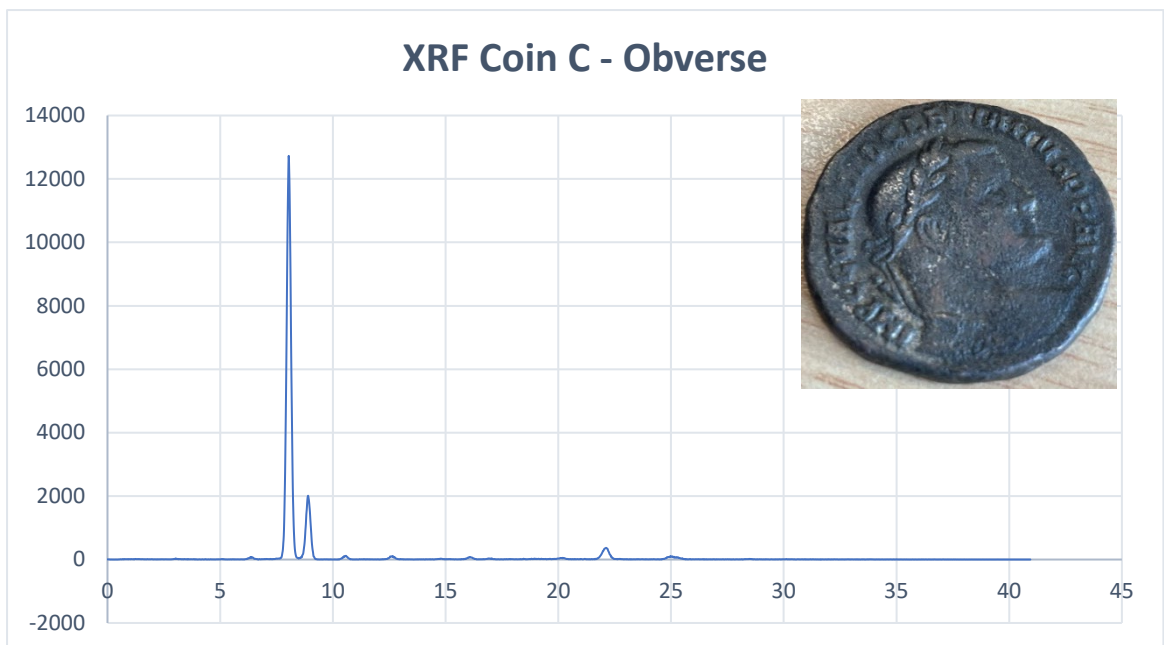


Figure 6.1.4 (above): XRF spectrum of the obverse of Coin C with its photograph.

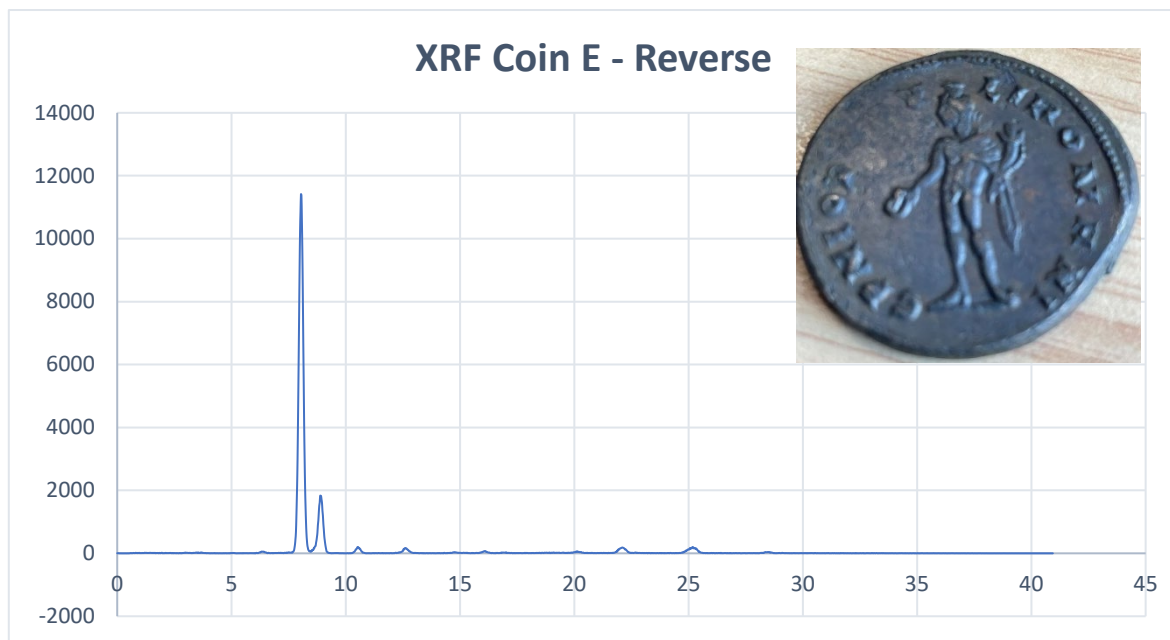


Figure 6.1.5 (above): XRF spectrum of the reverse of Coin E with its photograph.

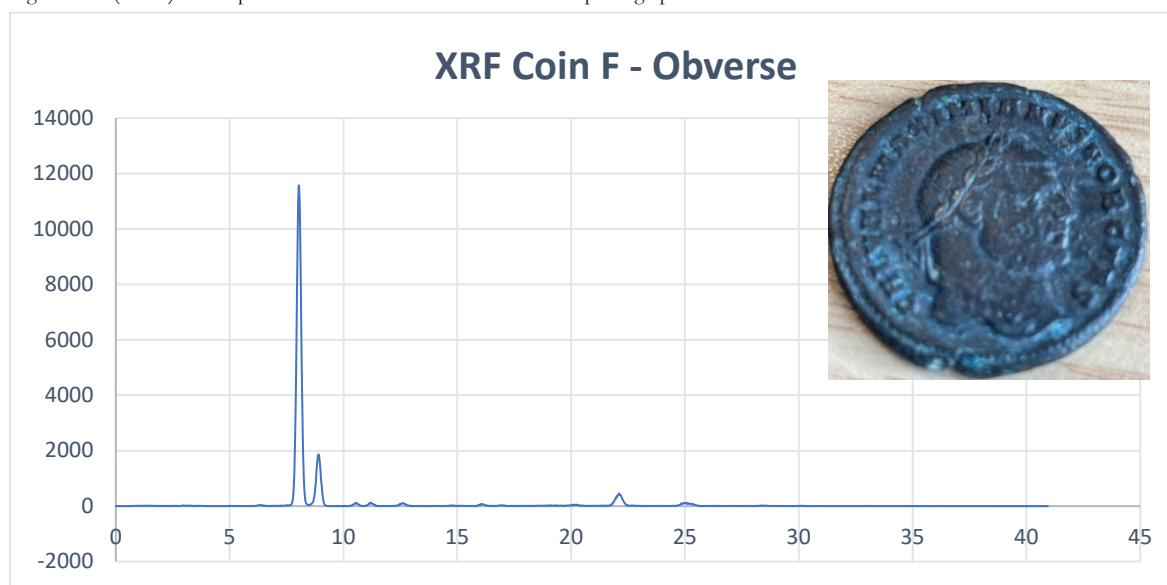


Figure 6.1.6 (above): XRF spectrum of the obverse of Coin F with its photograph.

The raw spectra of coins A, C, E and F remove the methodological error presented by the compositional data regarding the copper calibration and its artifacts such as the Sn-Ag crossover, yet still corroborate the initial supposition regarding overall erosion. In each graphs the peaks, read from the right, as Cu- K α , Cu-K β and Ag- α , which in their peak heights illustrate the same trend observed in the percentage composition data. Hence, conclusions regarding the relative erosion of each coin presented earlier are still reliable due to the repeated trend observed and accurate due to the elimination of the methodological concern regarding the copper calibration in the raw data.

Although unreliable due to the lack of data on any other coin, the XRF mapping data for the reverse of coin A further corroborates this conclusion particularly regarding the stark degree of erosion for this coin. The point-based nature of the XRF applied to the previous coins presents significant validity concerns regarding additional variables of potential changes in the fineness and presence of copper along the surface of the coin, such that a particular point selected in traditional XRF may be an outlier. This mapping data, seen in Figure 6.1.4 illustrates that along the section of the coin selected, there was little variation in presence of copper,

augmenting the accuracy of the data presented in the point-based XRF and percentage composition for Coin A and by extension, for the data set as a whole.

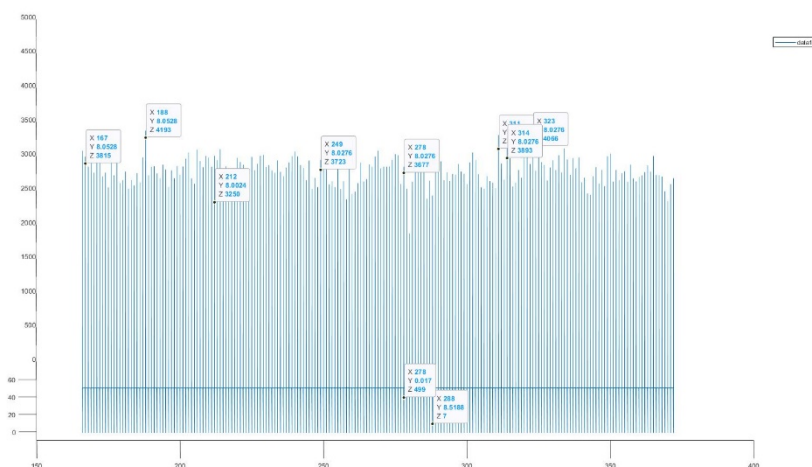


Figure 6.1.7 (above): variation in peak heights of copper across a section of Coin A.

6.2 Raman Scans

Two Raman scans were taken, one of Coin A and one of Coin E, on the initial assumption of a large contrast in silvering between the two as visual analysis initially indicated. The scans also present some notably validity and reliability issues in comparison to the XRF. Most notably, only 2 coins were scanned using Raman spectroscopy, meaning that any conclusions regarding the broader data set are unreliable and additionally, unlike XRF, coin A's obverse was scanned by XRF, invalidating any comparisons between the two due to the introduction of a new variable.

Despite these issues, the scans were significantly different in their peak heights and locations. Figure 6.2.1 and 6.2.2 (below) demonstrates this. Crucially, the two scans were very similar in their detection of copper (I and II) oxide, at approximately $500\text{-}650\text{cm}^{-1}$, with both spectra measuring a peak height of 300eV , indicating a some presence of oxidation and hence erosion. However, the spectra differed significantly throughout the rest of the graph, where the most significant peaks were for alcohols and other organic compounds. In both scans, this is evidence of severe biological contamination, likely from lipids from contemporary preparation and examination of the samples. However, this contamination appears much more present in Coin A than Coin E given the generally higher peak heights.

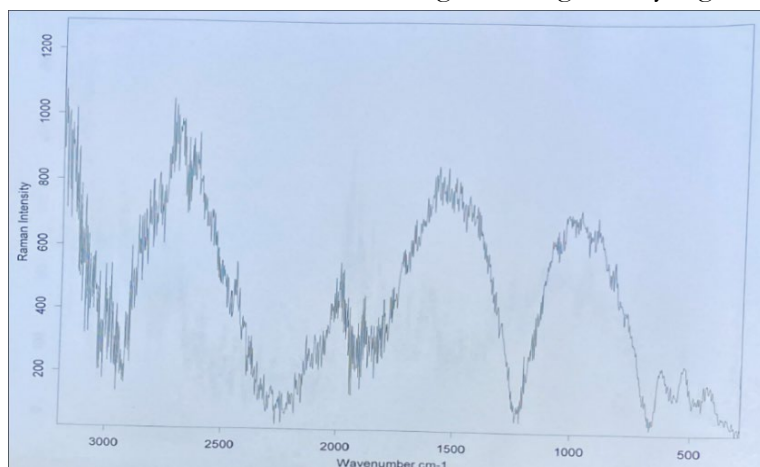


Figure 6.2.1 (above): Raman scan of the obverse of Coin A.

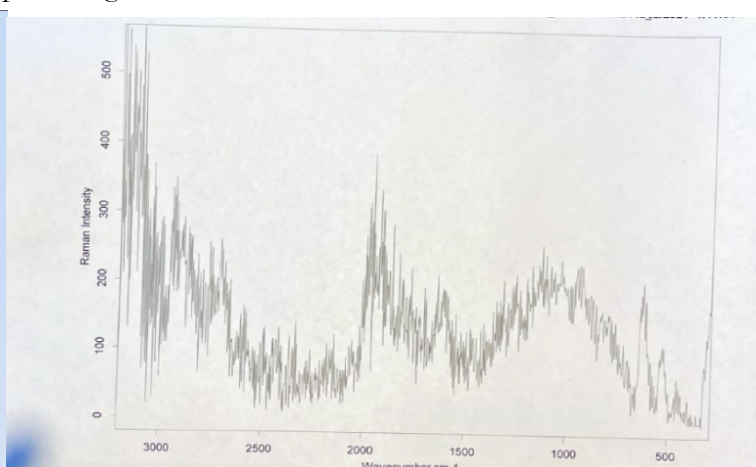


Figure 6.2.2 (Above): Raman scans of the reverse of Coin E

6.3 Alloying Agents and Contaminants

The key considerations regarding alloying agents and contaminants is regarding Figure 6.1.1 and the compositional XRF data. This data reveals significant unexpected peaks in Pb that likely represent significant contaminations in both the mining and refining process of the silver for the coins' patinas. Significantly, as illustrated by Craddock (Craddock, 2014), the primary means of Roman acquirment of silver was through a process known as 'cupperation'. This process separates Ag from Pb through the following reaction: $\text{Pb(s)} + \text{O}_2\text{(g)} \rightarrow \text{PbO}$ or $\text{PbO}_2\text{(s)}$, an oxidation of metallic lead. Ag, being unreactive, will not undergo this oxidation and can hence be easily separated from the lead oxide, often using its much lower melting point. However, often, trace amount of lead oxide remain, hence the contamination of the Ag with Pb and the presence of Pb as a contaminant in the XRF scans. The standard deviation within this result was comparatively low, indicating valid results that can be broadly extended.

6.4. Variation by Mint

As with the concerns regarding alloying agents and contamination, variation by mint will be considered as per the compositional data presented in Figure 6.1.1. Unfortunately, although significant variation appears to be present in the data, given that each coin demonstrates some variation from each other from another mint, conclusions regarding variations between mints are unreliable, as only one coin from each mint was present in the data set with the exception of coins A and B, both of which are from Siscia, meaning that further repeats must be undertaken to make these conclusions. Notably, Coins A and B differed greatly in their trends, meaning that a mint-based trend in composition is unlikely.

7. Conclusion: Archaeological Significance

Due to considerations regarding reliability and validity of conclusions for variation by mint, two primary archaeologically significant conclusions present themselves, in the widespread presence of lead contaminant agents in folles samples: and the relative durability of silver patinas in folles.

7.1 Presence of Lead Contaminants

As illustrated in 6.3, the sample of folles demonstrated a broad and universal presence of lead, likely from biproduct lead oxides within the samples. This is very significant in determining the details of Roman metallurgy. It suggests heavy presence of lead both in mining and processing, strengthening the accepted theory that silver was sourced primarily from argentiferous lead deposits and was separated primarily through cupperation.

7.2 Silver Washing Methods

The debate regarding the application of the silver wash of Tetrarchic folles, is currently quite large, with two major theories to be considered: the 'pickling' method illustrated by Vagi (Vagi, 1999); and the "coating" theory presented initially by Hedges and Robins (ROBINS, 1963) and then elaborated on by Sayles (Sayles, 2003). The former suggests that a fine coat of silver was "raised" to the surface of the coin through removal of copper using a strong acid, while the latter suggests that the coins were coated in molten silver. The overall high concentrations of silver presented by the XRF data and relatively low presence of copper oxides seen in the Raman data, as well as the within-sample consistency seen in the XRF mapping, suggests that only the latter could be possible, as argued by Hedges and Robins, such that the 'pickling' method would produce an inconsistent coating, while the molten silver would be much more consistent.

8. Conclusion: Future Research

This investigation into the metallurgical composition of Tetrarchic folles presents multiple major options for future research, most notably through investigations into larger data sets and further into the debate regarding silver washing techniques. With larger data sets, preferably from the same mint, more reliable determinations regarding trends between Roman mints can be made, allowing for further conclusions to be drawn regarding specific metal sourcing and processing. Furthermore, repetitions of the XRF mapping scans and Raman scans would significantly improve the reliability of results, allowing for further extrapolation. However, most critical is a further investigation into the historical context of the debate regarding the silver washing techniques, which may use the silver fineness results presented by this investigation to make determinations regarding the thickness of the initial wash and hence, potentially, the technique used to create it, which would only be supplemented by additional investigations into the consistency of the coat applied through repetitions of the XRF mapping.

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Appendices

Appendix A:

All source data, images, and drafts at GitHub permalink:

Appendix B:

Truncated table from (COPE, 1996) regarding metallurgic composition of Tetrarchic folles.
Truncated to only include silver composition by sample, with mean and standard deviation.

Silver Content in Tetrarchic F	Percentage Composition (%g) of Ag in Sa	\bar{x} (per mint)	σ
Mint of Loninium			
1	2.23	1.92	0.193080294
2	1.7		
3	2.07		
4a	1.85		
4b	1.83		
4c	1.84		
MINT OF TREVERI		1.687	0.495469474
5	2.56		
6	2.25		
7	1.73		
8a	1.2		
8b	1.32		
8c	1.26		
9	2.28		
10	1.52		
11	1.37		
12	1.38		
MINT OF LVGDVNVM		1.882727273	0.538666704
13a	2.61		
13b	2.7		
13c	2.66		
14	2.07		