A Re-evaluation of the Debasement of the Roman Silver Coinage as Presented in David Richard Walker's *Metrology of the Roman Silver Coinage*

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Thesis submitted to the University of Ottawa
in partial fulfillment of the requirements for the
Master's degree in Classical Studies.

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Abstract

David Richard Walker's *Metrology of the Roman Silver Coinage* analyzed the silver content of over 5000 Roman *denarii*, *antoniniani*, and *drachmae* using x-ray fluorescence (XRF) spectrometry. His results have been widely cited and used by scholars in the fields of Roman economic theory and numismatics. This thesis seeks to prove that Walker's XRF results were not only inaccurate, but inconsistently so.

Corrosion and surface enrichment on silver-copper coins have caused surface-level elemental examinations, like XRF, to produce incorrect results. The results from Walker's XRF analysis have been compared against results from four individual wet chemical studies. The comparisons display striking, and significant, differences. I am forced to conclude that Walker's data does not in any way align with the true silver content of the coins he analyzed. As a result, this thesis will re-examine several theories and hypotheses posed by scholars who used Walker's data and propose new, more appropriate, uses for Walker and XRF analysis outside of the examination of corroded silver-copper coins.

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Acknowledgements

First and foremost I would like to thank my thesis supervisor Richard Burgess for all of his help and guidance, and for seeing an opportunity when I saw a catastrophe.

I would also like to thank my brother, Ben Langmuir, whose French comprehension is much better than my own, for his assistance in translating a great deal of technical chemistry terms. A big thanks to Jason Lockhart for helping me pick an appropriate statistical significance test and for verifying the accuracy of the T-test calculator.

I am very grateful for parents, Judy Parkes and Blair Langmuir, and my sister, Cassandra Langmuir, for their continued support and encouragement. And finally, I would like to thank my boyfriend, Michael Tomlinson, who kindly acted as a sounding board for all of my ideas.

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Introduction

Since the publication of David Richard Walker's seminal study *Metrology of the Roman Silver Coinage* (*MRSC*) in 1976 it has been widely cited in the fields of economics, history, and numismatics alike.[1] Never before had such an all-encompassing study of Roman coins been attempted, nor has it been repeated since. Walker employed state of the art technology, i.e. x-ray fluorescence (XRF) spectrometry, to analyze the elemental make-up of over 5000 *denarii*, *antoniniani*, and *drachmae* dating from the first to third centuries AD. Each coin was categorized by imperial reign, year, and mint, with help from the British Museum archives and numerous volumes of *The Roman Imperial Coinage* (*RIC*). They were then weighed, cleaned, and x-rayed. The weight along with silver and copper content were recorded for each coin and averaged for each category. At times his weight calculations were supplemented with the weight records of the coins in the collection of the British Museum and re-averaged (he refers to these as 'corrected weights').[2] With this information Walker was able to produce a nearly year by year report on the progress of the Roman silver coinage across three centuries.

The information gathered from his study helped to confirm long suspected theories of debasement and inflation that took place across the Empire. Many new theories relating to how and why this debasement occurred, written by Walker himself as well as many other later scholars, were spurred by his publication. It had long been known – thanks largely to the survival of Diocletian's Currency and Price Edicts – that debasement of the silver coinage had been a problem in the late Empire. However the process of debasement preceding Diocletian's actions was only partially understood because it was based on only visual inspection of the coins and a few (much

[1] D.R. Walker, *The Metrology of the Roman Silver Coinage* 1-3 (Oxford, 1976-1978).
[2] The supplementary coins from the British Museum are unidentified.

smaller) attempts to determine the metal content of Roman coins. Walker's study allowed scholars to track debasement virtually as it happened. It enabled scholars to speculate on the economic and monetary policies of the emperors (something that was not possible from a visual examination of the coins). Thanks to the large quantity of coins he had access to, Walker was even able to provide multiple readings for single years. At times upwards of twenty coins were recorded for a single group. This information allowed scholars to theorize on more than just the process of debasement. He used the multiple recordings to calculate the differences between each coin and the yearly average in order to make speculations about the process of minting coins and the silver standards. How precisely these standards were adhered to and the accuracy of the minting process are questions that Walker's study was able to answer. Walker, and scholars using his data, found that in theory there were active silver standards in place across the empire, but in practice there was a lot of variation in the silver fineness of each coin even within a single standard, i.e. the standard deviation was consistently high, which was peculiar. These are merely a few of the theories and observations that were spurred by Walker's study.

When I began my thesis, I intended to write a study comparing the process of inflation in the Roman Empire against the debasement of the silver coinage. Walker's publication was an obvious, and necessary, place to start. I sought to determine how debasement affected, or was affected by, inflation by tracking the price of a staple commodity across two centuries. It was my plan to record the silver content of the *denarius* (which would become the standard unit of account in the later empire) over the same time period in order to track and compare the debasement against the inflation. I was by no means the first to attempt this comparison. Many notable scholars such as Bagnall, Jones, Duncan-Jones, Howgego, and Harl had already undertaken similar investigations, the latter three by directly employing Walker's figures in their comparisons. I

chose the third and fourth centuries for my study because of the massive inflation that existed at this time and the abundance of primary sources attesting to it. Since Walker's study only extends until the mid-third century, I had to seek out other sources for tracking debasement beyond that time.

I began with L.H. Cope whose 1974 PhD thesis, *The Metallurgical Development of the Roman Imperial Coinage during the First Five Centuries A.D*, included several small wet chemical studies of Roman coins dating to the late third and early fourth centuries.[3] From a preliminary examination it appeared that debasement quickly became extensive. Compared to Walker's figures for the first half of the third century Cope's figures for the silver content of the standard coin, the *antoninianus*, were strikingly low. In 253, the last year that Walker records, he lists the silver fineness of the *antoniniani* as 35.5 percent. This is a 28.56 percent decrease from its initial fineness of 49.69 percent in 215, when the coin was first introduced as an eventual successor to the *denarius*. And yet in 270 Cope recorded the fineness of the *antoniniani* as only 3.26 percent. If both Cope and Walker were to be believed the fineness would have to have dropped 90.82 percent in only seventeen years, which was over twice the amount Walker showed it dropping since the introduction of the coin, in less than half the length of time. While not impossible, it was surprising, and suspect.

I had read, as is so often stated by scholars who cite Walker, that XRF analysis is known to produce inflated figures. XRF is a surface level analysis and therefore prone to accidentally analyzing the corrosion that often accompanies silver-copper coins like the *denarius* and the *antoninianus*.[4] Corrosion causes copper at the surface of the coin to be eliminated, resulting in an

[3] L.H. Cope, *The Metallurgical Development of the Roman Imperial Coinage during the First Five Centuries A.D* (Liverpool, 1974).
[4] This will be covered in more detail in Chapter Two.

apparent proportional increase of silver in that area. Since scholars continue to use Walker's figures in spite of the warnings, originally I assumed that the elevated silver levels would be minimal and consistent. But Cope's data now showed that it was not minimal. My next step was to determine if it was consistent. In the process of gathering evidence I came across two scholars who had compared Walker's results against neutron activation analysis and atomic absorption spectroscopy,[5] and found that Walker was reporting silver levels that were far too high.[6] However this work only included one comparison of *denarii* minted under Septimius Severus and two comparisons of *denarii* minted under Vespasian.[7] This made it impossible for them to establish if there was any pattern or consistency to the difference, which in turn would determine whether or not the difference in reported results actually mattered. If Walker's figures were consistently a set percentage greater than the true silver content then they would still have value. If not, I would be unable to use Walker's work and therefore unable to complete my intended study. Without Walker there was not enough data for the third century to continue with my study. Moreover, if Walker's figures were inconsistent then all economic speculations that had been made based on his data would be called into question.

In order to solve this problem I selected four studies that all overlapped with the period Walker reported on. They were all wet chemical studies from reputable scholars and all without any major criticism of their results. Wherever possible I compared directly on a year to year basis.

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[5] Neutron activation analysis (NAA) and atomic absorption spectroscopy are two other methods of elemental determination. The original NAA analysis of the coins used by Butcher and Ponting was performed by Condamin and Picon for their paper, 'The Influence of Corrosion and Diffusion on the Percentage of Silver in Roman *Denarii*,' *Archaeometry* 7 (1964) 98-105.

[6] K. Butcher and M. Ponting. 'Rome and the East. Production of Roman Provincial Silver Coinage for Caesarea in Cappadocia under Vespasian, AD 69–79,' *Oxford Journal of Archaeology* 14 (1995) 63-77.

[7] Their following paper, K. Butcher and M. Ponting, 'The Roman *Denarius* under the Julio-Claudian Emperors: Mints, Metallurgy and Technology,' Oxford Journal of Archaeology 24 (2005) 163-197, compared the average silver content for the post-reform *denarii* of Nero against Walker's average.

When lack of data made this impossible I combined years and compared across time periods.[8] The results, as shown in Chapter Two, prove there to be a striking difference between Walker's XRF results and those from wet chemical studies. There was no discernible pattern or consistent difference between the results. Faced with this information, I was forced to conclude that Walker's work could not be relied upon as an accurate source for silver fineness and therefore any economic or numismatic arguments based on it would be invalid. Now that my original thesis plan was no longer a viable option, I shifted my focus, taking the work I had already done to evaluate Walker's results and expanding upon it. My new thesis became a critique of Walker and XRF in the study of Roman silver and billon coins.[9] In the following three chapters I will endeavour to prove not only that Walker, and XRF in general, are not reliable sources for silver fineness, but also that the way in which they have been used in the past is both inappropriate and detrimental to progress in numismatics and Roman economic history.

Chapter One will look at methods of elemental analysis. Before we can begin examining any data, it is necessary to explain how different methods of analysis determine the composition of a sample. This knowledge will allow us to understand what might make one method preferable to another depending on the type of sample being analyzed. This is a necessary place to begin for two reasons: first, to establish wet chemical analysis as the gold standard of elemental analysis, and thus an appropriate point of comparison to prove the inefficacy of XRF; and second, to understand why XRF may not give correct results when analyzing silver-copper alloys. The second chapter will present the data from Walker and four wet chemical studies and evaluate their differences. Finally, the third chapter will look at previous scholars who have used Walker as a

[8] I made the time periods as small as possible for greatest accuracy. The limitations of this will be discussed in Chapter Two.
[9] Billon is a metallic alloy comprised primarily of a base metal, like copper or bronze, mixed with a small portion of precious metal, like gold or silver.

source for silver fineness and how the conclusions drawn in Chapter Two affect the theories and conclusions drawn in their work.

Chapter One

Methods of Elemental Analysis

There are many different methods available for determining the elemental makeup of a sample, not all of which are suitable for the examination of artifacts. The method chosen should depend upon the needs of the experiment. Analytical techniques can be broadly split into two categories: destructive and non-destructive. As their names suggest destructive techniques work by grinding, dissolving or otherwise removing a substantial portion of the analyte- the sample being analyzed- in order to analyze the entire composition, whereas non-destructive techniques analyze only the exterior of the object negating the need to heavily damage or destroy it. In the case of homogenous substances the non-destructive techniques are preferred because it does not matter which portion of the object is analyzed. But for a heterogeneous substance, e.g. a two phase silver-copper alloy, the portion analyzed must be representative of the whole.[1] This can cause problems for non-destructive techniques since only a small portion of the exterior is analyzed. This is one reason wet chemical analysis is often considered the gold standard, since it negates the potential problems associated with heterogeneous samples.

For the examination of ancient coins an ideal method would provide both accurate qualitative and quantitative information- that is whether or not an element is present in the sample and how much of that element there is in the sample- while being completely non-destructive. Secondary considerations would be the ease of use and transportability, cost, and time required. These secondary considerations, alongside its non-destructive nature, are a driving force behind

[1] See n. 8. R. Jenkins, 'X-ray Techniques: Overview,' in R.A. Meyers (eds), *Encyclopedia of Analytical Chemistry* (2006) 9.

many analysists' choice to use X-Ray Fluorescence (XRF), even though it can only perform surface-level analysis, i.e. it analyses only a portion of the analyte's outermost layer. On the other hand, the choice to use wet chemical analysis, i.e. a method of analysis whereby the analyte is chemically dissolved in order to analyse its entirety, forgoes the latter considerations in favour of more accurate quantitative results. These two methods, XRF and wet chemical analysis, in theory should provide similar results. In reality, external factors associated with aging metal alloys, i.e. surface enrichment and corrosion, can alter the effectiveness of any surface-level analysis.[2]

Wet chemical analysis and XRF are a fundamental, but small subset of elemental determination techniques. Many more exist. I chose to discuss only the aforementioned techniques because they are most pertinent to the study of Roman coins. David Richard Walker's analysis, against which all other studies will be compared, employed energy dispersive (ED) XRF as the method of analysis. For this reason, a comprehensive understanding of XRF, and specifically ED-XRF, is necessary in order to understand how Walker analyzed his coins and why this method is problematic for silver-copper alloys. Wet chemical analysis was chosen as the basis of comparison because of its overwhelming accuracy even in the face of heterogeneous samples and because all studies compared against XRF in the following chapter employ a method of wet chemical analysis to determine the elements in their coins. Therefore, it is necessary to describe the various methods of wet chemical analysis in order for the reader to understand how they function and why the results from wet chemical analysis should be trusted over those from XRF in this application.

[2] E.T. Hall, 'X-Ray Fluorescent Analysis Applied to Archaeology,' *Archaeometry* 3 (1960) 33.

X-Ray Fluorescence

XRF is a virtually non-destructive method for analyzing the elemental makeup of a wide variety of materials. It is able to detect low levels of any element whose atomic number is greater than sodium (eleven), but has the greatest accuracy with elements between twenty-two and ninety-two on the periodic table (for elements with an atomic number lower than twenty-two XRF requires a vacuum).[3] In this range, which includes the common components of coins, i.e. silver, copper, and gold, XRF can detect amounts as low as 0.01 percent,[4] provided that there is an adequate surface area available for analysis. Unfortunately, for the examination of most artifacts a very small surface area must be used. This is because while XRF is mostly non-destructive, the cleaning process required to properly analyze ancient artifacts like coins can leave the object looking 'overly polished' or 'dull,'[5] which is something that the owners of such artifacts are rarely willing to accept. Most analysists will aim to make the damage as small as possible and therefore use a very small portion of the surface area, usually a few millimetres in diameter, or choose to sacrifice a less visible part of the object, like the reverse of a coin, to the cleaning process.[6] The sensitivity of XRF will decrease proportionately with the decrease in surface area.[7] Furthermore, when a sample is not a single phase,[8] homogeneity must be achieved by hand in order to gather a

[3] Ibid. 32.
[4] Ibid.
[5] G.F. Carter, 'Preparation of Ancient Coins for Accurate X-ray Fluorescence Analysis,' *Archaeometry* 36 (1964) 108.
[6] Ibid.
[7] E.T. Hall, 'X-ray Fluorescent Analysis Applied to Archaeology,' 32.
[8] Alloys can be either homogenous or heterogeneous, i.e. single phase or multiphase. Homogeneity occurs when the constituents of the alloy combine to form a single substance. These alloys have one phase. However some elements are insoluble or have a saturation point that, once reached, means they can no longer combine. Therefore, the elements remain separate and the substance is multi-phase. A heterogeneous alloy can be forcibly made into a single phase by dissolving it in acid and reducing it to a liquid state.

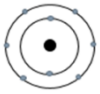
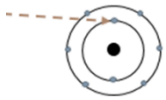
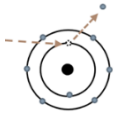
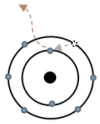
reliable reading.[9] This can be done by dissolving a portion of the sample in acid or grinding it down, but this will lose the crucial non-destructive element.

XRF is performed through the use of an x-ray spectrometer, which is comprised of three components: an x-ray source, a spectrometer, and the measuring electronics.[10] The basic principle behind XRF is that the composition of a sample can be determined by the measurement of either the specific wave lengths or the energy that is emitted by that sample when it is stimulated.[11] This is achieved through a process known as the photoelectric effect. In this process, high-energy photons (x-rays) are emitted from the x-ray source and strike the surface of the sample. These photons are absorbed by the atoms in the sample. Atoms are comprised of protons within the nucleus and electrons that surround the nucleus. The electrons encircle the nucleus in shells or layers. The farther a shell is from the nucleus the more energy is required to keep its electrons in orbit. If the energy of the striking x-ray photon is equal to or greater than the energy that binds the electrons to the atom, then an electron from the inner-shell of the atom will be ejected. This is known as ionization. The atom, now an ion, is left in an excited state. In order for the atom to return to a more normal and stable electron configuration an electron from an outer shell is pulled in to fill the vacancy left by the ejected electron in the inner shell. Since electrons in outer shells are farther away from the nucleus and therefore require more energy to stay in orbit, there is a discrepancy in energy required by the electron to remain in place once it moves from an outer to an inner shell. This excess energy is emitted from the atom in the form of an x-ray photon, also known as a secondary x-ray. The x-ray that is emitted is directly related to the type of atom that

[9] K. Janssens, 'X-ray Fluorescence Analysis,' in G. Gauglitz, D.S. Moore (eds), *Handbook of Spectroscopy* [2] (Weinheim, 2014) 452.
[10] Ibid. 465.
[11] Ibid. 451.

it originates from, which enables the practitioner to analyze either the energy or the wavelength of the x-ray and determine its elemental source.[12]

Figure 1

1. Stable atom	2. X-ray photon strikes the electron	3. Electron in the inner shell is ejected in highly excited state	4. Outer shell electron takes the place of ejected electron. Secondary x-ray is emitted.
			

WD-XRF was developed in the 1950s and is the most widely used method of x-ray analysis.[13] As the name indicates, WD-XRF determines the elemental composition by examining the wavelengths of the secondary x-rays as they leave the sample. The secondary x-rays are directed towards a single crystal which uses what is known as Bragg's Law to diffract and isolate individual wavelengths towards the spectrometer.[14] Since the relationship between wavelengths and elements is known, the measuring electronics are easily able to identify which element produced which wavelength. The intensity of the wavelength is proportional to the quantity of each element present in the sample. In contrast, energy dispersive (ED) XRF, developed in the 1970s, does not use a crystal but instead the secondary x-ray is converted into a voltage pulse by a pulse processor.[15] The amplitude of the pulse is proportional to the energy of the received x-ray. The pulse processor sorts the pulses by energy (indicative of the element) and amplitude

[12] See Moseley's Law: R. Jenkins, 'X-ray Techniques: Overview,' 1; K. Janssens, 'X-ray Fluorescence Analysis,' 465.
[13] R. Jenkins, 'X-ray Techniques: Overview,' 2.
[14] Bragg's Law ($\theta = n\lambda/2d$) is the relationship between the diffraction of an x-ray and the distance between parallel atoms in a crystal. The angle of diffraction can be manipulated by changing the angle of the crystal. When the crystal is set to the Bragg angle the secondary x-ray from the sample can be directed at the detector. See E.T. Hall, 'X-Ray Fluorescence Analysis Applied to Archaeology,' 30 for further details.
[15] R. Jenkins, 'X-ray Techniques: Overview,' 8.

(indicative of the quantity).[16] The pulses are analyzed by the measuring electronics to create a histogram of the elements and their quantities. Both methods are able to gather qualitative and quantitative information simultaneously.

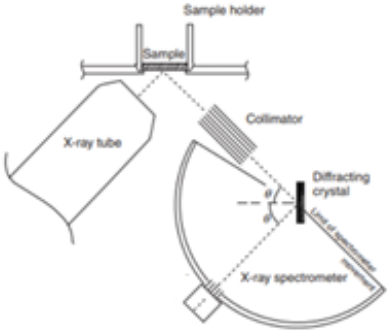


Figure 2 Schematic of a WD-XRF Spectrometer. Modified from a Schematic found in K. Janssens, 'X-ray Fluorescence Analysis,' 476.

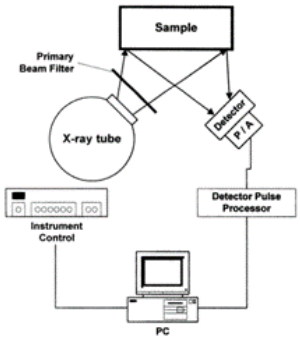


Figure 3 Schematic of a ED-XRF Spectrometer taken from R.E. Van Grieken, A.A. Markowicz (eds), *Handbook of X-Ray Spectrometry* [2] (New York, 2002) 200.

XRF is often chosen for its ease of use. XRF spectrometers range in size from large laboratory equipment to portable hand-held devices.[17] While the larger models are often more accurate, all models employ the same method of analysis.[18] All must be calibrated before quantitative determinations can be made, i.e. a sample of known elemental makeup must be analyzed in order for the spectrometer to accurately differentiate specific elements.[19] The cost of XRF is relatively low compared to other methods, and it is extremely fast.[20] Analysis usually takes a matter of minutes to complete. The biggest advantage to using XRF in the study of Roman coins is its non-destructive nature. For this reason analysists have a much better chance of acquiring

[16] M. Yao, *et al*., 'Element Analysis Based on Energy-Dispersive X-Ray Fluorescence,' *Advances in Material Science and Engineering* (2015) 2.
[17] K. Janssens, 'X-ray Fluorescence Analysis,' 452.
[18] Ibid.
[19] J.P. McKaveney, 'Gravimetric Analysis-General Theoretical and Applied Concepts in the Preparation of Standard Methods of Metals,' *Some Fundamentals of Analytical Chemistry* 564 (1974) 6.
[20] K. Janssens, 'X-Ray Fluorescence,' 452.

coins from museums or private collections than when employing a more destructive technique. A major drawback to this method relates to the non-homogenous nature of many Roman coins and the frequent presence of enrichment on their surfaces. Since this method only penetrates a short distance into the sample nothing beyond the surface level will be analyzed.[21]

For these reasons E.T. Hall believes that XRF should only be used qualitatively, not quantitatively, for examining ancient metals.[22] For instance, XRF could be used to determine the elemental make-up of a sample, but not to determine the quantities of those elements. It is only the measurement of quantities that is affected by corrosion and surface enrichment. He argues that such a large portion of the coin would need to be cleaned and analyzed in order to get an accurate quantitative reading that it would be less destructive, and more accurate, to drill a small hole in the edge of the coin and examine the shavings. Proponents of XRF argue that cleaning the surface of a coin, either chemically or mechanically, is effective enough to overcome the potential problems of surface enrichment and corrosion.[23] The more pervasive problems associated with analyzing heterogeneous coin alloys with XRF will be covered in more detail in the following chapter.

Wet Chemical Analysis

Wet chemical analysis is a general term for a category of analysis where the sample is chemically dissolved and analyzed in a liquid or gaseous state. For obvious reasons it is a highly destructive technique. Wet chemical analysis can be split into two broad categories: classical and instrumental. Classical wet chemical analyses were the first methods developed for such analysis

[21] Ibid.
[22] E.T. Hall, 'X-ray Fluorescent Analysis Applied to Archaeology,' 33.
[23] See G.F. Carter's article, 'Preparation of Ancient Coins for Accurate X-Ray Fluorescence Analysis,' 106-113 for arguments in favour of XRF on ancient coins.

and remained the most popular until their gradual phasing out in the latter half of the twentieth century in favour of instrumental methods.[24] However, classical wet chemistry remains the most highly regarded and accurate option for elemental determination when analyzing major constituents, i.e. over ten percent of the whole.[25] In contrast, instrumental analysis has a lower detection limit and is therefore often used to identify trace elemental components.[26] Classical and instrumental analysis can be used in conjunction to determine both major and minor constituents for the greatest accuracy.

While the theory behind classical and instrumental wet chemical analysis is the same, the methodologies are distinct. Classical wet chemical methods function on the principle of stoichiometry, i.e. the volumetric measure of reactants and products in chemical reactions, and relies greatly on the ability of the chemist. In contrast, instrumental methods, similar to XRF, rely on electron displacement. Within the broad category of classical wet chemistry there are two main methods: 1) gravimetric analysis; and 2) titration. Instrumental analysis is also divided into two main methods: 1) inductively coupled plasma (ICP) atomic emission spectroscopy (AES); and 2) ICP mass spectroscopy (MS).[27]

[24] J.P. McKaveney, 'Gravimetric Analysis- General Theoretical and Applied Concepts in the Preparation of Standard Methods of Metals,' 6.
[25] L.L. Lewis, 'A Comparison of Atomic Absorption with Some Other Techniques of Chemical Analysis,' *Atomic Absorption Spectroscopy, ASTM STP* 443 (1969) 49.
[26] J.R. Dean, 'Inductively Coupled Plasma Spectrometry,' in A. Seidel (eds), *Encyclopedia of Chemical Technology* 5 (2007) 27; A. Brumby, *et al.*, 'Silver, Silver Compounds, and Silver Alloys,' *Ullmann's Encyclopedia of Industrial Chemistry* 33 (2012) 86; J.A.C. Broekaert, 'Inductively Coupled Plasma Spectrometry,' in G. Gauglitz and D.S. Moore (eds), *Handbook of Spectroscopy* [2] (Weinheim, 2014) 584.
[27] Other methods of both classical and instrumental analysis exist, but they are not used by any of the studies discussed in this paper.

Classical Wet Chemistry

i. Gravimetric Analysis

Gravimetric analysis is the quantitative determination of elements in a sample based on the law of conservation of mass, i.e. the total mass of reactants will be equal to the total mass of products after a chemical reaction.[28] In the gravimetric analysis of a metal alloy, the first step is to convert the solid metal into a liquid solution through the addition of an acid, e.g. nitric acid. Next, the chemical reaction is initiated by the addition of a precipitating agent, i.e. an acid, to the sample. When a precipitating agent is added to a liquid solution it causes a portion of the solution to solidify. The solid particles are the precipitate. In gravimetric analysis the precipitating agent differs depending on the element that one wishes to analyze, and as a result the precipitate will be a compound of that element. For the examination of silver, for instance, hydrochloric acid is added to create a precipitate of silver chloride.[29] The precipitate is collected into a ceramic crucible where it is filtered and washed. A reducing agent is used to remove the oxide or chloride that was attached to the element in the precipitation stage, e.g. for the isolation of silver from silver chloride electrolytic reduction is employed.[30] Afterward the crucible containing the precipitate is dried in an oven, and finally they are weighed together. The mass of the crucible is subtracted and the total mass of the isolated element is left. Since the mass of the original sample and the mass of the precipitate are known, it is possible to calculate the percentage of the former that the latter made up. For the analysis of silver, the mass of the isolated silver would be subtracted from the mass of the initial sample in order to determine what percent of the original sample was silver. In the hands

[28] M. Widmer, 'Gravimetry,' in *Encyclopedia of Analytical Chemistry* (2006) 1.
[29] E.R. Caley, *Analysis of Ancient Metals* (New York, 1964) 73; D.A. Skoog, et al., 'Gravimetric Methods of Analysis,' in S.R. Crouch and F.J. Holler (eds), *Fundamentals of Analytical Chemistry* [9] (Belmont, 2013) 295.
[30] Reducing agents can also be acids, see D.A. Skoog, 'Gravimetric Methods of Analysis,' 295.

of a skilled chemist gravimetric analysis can be more accurate than 0.1 percent.[31] However, since the process requires each element to be analyzed separately it is both lengthy and costly, and requires many samples.

ii. Titration

Titration, also referred to as titrimetry or volumetric analysis, is the addition of liquid reactants to a sample until a chemical reaction, e.g. change in colour, loss of colour, or turbidity, occurs to indicate completion.[32] Before analysis the sample must be converted to a liquid solution through the addition of an acid, e.g. nitric acid. A chemical reacting agent, such as sodium chloride for the titration of silver,[33] is added to the solution until a reaction can be visually observed. Direct electrical current can also be used as a reagent; this is known as coulometric titration.[34] Either the volume of reactant or the quantity of charge required to reach the necessary visual change indicates the concentration of the element within the solution. Like gravimetric analysis titration is highly accurate when it comes to analyzing large components in a sample. Most titrations are precise to 1-0.1 percent.[35]

[31] M. Widmer, 'Gravimetry,' 1; D.A. Skoog, 'Gravimetric Methods of Analysis,' 280.
[32] D.A. Skoog, 'Titrations in Analytical Chemistry,' in S.R. Crouch and F.J. Holler (eds), *Fundamentals of Analytical Chemistry* [9] (Belmont, 2013) 302-305.
[33] A. Brumby, 'Silver, Silver Compounds, and Silver Alloys,' 86.
[34] D.A. Skoog, 'Titrations in Analytical Chemistry,' 302.
[35] M. Widmer, 'Titrimetry,' in *Encyclopedia of Analytical Chemistry* (2006) 1.

Instrumental Wet Chemistry

The foundation of the instrumental systems discussed in this paper is ICP. ICP uses the energy from argon plasma to excite atoms in a sample and induce ionization, which was described above.[36] The appearance of this plasma has resulted in this instrument being referred to as an ICP torch. The instrumentation for an ICP torch is comprised of concentric quartz tubes and an induction coil.[37] The induction coil wraps around the outside of the ICP torch and is the source of its power. It is attached to a high frequency generator; when ignited it causes a current to move through the coil producing an electromagnetic field. Before the electromagnetic field is induced, argon gas is introduced tangentially into the quartz tubes, and it is then momentarily turned off in order to initiate a high voltage spark. This spark causes free electrons to become intertwined with the argon gas, which initiates the transition from argon gas to plasma. The electromagnetic field interacts with the free electrons and causes them to move rapidly producing extreme heat. The high temperature in the torch causes some of the argon gas to become ionized, resulting in the formation of plasma. Since the ionized argon, argon atoms, and free electrons co-exist within the plasma it is itself electrically neutral[38]. The entire process takes place almost instantaneously.

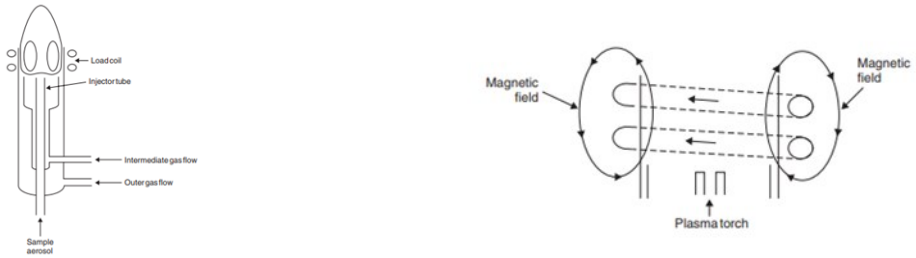


Figure 4 Schematic of an ICP torch, and a close up of the induction coil and magnetic field taken from J.R. Dean, 'The Inductively Coupled Plasma and Other Sources,' in *Practical Inductively Coupled Plasma Spectroscopy* (Chichester, 2005) 59.

[36] T.J. Manning and W.R. Grow. 'Inductively Coupled Plasma- Atomic Emission Spectrometry,' *The Chemical Educator* 2 (1997) 3.
[37] J.R. Dean. 'Inductively Coupled Plasma Spectrometry,' 3.
[38] J.R. Dean, 'Inductively Coupled Plasma Spectrometry,' 3.

At this point a sample can be introduced into the ICP torch. For ICP to function properly the sample must be introduced as an aerosol. For solids, as in the case of coins, the sample must be pretreated.[39] This could involve either the addition of an acid to revert it into a liquid solution or laser ablation. Once in a liquid state, a nebulizer is used to inject the sample into the ICP torch. When the sample comes into contact with the argon plasma the high temperature of the plasma ionizes the elements in the sample. The final step in ICP is the elemental identification and analysis of the sample. The difference between ICP-AES and ICP-MS lies in their methods of detection. Like XRF, both systems require their spectrometers to be calibrated with known elemental standards before analysis.[40]

i. ICP-AES

For ICP-AES the ICP torch is connected to a spectrometer that separates and detects the wavelengths emitted by different elements.[41] When the elements in the sample are ionized inside the ICP torch they emit a characteristic x-ray, just as in XRF. However, this system differs from a WD-XRF spectrometer in the method of wavelength separation. Rather than using the Bragg effect via a single crystal, this spectrometer has a saw tooth pattern of grooves scratched onto a mirror to create a 'diffraction grating.'[42] As the x-rays emitted from the sample hit the mirror they are diffracted at angles specific to the element. These ricocheting wavelengths are then read by the detector. There are two types of atomic emission spectrometers: sequential and simultaneous. While sequential is the most accurate, simultaneous is the most efficient.[43]

[39] Ibid. 5.
[40] Ibid. 10 and 15.
[41] Ibid. 10.
[42] Ibid. 10.
[43] Ibid. 12.

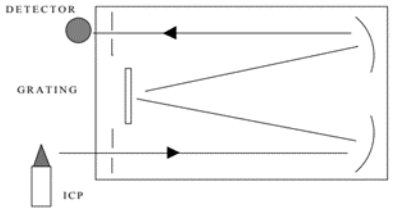


Figure 5 Simplified view of the sequential AES process taken from T.J. Manning, and W.R. Grow, 'Inductively Coupled Plasma-Atomic Emission Spectrometry,' *The Chemical Educator* 2 (1997) 13.

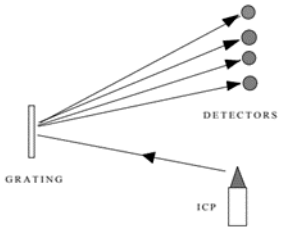


Figure 6 Simplified view of the simultaneous AES process taken from T.J. Manning and W.R. Grow, 'Inductively Coupled Plasma- Atomic Emission Spectrometry,' 14.

ii. ICP-MS

Like ICP-AES the mass spectrometer aims to separate and detect the elements present in the sample. The spectrometer is able to filter ions based on the mass/charge ratio.[44] The mass/charge ratio is the ratio of the mass of the atom to its charge. When atoms lose or gain an electron they become positively or negatively charged. The more electrons lost or gained the greater the charge. In ICP-MS the ions will all be positively charged from losing electrons. A magnetic field inside the mass spectrometer deflects the ions: the lighter and more charged an ion is the greater the deflection. This allows the spectrometer to filter specific ions based on their identifiable mass/charge ratios. The mass/charge ratio is indicative of the element. It is recorded by the detector and, just like XRF, the signal intensity is proportional to the element's concentration in the sample.

[44] K. Jassens, 'X-Ray Fluorescence Analysis,' 476.

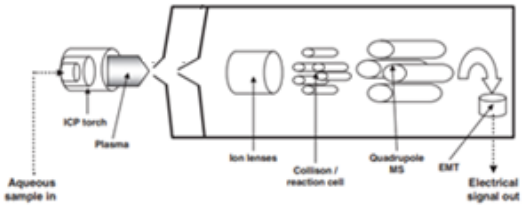


Figure 7 Schematic of an ICP-MS system taken from J.R. Dean, 'Inductively Coupled Plasma Spectrometry,' 6.

In terms of cost and efficacy ICP-AES and ICP-MS are comparable. Both are able to determine a multitude of elements at the same time, although ICP-MS is able to detect more elements than ICP-AES, and both take only a few minutes to produce a complete analysis once the sample has been prepared.[45] ICP-MS has slightly better precision and lower detection limits than ICP-AES when analyzing trace elements.[46] ICP-MS is precise from 0.5-2 percent, while ICP-AES is precise from 0.1-2 percent.[47] The detection limit for silver and copper, the main constituents of a Roman *denarius*, is 0.6 μg/L and 0.00009 μg/L, and 0.4 μg/L and 0.002 μg/L for ICP-AES and ICP-MS respectively.[48] The sensitivity is impressive, but it is more than what is required to analyze Roman silver-copper alloyed coins of the first to third centuries. The main drawback to both methods is their high cost and destructive nature.[49] In comparison with classical wet chemistry, these instrumental methods are faster, have lower detection limits, and do not require a skilled chemist. However, classical wet chemistry remains the most precise option for large constituents, and since it does not require expensive instrumentation it has a lower cost than instrumental analysis.[50]

[45] AES can detect up to 60 elements, MS can detect over 80 elements: J.R. Dean, 'Inductively Coupled Plasma Spectrometry,' 26.
[46] Ibid. 27.
[47] Ibid. 26.
[48] Ibid.
[49] Ibid.
[50] G.F. Carter, et al., 'Comparison of Analyses of Eight Roman Orichalcum Coin Fragments by Seven Methods,' *Archaeometry* 25 (1983) 202; L.L. Lewis, 'A Comparison of Atomic Absorption with Some Other Techniques of Chemical Analysis,' 49.

Conclusions

In the context of the analysis of ancient coins, strong arguments can be made in favour of both wet chemical analysis and XRF. The core of the argument lies in the need for non-destructive analysis versus the need for precision. There is no doubt that wet chemical analysis is more precise than XRF, and that the heterogeneous nature of ancient coins poses a problem for surface level analysis. The full extent of the problems with XRF that must be overcome in order to achieve accurate results, i.e. corrosion and surface enrichment, will be discussed in detail in the following chapter. On the other hand, the extreme rarity of many ancient coins makes the idea of destroying them incomprehensible to most. Hence the prevalence of XRF in the field of numismatics. With the above information in mind, it is now possible to commence a comparison of Walker's XRF results with that of wet chemical analysis.

Chapter Two

Data Comparisons

In this chapter I aim to compare the results from David Richard Walker's XRF analysis with data from four separate wet chemical studies, the purpose being to see if the chemical analyses can corroborate Walker's results and thereby allow us to employ them in further historical and economic analyses. If XRF is as accurate as its proponents claim, its results should compare favourably with those derived from wet chemical analysis. At the very least there should be a consistent perceptible pattern in the differences between Walker's XRF results and those from wet chemical analysis. Unfortunately, in the preliminary comparisons that I undertook when first researching this thesis I did not find this to be the case. Walker's results differed greatly from those of wet chemical analysis. However, it should be possible to confirm or deny this initial impression with a larger sample size. Before I get into the comparisons I will overview the known, and lesser-known, problems of XRF analysis. This information may help us to better understand our results when we compare the data.

Corrosion and Surface Enrichment

The main problem with using surface-level analyses, like XRF, is that they report a higher silver content than is actually present in the interior of the coin. This phenomenon is widely known to be a result of corrosion, i.e. the oxidization of surface metals. When there is less than ninety percent silver present in a silver-copper alloy it is at risk of corrosion.[1] That is because when the

[1] K. Butcher, M. Ponting, and G. Chandler, 'A Study of the Chemical Composition of Roman Silver Coinage, AD 196-197,' *American Journal of Numismatics* 9 (1997) 20; K. Butcher and M. Ponting, 'The Roman *Denarius* under the Julio-Claudian Emperors: Mints, Metallurgy and Technology,' *Oxford Journal of Archaeology* 24 (2005) 173.

silver fineness is above ninety percent the copper and silver combine to form a single homogenous phase, but below ninety percent the copper and silver are unable to combine; instead the elements remain separate and form two distinct phases.[2] At this point, the copper becomes susceptible to corrosion. In a silver-copper alloy, corrosion will occur in the copper layer, while the silver will be mostly unaffected. This is because the element that is oxidized is determined by its electrode potential: whichever element is more electro-negative, i.e. less noble, will be the one to oxidize.[3] Oxidization occurs when copper on the surface of the coin is exposed to the oxygen in the air.[4] Over time the atoms of copper will exchange electrons with oxygen atoms resulting in the formation of copper oxide. Because copper oxide has a greater volume than copper, it forces copper atoms to diffuse from the surface, i.e. the added volume pushes the copper out of the coin to make room.[5] The result is an overall decrease in the amount of copper in the affected area, and in turn an increase in silver, in proportion to copper, present in that area.

Besides an overall decrease in the amount of copper, corrosion can also develop into 'pits'. These corrosion pits are areas where a pronounced amount of copper has been forced out of the coin in relation to the surrounding area.[6] They are mostly seen at the surface level of the coin. In these pits, there is often less than one-third of the original copper left, resulting in extreme levels

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[2] See n. 8 above for an explanation of homogenous and heterogeneous alloys. See also Butcher and Ponting, 'The Roman *Denarius* under the Julio-Claudian Emperors: Mints, Metallurgy and Technology,' 173.

[3] G.F. Carter, 'Preparation of Ancient Coins for Accurate X-Ray Fluorescence Analysis,' *Archaeometry* 7 (1964) 107; Butcher, et al., 'A Study of the Chemical Composition of Roman Silver Coinage, AD 196-197,' 21; H. Gitler and M. Ponting, *The Silver Coinage of Septimius Severus and His Family (193-211 AD): A Study of the Chemical Composition of the Roman and Eastern Issues* (Milan, 2003) 11; K. Butcher and M. Ponting, 'Rome and the East: Production of Roman Provincial Silver Coinage for Caesarea in Cappadocia under Vespasian, AD 69–79,' *Oxford Journal of Archaeology* 14 (1995) 66.

[4] Some metals that appear in trace quantities inside the silver or copper ore, e.g. tin or lead, also oxidize. But as they are present at extremely low levels and their quantities are not recorded by Walker or many wet chemical studies, this will not be discussed here.

[5] J. Condamin and M. Picon, 'The Influence of Corrosion and Diffusion on the Percentage of Silver in Roman *Denarii*,' *Archaeometry* 7 (1964) 99.

[6] Ibid. 100.

of silver enrichment.[7] Additionally, it makes analyzing these areas extremely difficult because the copper level inside the pits is much lower than the surrounding area, which means that there is a great deal of variability within the same layer of the coin's surface.[8] The pits themselves are not normally visible to the naked eye; without fragmentation and examination with a scanning electron microscope it would be virtually impossible to detect their presence. But they are easily penetrated by x-rays.

In order to negate the problem of corrosion, analysts who use surface level techniques will attempt to remove the corroded areas of the surface of the coin by either chemical cleaning or physical abrasion. Walker used mechanical abrasion in order to bypass the surface layer of the coins he studied.[9] Researchers like G.F. Carter have argued for the efficacy of mechanical abrasion in XRF studies over chemical cleaning.[10] In his study, he looked at seven coins and air-abraded the surface. He removed sixty microns (the amount it took to achieve three consistent readings from XRF) from the surface of each coin, and examined the area beneath the abrasion, believing it to be representative of the interior of the coin. In theory, this should be effective, but Carter failed to account for interior corrosion and silver blanching.[11]

While corrosion occurs mostly on the surface of a coin it can also be present well into the interior depending on how deep the oxidization reaches.[12] The depth will vary from coin to coin

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[7] Ibid.
[8] Ibid.
[9] Butcher, et al., 'A Study of the Chemical Composition of Roman Silver Coinage, AD 196-197,' 25 and R. Klockenkämper, H. Bubert, and K. Hasler, 'Detection of Near-Surface Silver Enrichment on Roman Imperial Silver Coins by X-Ray Spectral Analysis,' *Archaeometry* 41 (1999) 312 and 318 both report that Walker used physical abrasion to prepare his coins, Walker himself only states in his first volume that he repeatedly cleaned and tested his samples.
[10] G.F. Carter, 'Preparation of Ancient Coins for Accurate X-Ray Fluorescence Analysis,' *Archaeometry* 7 (1964) 106-13.
[11] Butcher, et al., 'A Study of the Chemical Composition of Roman Silver Coinage, AD 196-197,' 25.
[12] Condamin and Picon, 'The Influence of Corrosion and Diffusion on the Percentage of Silver in Roman *Denarii*,' 98-105.

depending on the context in which the coin was deposited. The second aspect that Carter failed to account for, silver blanching, was first theorized by L.H. Cope in the early 1970s.[13] Silver blanching, as described by Cope, is a process that involves chemically polishing the outer layer of a coin using an organic acid at the time of minting. It differs from silver washing or silver plating in that it does not involve the addition of silver to the coin. It was used to hide the physical evidence of silver debasement.[14] When the silver content of the *denarius* fell below ninety percent, the silver and copper separated into two distinct phases, as described earlier, and this resulted in a pinkish outer layer caused by the oxidization of the copper. Silver blanching would disguise this pink layer and make the coin appear to be pure silver.[15]

This, of course, theorizes that the Roman officials in charge of minting where aware of the potential negative economic effects of fiduciary coins.[16] What this implies is that they were worried that having a coin that obviously contained less silver would result in decreased confidence in the coin's purchasing power. Therefore, they blanched the outside of the coin to make it appear to have a higher silver content than it actually contained. The result of this process is that the cross section of a blanched coin will show two distinct layers of silver enrichment:[17] an outer layer, the result of acid washing, and a secondary layer, the result of later corrosion. This secondary layer will extend an unknown depth into the coin, and could possibly extend throughout the entire coin. Therefore, when Carter removed the surface corrosion on such coins to a depth of

[13] L.H. Cope, 'Surface-Silvered Ancient Coins,' in E.T. Hall and D.M. Metcalf (eds), *Methods of Chemical and Metallurgical Investigation of Ancient Coinage- A Symposium Held by the Royal Numismatic Society in London on 9-11 December 1970* (London, 1972) 266-71.
[14] As a result, silver washing becomes more common as debasement gets worse. It would have been particularly common in periods like the third century when debasement was notably high.
[15] Butcher and Ponting, 'The Roman *Denarius* under the Julio-Claudian Emperors: Mints, Metallurgy and Technology,' 173-174.
[16] Cope, 'Surface-Silvered Ancient Coins,' 267-268.
[17] Gitler and Ponting, *The Silver Coinage of Septimius Severus and His Family (193-211 AD): A Study of the Chemical Composition of the Roman and Eastern Issues*, 12-14.

sixty microns he would only have succeeded in removing the blanched zone.[18] As a result, he was analyzing the corroded zone beneath.

But, as discussed in the introduction, most scholars are aware that the figures Walker reports for silver are too high. When his data is used for economic and numismatic analyses the problems with corrosion for surface level analysis are often cited as a kind of disclaimer, but that does not stop scholars from using the data as he reported it. The rationality for the use of his data lies in the assumption that while the numbers he reports are too high, they are consistently a certain percentage higher than the true value (that percentage is not always stated), and so, while incorrect, his results still reflect the true trends of the changes in the silver levels. This assumption is aptly summed up by Carradice and Buttrey in *RIC 2* where they argue that "[without more reliable analysis, Walker] remains a valuable resource for gaining overviews of different reigns assuming his methods were consistent and therefore valid for relative comparison."[19] There are two problems with this conclusion: 1) it assumes that consistent methods of analysis will produce correct results, and 2) it assumes consistency of corrosion across samples.

These two problems are closely linked. If one believes corrosion to affect only the exterior of the coins and do not take into account silver blanching, then it is easy to assume that the depth and severity of corrosion will be relatively consistent across samples. Once the corrosion is bypassed by abrading the surface of the coin, the true interior can be examined. However, depending on the context in which the coins were discovered the severity of corrosion will be different, and corrosion inside the coin can extend for an unknown depth (in some cases for the

[18] Ibid. 14.
[19] I.A. Carradice and T.F. Buttrey, *The Roman Imperial Coinage*, 2.1[2] (London, 2007) 2-3.

entirety of the coin).[20] Indeed, the presence of corrosion pits means that copper levels can vary greatly even within the same layer of the coin. Therefore, even if one removes the corroded layers of one coin, removing the same amount of surface material from another coin may not bypass its corrosion. Without fragmenting or drilling into the coin to see the changes in the composition layers it is simply not possible to determine whether the layer being examined is corroded or not.[21] As a result, there is good reason to assume that Walker's results will differ from the results obtained through wet chemistry. In fact, as we will see when we compare Walker's data against those of wet chemical analysis, the true problem with Walker's data is inconsistent incorrectness.

Mints

Another variable to consider when examining Roman coins is the mint the coin came from. When there is no mint mark present, the mint of a particular coin sometimes can be a subject of debate amongst numismatists, as is the question of where those mints were actually located. For the majority of the Roman Empire the main mint was located in Rome.[22] Before this, the main mint is widely thought to have been in Lugdunum and there is some controversy over when the switch to Rome took place.[23] The general consensus is that the switch occurred sometime during the reign of Nero, likely coinciding with his initial lowering of the silver fineness.[24]

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[20] Butcher and Ponting, 'Rome and the East. Production of Roman Provincial Silver Coinage for Caesarea in Cappadocia under Vespasian, AD 69–79,' 66.
[21] L.H. Cope, 'The Metallurgical Analysis of Roman Imperial Silver and *Aes* Coinage,' in E.T. Hall and D.M. Metcalf (eds), *Methods of Chemical Metallurgical Investigation of Ancient Coinage- a Symposium Held by the Royal Numismatic Society in London 9-11 December 1970* (London, 1972) 10.
[22] Butcher and Ponting, 'The Roman *Denarius* under the Julio-Claudian Emperors: Mints, Metallurgy and Technology,' 164.
[23] Ibid. 194.
[24] W. Metcalf, 'Rome and Lugdunum Again,' *American Journal of Numismatics* 1 (1989) 68-69.

Apart from mint marks and stylistic differences, mint location can be determined by the presence of trace elements in the coins which would have been present in the ore taken from the mine.[25] For instance, silver coins from Rome have a higher lead content than coins from Laodicea or Emesa, but *denarii* from Laodicea have a higher nickel content than ones from Rome.[26] The Roman moneyers lacked the sophisticated alloying equipment necessary to strip the ore of trace elements, and given that the level of impurities were low it is unlikely they would have removed them even if they had been able.[27] Therefore, what they would consider to be 'pure' silver bullion was not elementally pure, but contained small amounts of other metals that were either located in the silver ore or accidentally added in the refining process.[28] For this reason, in order to determine the amount of silver that the Romans believed was being added to their coins we should be including the trace elements in addition to the elementally pure silver. In Butcher and Ponting's 2005 study they measured the trace elements present in the silver ore in addition to the elementally pure silver in the coinage struck between Augustus and the reform of Nero. They found that, with the trace elements added to the pure silver, the 'silver' content was essentially 100 percent.[29] The addition of the trace elements increased the fineness by approximately two percent per coin above what was found when only the elementally pure silver was recorded. Unfortunately, Walker did not report the trace elements alongside the silver fineness. Therefore we can only compare the pure silver content.

[25] H. Gitler and Ponting, *The Silver Coinage of Septimius Severus and His Family, 193-211 AD. Study of the Chemical Composition of the Roman and Eastern Issues*, 23.
[26] Ibid. 23-24.
[27] Ibid. 21.
[28] Butcher and Ponting, 'The Roman *Denarius* under the Julio-Claudian Emperors: Mints, Metallurgy and Technology,' 175.
[29] Ibid. 178.

And since each mine varied in both the type and amount of trace elements present in its silver ore, comparisons of the pure silver content of coins from two different mints can cause potential problems. For instance, if the bullion at one mint was more elementally pure than the bullion used at another mint it would give the false impression of higher silver standards being used at that mint. Furthermore, monetary unity between the eastern and western empire was not achieved until the reign of Septimius Severus in 194.[30] This creates the potential problem of different silver standards being utilized in different parts of the Empire.[31] To negate these problems I will not be comparing across mints. Instead only evidence from the mint of Rome will be analyzed and compared (with the exception of coins from before Nero's monetary reform which will be taken from Lugdunum).

Data

Now that the difficulties with using XRF when faced with silver-blanched or corroded coins have been laid out, the expectation is that Walker's results will both report a higher fineness than wet chemistry and the degree of difference will vary coin by coin. In this section I will test this theory by directly comparing Walker's results against those of several studies that involve wet chemical analysis. These studies were selected for two reasons: 1) they each employed a form of wet chemical analysis; and 2) they each overlapped with a period of time that was also analysed by Walker. Each table presents the data from a chemical analysis and then presents Walker's data

[30] Ibid. 52.
[31] Once monetary unity was achieved, coins from a variety of mints would have been melted down and reminted along with new silver and then produced in other mints, often not the mint it originally came from. Thus over time the silver became homogenized.

for the coins of the same time period.[32] Where more than one coin is presented for a time period, as is the case for all of Walker's data, the fineness has been averaged to both present a more concise comparison and to account for small variations among single coins (the number of coins that were analyzed will be shown in brackets next to their averages). For visual clarity, the final column will present the difference between the chemical analysis and Walker's analysis.

Table 1

	Butcher & Ponting	Walker	
Emperor	**Ag (%)**	**Ag (%)**	**Diff. (%)**
Augustus	98.6 (10)	97.81 (25)	-0.81
Tiberius	98.83 (18)	98.07 (7)	-0.77
Caligula	98.75 (2)	97.69 (4)	-1.09
Claudius	98.98 (6)	98.00 (18)	-1.00
Nero, pre-reform	97.63 (7)	97.35 (13)	-0.29
Nero, post-reform	82.22 (31)	93.48 (24)	12.05
Otho	87.07 (3)	93.59 (21)	6.97

The first study used for comparison is from Butcher and Ponting, who analyzed seventy-eight *denarii* of the Julio-Claudian dynasty.[33] For each coin they drilled a small hole (approximately half a millimetre in diameter) and discarded the first millimetre of turnings most likely to be affected by corrosion. They then performed ICP-AES analysis on the dissolved metal.

[32] With such a small amount of data it was impossible to compare strictly against single years. Multiple years often had to be combined in order to create overlaps for comparison. The potential problem with this is that the averages could be skewed based on which years each study has more data for. If the silver standard for one year in a grouping is notably higher than the silver standards for the other years and one study has more data for that year than the other study, the first study will have a higher average even if there are no discrepancies in results. To negate this problem, I made the groupings as small as possible. The comparison of Gitler and Ponting and Guey's wet chemical results for 194-217, found on pages 35-36, showed them to be virtually identical (and Walker's results to be much higher), leading me to believe the groupings did not skew the results of this study.

[33] Butcher and Ponting, 'The Roman *Denarius* Under the Julio-Claudian Emperors: Mints, Metallurgy and Technology,' 163-197.

One critique of their method is that without fragmenting the coin they were unable to determine how deep any corrosion reached and therefore how much more of the turnings could have been discarded. However, since the majority of the coins examined have a silver content of over ninety percent excessive corrosion is unlikely to have occurred and there would have been no reason at all for any acid wash to have been applied by the Romans. Furthermore, five of the seventy-eight coins were completely destroyed in order to analyze their microstructures, which allowed Butcher and Ponting to determine without doubt the extent and depth of any corrosion, on the assumption that these coins are representative of the majority.

As we would expect, when the silver content is ninety percent or higher Walker's data is considerably more accurate. Butcher and Ponting themselves attribute XRF's greater reliability with coins of a higher silver content to the lack of silver blanching on coins with an already high silver content.[34] But it should also be in part because when the silver makes up ninety percent or more of the alloy it creates a homogenous phase rather than the separate copper and silver phases that occur when the silver content is lower. A single phase would prevent the copper from oxidizing and thereby creating a corroded layer to interfere with XRF analysis. However, once the silver content drops below ninety percent, i.e. after Nero's debasement, Walker's results begin to differ significantly, from -0.29 to 12.05 percent. This indicates that Nero's debasement of the silver currency was much more significant than Walker's results indicate.[35]

[34] Ibid. 175.
[35] Ibid. 179.

Table 2

	Cope	Walker	
Year	**Ag (%)**	**Ag (%)**	**Diff. (%)**
70-74	94.85 (2)	89.25 (56)	-6.27
75-78	86.12 (2)	90.41 (40)	4.75
103-111	90.8 (1)	90.82 (120)	0.02
112-117	81.4 (3)	88.99 (130)	8.53
132-138	88.39 (3)	89.11 (61)	0.81
141(+)-151	78.84 (3)	84.45 (10)	6.64
161	68.36 (1)	77.81 (13)	12.14
235-236	22.75 (1)	49.47 (30)	54.01

L.H. Cope used gravimetric analysis to determine the metallurgical makeup of several silver and *aes* coins of the Roman imperial period.[36] As with all methods, the sample must be cleaned before analysis. Cope advocates for mechanical cleaning of the coins surface rather than chemical. He argues that chemical cleaning can inadvertently cause internal corrosion of the coin that will not be visible to the eye and therefore go undetected. The full process Cope employs is a variation of E.R. Caley's procedure for wet chemical gravimetric analysis.[37]

The comparison between Cope and Walker's analysis is striking. In a broad sense they do appear to be following the same trajectory. However when analyzed more closely it is apparent that there are key differences. Walker's analysis presents a picture of relatively stable silver standards down to the 130s followed by a decline between ca. 140 and ca. 160. If we look at Walker's full report, we can see that it shows the silver standard staying relatively consistent after this (hovering in the high seventy to low eighty percent range) until the start of the third century. At this point, it again begins to drop, eventually lowering to the near fifty percent around 235 seen

[36] Cope, 'The Metallurgical Analysis of Roman Imperial Silver and *Aes* Coinage,' 3-47.
[37] For a description of Cope's modification to E.R. Caley's method, see Cope, 'The Metallurgical Analysis of Roman Imperial Silver and A*es* Coinage,' 20-22.

in Table 2. In contrast, Cope's analysis shows a relatively steady drop, with one peak in the first decade of the second century and another in the 130s. The fineness in 235 is less than half of that reported by Walker. One can also see that once the silver content drops below fifty percent the difference between Cope and Walker's results increases quite starkly. The two different studies therefore present two distinct narratives of coin debasement.

J. Guey's study effectively picks up where Cope's left off, providing us with a convenient continuation. Guey based his evaluation on ninety-nine coins that underwent classical wet chemical analysis at the Laboratoire de la Monnaie in Paris and the Pourquery Laboratoire in Lyon.[38] For each coin, a 500-1000 milligram fragment was examined rather than shavings. Fragments of the same coins were later used by Condamin and Picon for their study on the effects of corrosion, oxidization and diffusion on silver-copper alloys. In an unpublished letter to Guey Condamin wrote that twenty-three of the ninety-nine coins he analyzed showed an elevated silver content.[39] Internal corrosion had caused the inner portion of the coin to contain a higher silver content than would have existed at the time of minting. Guey subsequently re-evaluated his results and proposed corrected (lowered) levels of silver. The corrected fineness has been averaged and added to the following table.[40]

Table 3

	Guey	Walker	
Years	**Ag (%)**	**Ag (%)**	**Diff. (%)**
176-179	75.77 (10)	79.37 (28)	4.54
179-181	72.88 (6)	76.94 (13)	5.28
181-182	72.55 (2)	77.4 (10)	6.27
183-184	73.75 (2)	75.78 (27)	2.68

[38] J. Guey, 'L'aloi du denier romain de 177 à 211 après J.-C. Étude descriptive,' *Revue Numismatique* 6 (1962) 73-140.
[39] J. Guey, 'Peut-on se fier aux essais chimiques? Encore l'aloi du denier romain de 177 à 211 après J.-C.,' *Revue Numismatique* 6 (1965) 110.
[40] Ibid. 110-122.

184-185	70.7 (2)	75.12 (17)	5.88
186-187	72.45 (2)	75.26 (32)	3.73
187-189	73.72 (4)	75.33 (22)	2.14
190-191	70.95 (2)	72.12 (21)	1.62
192	65.95 (8)	73.44 (28)	10.20
193	71.95 (6)	80.82 (40)	10.98
194-196	50.69 (9)	66.34 (48)	23.59
196-198	46.85 (13)	57.13 (60)	17.99
198-200	47.28 (4)	55.53 (26)	14.86
200-205	46.96 (12)	57.04 (66)	17.67
206-207	46.5 (4)	56.32 (31)	17.44
208-213	46.72 (6)	54.31 (109)	13.98

All of Guey's results range between 1.62 and 23.59 percent lower than Walker's. None is above. The difference appears somewhat negligible between 176 and 191, ranging just between 1.62-6.27 percent, but then it sky rockets to 10.20 percent in 192 and remains high thereafter. This is no doubt a result of the increased corrosion caused by higher copper levels, which then leads to less accurate XRF analysis. Both evaluations show a rise in fineness in 193, although Walker's results are 10.98 percent higher than Guey's, before silver standards drop considerably.

Table 4

	Gitler & Ponting	Walker	
Years	**Ag (%)**	**Ag (%)**	**Diff. (%)**
193-198	49.04 (32)	66.13 (136)	25.84
198-211	44.87 (35)	56.25 (184)	20.23
211-217	46.2 (1)	51.6 (104)	10.47

In their study of the coins of the Severan dynasty Gitler and Ponting used a combination of atomic absorption spectroscopy and ICP-AES to determine the elemental makeup of eighty-three coins.[41] The difference between Gitler and Ponting's results and Walker's is strikingly high

[41] Atomic absorption spectroscopy is another destructive technique for elemental determination. In this method, the sample is atomized and then irradiated. The resulting radiation emitted from the atomized sample is characteristic to

across the board. It is especially interesting when we consider the results from Guey's study as well. If we separate Guey's data across the same years as Gitler and Ponting, the similarities are striking.

Table 5

Years	Gitler & Ponting	Guey	Walker
193-198 (194-198)	49.04 (48.38)	53.622 (48.39)	66.13 (61.22)
198-211	44.87	46.86	56.25
210-217[42]	46.2	47.6	51.6
194-217	**46.78**	**47.58**	**57.31**

At first glance, it appears that Guey's average for 193-198 is notably higher than Gitler and Ponting's,[43] but this is likely due to an uneven dispersion of data for the single year of 193. Guey analyzed six coins for 193, while Gitler and Ponting only analyzed one. Therefore, Guey's average for 193-198 is influenced more by the coins of 193 than Gitler and Ponting's average is. If we exclude the data from 193, then Gitler and Ponting and Guey's averages for 194-198 become 48.38 and 48.39 respectively. In contrast, Walker's average for 194-198 is still over twenty percent higher than either Gitler and Ponting or Guey.[44] Furthermore, excluding the year 193, Gitler and Ponting's averages for the entire Severan period are within one percent of each other, while

its elemental source. See M.J. Hughes, M.R. Cowell, and P.T. Craddock, 'Atomic Absorption Techniques in Archaeology,' *Archaeometry* 18 (1976) 19-37 for more details on this technique.

[42] Guey does not give separate data for 211.

[43] His data is 8.55 percent higher than Gitler and Ponting, but still 18.91 percent lower than Walker.

Walker's average is nearly 10 percent higher than either data set. Nevertheless, the difference seen in 193, the first year of Septimius Severus' reign, is important. It appears that Severus increased the silver standard in that year, an act that was not uncommon for a new emperor.[45] Unfortunately, like his predecessors before him, he was soon forced to drop the standards again: compare Guey's average of 71.95 percent for 193 to his average of 50.69 percent for 194-196.

The overlap between Gitler and Ponting and Guey's examinations of the *denarius* provides us with an important opportunity to display the uniformity between wet chemical studies and highlight the error of XRF. Without an overlap in chemical studies it could be easy to make the assumption that part of the differences seen between XRF and the chemical studies is simply due to chance, or different practitioners, and that no two studies of any methodology would align well. However, this overlap shows that this is not the case. Chemical studies have provided consistent and correct results that deviate greatly from Walker's XRF results. It is unfortunate that more overlaps in the data do not exist, but the Severan dynasty is perhaps the best period to demonstrate the consistency of chemical analysis as it is the subject of much numismatic interest.

To summarize: an analysis of the data in this section shows results in line with expectations. Walker's data is consistently higher than the data from wet chemical studies (when the fineness is below ninety percent), but the amount that it differs by is shockingly inconsistent. Finally, in the last comparison we were able to show the consistency between two different wet chemical studies. In the following section we will expand upon the variations in Walker's results and further prove the consistency in results taken from wet chemical studies.

[45] E.R. Caley and H. McBride, 'Chemical Compositions of *Antoniniani* of Trajan Decius, Trebonianus Gallus, and Valerian,' *Ohio Journal of Science* 56 (1956) 287.

Statistical Significance

In the final comparison among Walker, Gitler and Ponting, and Guey it was clear that Walker's data differed greatly from the results of both wet chemical studies. While the variability is clearly a problem, some differences are to be expected. Given the technology available to the Romans we cannot expect every coin to be identical nor any process to be perfect. There is still variation even between coins of Gitler and Ponting and Guey, albeit much smaller. The question then becomes whether these small difference are still significant or can they be accounted for by a reasonable margin of error or random chance? To answer this, we must first determine and define what is 'significant.'

Statistical significance occurs when the probability that the result could have been reached by chance, i.e. the p-value, is less than the error rate, i.e. the alpha level. In other words, the aim of statistical significance testing is to disprove the 'null hypothesis.' This hypothesis states that there is no difference between the two data sets beyond what can be accounted for by a reasonable margin of error. If significance is found, the null hypothesis is disproven. Statisticians generally set the alpha level at five percent;[46] therefore, to be considered significant the p-value must be less than 0.05. A p-value of 0.05 or less indicates that there is less than a five percent chance that the result occurred accidentally. However, in the case of multiple pair-wise comparisons, as seen below, the p-value must be adjusted. Performing multiple pairwise comparisons increases the chances of finding a statistically significant result, thereby invalidating the test. In order to negate this problem, the Bonferroni correction must be applied. The Bonferroni correction divides the alpha level by the number of comparisons being made, thus giving a new (higher) threshold for

[46] T. Dahiru, '*P* – Value, A True Test Of Statistical Significance? A Cautionary Note,' *Annals of Ibadan Postgraduate Medicine* 6 (2008) 21.

significance. For the following comparisons, significance would be achieved when the p-value is less than 0.0167.

If the differences between Gitler and Ponting and Guey are significant, then it stands to reason that either 1) the minting process of the Romans was so imperfect that significant variation will be found among all coins regardless of the method of analysis employed, or 2) even wet chemical analysis does not yield consistent results. In either case, finding significance between the differences in Gitler and Ponting and Guey's data would undermine the results found in the previous section and mean that the results of wet chemical analysis may be no more reliable than XRF, even if the differences appear smaller. Should the results be insignificant it would demonstrate consistency in results taken from wet chemical analyses and, moreover, consistency in the minting process and silver standards of Roman silver coins. It would also further prove wet chemical analysis to be the 'gold standard' of elemental analysis and an appropriate methodology choice for examining ancient coins.

Table 6

	Gitler & Ponting	Guey	
Years	**Ag (%)**	**Ag (%)**	**P-Value**
194-198	48.38	48.39	0.356376
198-211	44.87	46.86	0.121987
211-217	46.2	47.6	Cannot be calculated on account of insufficient data.[47]
194-198	46.78	47.58	0.178979

[47] It is impossible to perform a statistical significance test with only one data entry.

We can make three comparisons between Gitler and Ponting and Guey's data.[48] Of these, not one could be deemed statistically significant. Therefore, we can conclude that even though small differences exist between the data collected by Gitler and Ponting and the data collected by Guey, the differences are simply the result of a reasonable margin of error or random chance. Ideally, I would like to do an additional test to determine if the differences between Walker's results and the corresponding wet chemical studies are statistically significant. Unfortunately this is not possible because his results do not adhere to a normal pattern of distribution.

Statistical significance tests, like the T-test, work on the assumption of normality. Under 'normal distribution' the assumption is made that the mean of a sample set is also the number that occurs most often in that set. It also assumes that the majority of data will fall within one standard deviation higher or one standard deviation lower than the mean. For this reason, normal distribution takes the form of a bell-curve. If there is an insufficient amount of data the distribution will not appear as a perfect curve because there are not enough data points to create the bell curve. The assumption is made that with more data it would form a bell curve, and therefore we can make the assumption of normality. Take, for example, the histogram below which displays the distribution of Guey's data for the Severan Period. While it does not make a perfect bell curve, the data is clearly in the preliminary shape of a bell curve. However, with Walker's data we cannot make an assumption of normality. If, as I have presumed, he is mistakenly examining the corroded outer layer of his samples then his data points will have too many outliers to create a normal distribution.

[48] Statistical significance results were obtained using a standard T-test calculator for two independent means. This is a common statistical significance equation that utilizes the mean and standard deviation of each sample to obtain the p-value. I would like to thank Jason Lockhart for his assistance in checking the T-test to assure correct results.

Chart 1

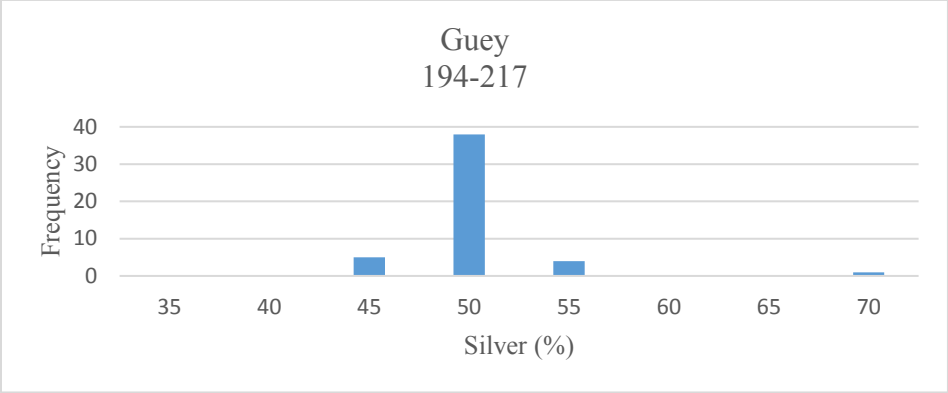
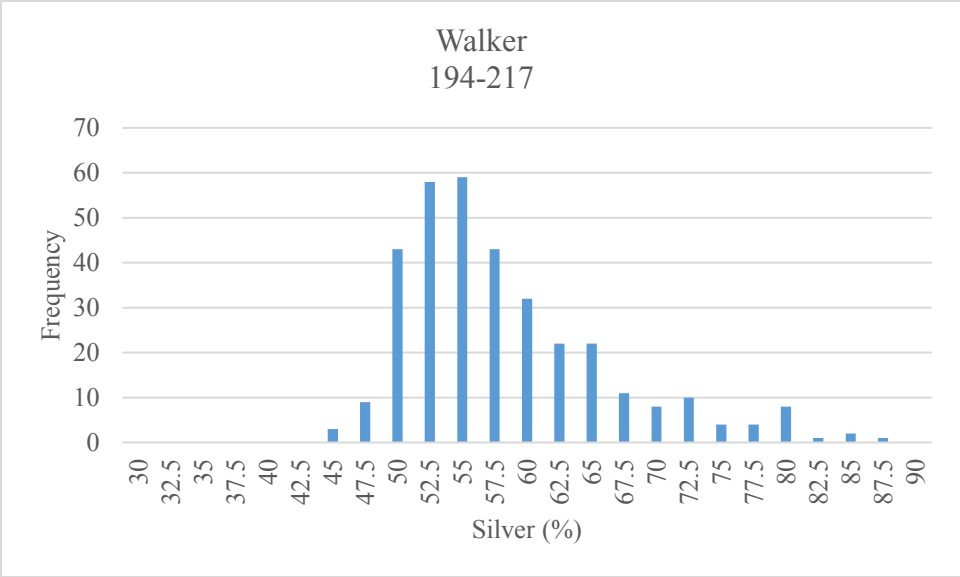


Chart 2



In the above histogram one can see that instead of the data being normally distributed in the shape of a bell curve it leans strongly to the right. This is not unexpected given that Walker's data tends to report the silver fineness too high. As stated earlier, it is possible for normally distributed data to not form a perfect bell curve if there is insufficient data. However, given that Walker's data for this time period includes 340 separate entries there should be more than enough

data to form a bell curve if it is distributed normally. Given the abnormal distribution of this graph, we are not able to complete the desired statistical significance tests with Walker's data.

Standard Deviation

While we cannot perform a statistical significance test with Walker's data, we can examine the standard deviation. Standard deviation measures the differences between each data point and the mean. The greater the standard deviation the more variability there is among coins and vice versa. I have calculated the standard deviation for each study and each time period that was examined in the previous section (the results are listed below in Table 7). Theoretically, coins coming from the same time period and location should have been minted to the same standard. In this case the standard deviation would be close to zero. There is guaranteed to be slight variations among coins due to imperfections in the production process at the time of minting. Otherwise, a higher standard deviation can be attributed to improper analysis of the coins. Given the aforementioned problems with coins affected by corrosion and surface enrichment, we would expect any surface level examination that does not fully and consistently breach the corroded area to have a high standard deviation.

After determining the standard deviation for the coins of each time period and author, I can conclude that, as expected, Walker tends to have a higher standard deviation than the authors of any wet chemical study. The breakdown is as follows: in four cases a comparison was unable to be made as a result of low sample size in the wet chemical studies; in twenty-two comparisons Walker's work shows a higher standard deviation than wet chemical; and there are only eight instances where wet chemical results show a higher standard deviation than XRF. Walker himself

attributed the high standard deviation across his study to small sample sizes.[49] However, this logic does not hold since in all but two comparisons I have listed Walker's sample size is much larger than the wet chemical sample sizes. It is likely that Walker's high standard deviation is really the result of examining the improperly cleaned surfaces of corroded and silver blanched coins.

Table 7[50]

Year	Butcher and Ponting	Walker	Year	L.H. Cope	Walker	Year	Guey	Walker	Year	Guey	Walker	Year	Gitler & Ponting	Walker
Augustus	0.44	1.02	70-74	0.49	4.22	176-179	3.32	5.9	192	8.98	6.72	193-198	9.15	12.25
Tiberius	0.78	0.67	75-78	1.03	4.04	179-181	2.4	4.5	193	1.55	6.87	198-211	8.93	6.86
Caligula	0.49	0.94	103-111	NA	3.7	181-182	1.77	6.69	194-196	5.9	9.57	211-217	NA	4.99
Claudius	0.34	0.76	112-117	4.41	3.997	183-184	7.14	5.07	196-198	1.77	6.24			
Nero Pre-Reform	1.24	0.83	132-138	4.92	3.89	184-185	2.83	3.88	198-200	2.11	8.42			
Nero Post Reform	4.92	1.1	141-151	0.64	5.56	186-187	1.91	4.8	200-205	1.56	6.4			
Otho	0.65	0.7	161	NA	4.61	187-189	2.57	3.97	206-207	1.09	7.63			
			235-236	NA	4.8	190-191	1.06	3.18	208-213	2.89	5.96			

Conclusions

Even without the explanation and understanding of the effects of corrosion and silver blanching on Roman coins, it is clear that Walker's data varies greatly from wet chemical results. While his values follow the same broad trend of decline in silver standards that is shown by wet chemical analysis – a decline that is visible to the naked eye – it presents a completely different history of both the detailed process of debasement and the silver standards being used. In the initial comparison we saw that Walker's results varied from -6.27 to 54.01 percent from the wet chemical results. It would be incorrect to state, as some might, that Walker's results are on average 2.15 percent higher than Butcher and Ponting's, 10.08 percent higher than Cope's, 9.93 percent

[49] D.R. Walker, *The Metrology of the Roman Silver Coinage* 1, 154.

[50] The standard deviation calculations are achieved by finding the mean average silver fineness for each group, and then subtracting the mean from each individual silver recording and squaring the results. The squared results are added together and averaged. The standard deviation is the square root of this average.

higher than Guey's, and 18.85 percent higher than Gitler and Ponting's; or to say that Walker is on average 9.15 percent higher than results from wet chemistry. To say this would imply a consistency that does not exist. If Walker's results were consistently higher than wet chemistry, it would not matter how much higher they were because we would know the amount to subtract in order to find the true fineness. It is for this reason that the most important finding in the comparison between XRF and wet chemistry is the variability of the differences. Because of the variability it is impossible to determine the true silver content solely from looking at Walker's results. Furthermore, by comparing the standard deviation for groups of coins analyzed by Walker against those of wet chemistry it becomes clear that troubling variations exist not only between the studies but between the coins themselves. This conclusion further supports the theory that Walker was mistakenly reporting the silver content of the corroded area of his coin samples, rather than the inner portion which should display more consistency.

Furthermore, the statistical significance calculations prove that the results from different wet chemical analyses are consistent. The small differences that occur between different wet chemical studies are negligible and not statistically significant. I felt this was important to establish because small differences do exist between the wet chemical studies and between the individual coins examined with wet chemical analysis. However, as shown by the statistical significance results, these differences do not mean that wet chemical analysis is flawed. Instead, the results prove two points. First, they prove that with proper analysis there will be no significant difference between coins of the same time period and location, i.e. the lack of significant differences demonstrates that it is possible to have consistent results when analysing ancient coins. And second, the results prove the validity of the results obtained through wet chemical analysis.

In conclusion, I am forced to advise extreme wariness in the use of Walker's data. Given the errors in his data, any theories or statements based on it will inevitably be flawed. Since these errors have so far been largely unrecognized, the theories based on his data have already permeated both the fields of Roman economic history and numismatics. In the following chapter I will examine some of these prevalent theories, and discuss how Walker and XRF analysis can still be used appropriately in the future.

Chapter Three

Past and Present Applications of Walker and XRF

Now that the inaccuracies in Walker's data have been revealed, it is easy to imagine how these issues could have a lasting effect on not just the study of Roman numismatics, but Roman economic history as well. And this is the crux of the problem, the reason why his inaccuracies matter. If a theory's foundation is flawed then so too by necessity is the theory. To say that Walker's publication was a seminal work in the field would be an understatement: Walker's XRF data has been cited in over one hundred scholarly papers, articles, and books ranging on topics from pure numismatics to Roman economic theory. Some scholars, like Carradice and Buttrey, who were discussed in Chapter Two, were aware of the potential problems in Walker's data and included disclaimers alongside their citations.[1] Others, either by publishing before the problems of surface enrichment started to be widely recognized, or by ignorance, merely quote Walker's data as fact. From his data theories about the Roman economy have been formed and have proliferated. In this chapter I intend to examine some of the ways in which Walker's research has been used in the past and present, and to finish with suggestions for moving forward.

Before I begin a critique of the use of Walker's data, it should be noted that not all applications of his work are inappropriate, nor are all theories based upon his data necessarily incorrect. Walker's data correctly displays an overarching pattern of debasement beginning with Nero in 64 and a progressive worsening over time.[2] If one is only seeking to show the existence of debasement and its general downward trend, it is perfectly appropriate to cite Walker. However,

[1] I. A. Carradice and T. F. Buttrey, *The Roman Imperial Coinage* 2.1[2] (London, 2007) 2-3.
[2] See Chapter Two.

it is unnecessary because the existence of debasement had already long been established by visual examination of the coins by numismatists. Furthermore, Walker's study also includes a comprehensive list of coin weights alongside its fineness measurements. There is no reason to believe, as far as I am aware, that the weights he recorded are not accurate and usable. That being said, corrosion and surface enrichment, not to mention simple wear from being handled, can significantly reduce the weight of a coin, but this is true of all coins, not just the ones Walker recorded and there are methods for minimizing this problem. As Walker's compilation is by far the most all-encompassing and wide-ranging study on silver fineness, there is often little alternative to using his data. This in turn means that there is little data to challenge or correct theories based upon Walker's work. This does not mean that any such theory is ipso facto correct, but neither does it mean that it is incorrect. In most cases we simply do not have the appropriate data to definitively establish validity one way or another. Obviously, that is not a good enough reason to use the data in the first place.

Critique

The first author to use Walker's research to speculate about the progress of the Roman economy was Walker himself. He includes a section at the end of *MRSC III* in which he discusses the results of his data and its applications to Roman economic history.[3] I will not discuss Walker's own theories here any further as his data's influence on them goes without saying, and they are seldom mentioned outside of his own work. Instead I will focus on how his data has been used

[3] See Chapter 4 and Appendices 1-4 in D.R. Walker, *Metrology of the Roman Silver Coinage* 3 (Oxford, 1978) 106-159.

and interpreted by other scholars, particularly focusing on scholars who are well known and influential in the broader field of Roman history.

The first theory I intend to examine is presented by Duncan-Jones in his 1994 book *Money and Government in the Roman Empire*. In this work he proposes the idea that a new emperor was under pressure to produce much coinage very quickly at the start of his reign, i.e. for commemorative pieces or to pay the army, and therefore silver fineness temporarily dropped at the start of a reign and recovered later.[4] This theory is based upon Walker's data which shows coin fineness dropping at the start of the reign for five of the seven emperors from Vespasian to Commodus, before rising again later in their reigns. Since Walker's data is inaccurate, for Duncan-Jones' theory to be true it would also have to be substantiated by independent and more reliable data.

Sporadic evidence for the period between Vespasian and Commodus exists within Cope and Guey's wet chemical studies, and what we find there paints a very different picture. For example, according to Guey's study the silver fineness during the first year of the reign of Marcus Aurelius is 68.36 percent,[5] it then rises and averages out to be 77 percent in his final year.[6] On the other hand, while the silver fineness did drop during the first year of Commodus' reign from 77 to 74.4 percent, it continued to drop and by the end of his reign had reached 66.85 percent. No coins from either of their wet chemical studies are dated exactly to the beginning or end of Vespasian's reign (69 and 79), but Cope gives a silver fineness of 95.2 percent for 70-72, and 85.4 percent for

[4] R. Duncan-Jones, *Money and Government in the Roman Empire* (Cambridge, 1994) 238.
[5] The coin Guey examined is one of Lucius Verus, co-emperor to Marcus Aurelius.
[6] These are imperial coins of Commodus minted before the death of Marcus Aurelius. The final imperial coin listed by Guey for Marcus Aurelius is for 179 and has a silver fineness of 74.6 percent. Therefore the conclusions do not change.

78.[7] Finally, Cope measures the *denarii* from the first year of Antoninus Pius' reign as 92.05 percent silver and those of his final year as 68.36 percent silver.[8] As a result, from the wet chemical data for these four emperors only Marcus Aurelius' reign fits into Duncan-Jones' theory. However, this is neither enough evidence, nor are there enough examples, to definitively prove or disprove Duncan-Jones. On the other hand, it is enough to cast strong doubt on Duncan-Jones' hypothesis and therefore force scholars to set it aside until such a time as more accurate measurements of a wider selection of coins can be undertaken.

One might assume that given the hypothesis he builds upon Walker's work Duncan-Jones was unaware of the problems with using a surface-level analysis for silver-copper alloys, but he refers to such problems throughout *Money and Government in the Roman Empire*.[9] He mentions that there are technical problems with surface-level techniques that result in Walker's data having inexact and inflated figures. And yet, he goes on to make the above claim and presents several other hypotheses based on Walker's data throughout his book. For example, Walker's data for the years 138-161 (the reign of Antoninus Pius) has a lot of variation. Some coins appear to have a high silver content, while others of the same year have a much lower silver content. Based on this data, Duncan-Jones hypothesizes that by the reign of Antoninus Pius there were two distinct silver standards in use: a high standard and a low standard.[10] He is unsure of the reason for the bimodal system, but further hypothesizes that it may have been in order to give better coins to the upper class, or because mints were not receiving the same quantity of silver bullion, or that the recycling

[7] The coin of 78 belongs to Domitian. The last coin that Cope has of Vespasian is dated to 75. But the silver content it 86.85 percent, so this does not affect these conclusions.
[8] The coin of 161 is an imperial coin of Lucius Verus. Cope has no imperial coins for Antoninus Pius that date to later in his reign. However, he did record two coins that date to sometime after 141 and are minted in the name of Faustina I, Antoninus Pius' wife. Their silver content averages to 78.49 percent.
[9] Duncan-Jones, *Money and Government in the Roman Empire*, 223: n. 42, 224: n. 46, and 234.
[10] Ibid. 244.

of old (already debased) silver coins meant that coins made from the recycled silver came out more debased than coins that were made with new silver bullion. In reality, I believe it is more likely to be the result of sampling error and inconsistency of corrosion. As was discussed in Chapter Two, there is a high degree of variation between Walker's reported fineness levels for coins of the same year, i.e. they have a high standard deviation. This gives the illusion of a bimodal system.

Similarly, according to Walker's data for the reign of Vespasian there was a lot of variation in the silver content of the *denarius*. Lo Cascio used Walker's figures to propose that Vespasian created an 'incomplete bimetallic' system by having two standards of silver fineness active in the same issue of coins.[11] Once again, without more reliable data to back up the idea of a bimodal system, it is more likely to be the result of Walker's XRF results being hindered by inconsistent corrosion and surface enrichment. Furthermore, Lo Cascio makes two other observations based upon Walker's data. First, he concludes that not all debasement took place during periods of financial strife.[12] He bases this observation on Walker's figures which show a debasement directly after the Dacian conquest in 107 when Lo Cascio expects there to have been a massive infusion of wealth into the Roman treasury. And second, he states that Walker's dating of the debasement to 107 disproves A.H.M. Jones' theory that Trajan had debased the *denarius* in order to pay for his military expenses, and that the success of the Dacian conquest led to lower prices for gold soon after.[13] Both of these statements depend on Walker having reported the silver standards with extreme accuracy: not just accurate enough to show a process of specific debasement, but to show that the debasement occurred in a specific year. None of the wet chemical studies report silver

[11] A.H.M. Jones and P.A. Brunt (eds.) *The Roman Economy: Studies in Ancient Economic and Administrative History* (Oxford, 1974) 191 n. 3 cited in E. Lo Cascio, 'State and Coinage in the Late Republic and Early Empire,' *Journal of Roman Studies* 71 (1981) 79.
[12] E. Lo Cascio, 'State and Coinage in the Late Republic and Early Empire,' 79.
[13] Ibid. 80.

fineness for the *denarius* in 107 (and we would need reliable figures for the years leading up to 107 as well in order to prove that this was the year of debasement). Without more reliable data to attest to a debasement in 107, there are no grounds for excluding the likelihood that the apparent lowering of the silver standard in that year was not just the result of corrosion and sampling error. As it stands, there is simply not enough evidence to exclude Jones' hypothesis.

Moreover, as we saw in Chapter Two, the differing levels of corrosion and surface enrichment among the coins analyzed resulted in a high standard deviation even among coins of the same issue within a single reign. This means that theories about a bimodal *denarius*, as both Lo Cascio and Duncan-Jones proposed, cannot be proven by Walker's data. In short, there is a misunderstanding about how corrosion affected Walker's data. In his 1998 book, *Towards a New Introduction to the Flavian Coinage,* Carradice also assumes a consistency in Walker's figures when they describe coins of the same year. He states that even though Walker's analysis has been proven by Butcher and Ponting to contain errors, the multiple minting standards Walker's data seems to reveal during the Flavian period are still valid because the standards are different relative to each other.[14] By making this statement, and then going on to use Walker's data in his investigation, Carradice implies that the errors in Walker's data do not affect its internal consistency. As we have shown in Chapter Two, this is incorrect.

The acknowledgement of the errors of XRF while simultaneously continuing to use Walker as a source, a phenomenon briefly discussed in Chapter Two, is not uncommon among modern scholars. As discussed in the previous chapter, it boils down to a fundamental misunderstanding of what is wrong with XRF analysis: it is believed that the problem is simply that the reported

[14] I.A. Carradice, 'Towards a New Introduction to the Flavian Coinage,' *Bulletin of the Institute of Classical Studies* 71 (1998) 107.

silver fineness is too high, not that there is a problem with the overall consistency. For example, in his paper 'The *Denarii* of Septimius Severus and the Mobility of Roman Coin,' Duncan-Jones claims that Walker's XRF results are ten percent too high for the eastern coins of Septimius Severus.[15] Therefore he concludes that Walker's figures for later Severan *denarii* should be reduced by the same amount. As we saw in the previous chapter, this is not a valid assumption. We cannot base theories on the assumption of consistency in the difference between Walker's results and the true silver fineness, because there is no consistency.

Another misunderstanding of the problems of XRF leading to the proliferation of false conclusions and hypotheses can be found in Harl's 1996 book *Coinage and the Roman Economy*. Harl also concedes the problems of XRF and surface enrichment, but continues to use Walker as a primary source for silver fineness.[16] When Harl sets out to track the debasement of the *antoninianus* from 215-274 he relies heavily on Walker's data.[17] He begins with Walker's figures for the years 215 to 253 and then uses other sources and data for the next twenty-one years since Walker's figures run out.[18] This creates a serious problem that Harl does not realize because apart from Walker's study all the other data that Harl presents in his table come from wet chemical studies.[19] As such, the silver fineness in the table appears to drop drastically in 253 when his

[15] R. Duncan-Jones, 'The *Denarii* of Septimius Severus and the Mobility of Roman Coin,' *The Numismatic Chronicle* 161 (2001) 77: n. 9. He makes a nearly identical claim in *Money and Government in the Roman Empire*, 224: n. 46.
[16] K.W. Harl, *Coinage and the Roman Economy 300 BC to AD 700* (London, 1996) 130: n. 15.
[17] Ibid. 130.
[18] L.H. Cope, 'Roman Imperial Silver Coinage Alloy Standards: the Evidence,' *The Numismatic Chronicle* 7 (1967) 129-130; L.H. Cope, 'The Nadir of the Imperial *Antoninianus* in the Reign of Claudius II Gothicus AD 268-70' *The Numismatic Chronicle* 9 (1969) 150-153; P. Tyler, *The Persian Wars of the Third Century AD and Roman Imperial Monetary Policy 253-268* (Weisbaden, 1975) appendix 2; E. Besly and R. Bland, *The Cunetio Treasure: Roman Coinage of the Third Century AD* (London, 1983), 37. It should be noted that Harl is citing Cope, 'Roman Imperial Silver Alloy Standards' for the years 271-293. However Cope's paper only covers years 253-268, not the years Harl says he is using it for.
[19] P. Tyler, *The Persian Wars of the Third Century AD and Roman Imperial Policy 253-268* also uses cupellation alongside wet chemical analysis. Cupellation is another destructive method of elemental analysis.

sources switch from XRF to wet chemical. According to Harl's table, silver fineness dropped 38.42 percent within that one year.[20] For context it should be noted that the second largest jump in fineness listed in the table is only 12.64 percent. This drop in fineness should not be surprising to anyone who is aware of the change in methodologies, but Harl does not mention this as a possible explanation. One would expect him to have anticipated this drop in fineness or at least acknowledged the potential for problems in his table.

The problem is not just that these authors were at least partially aware of the problems with XRF analysis and chose to use Walker's figures anyway, but that despite their acknowledgement of XRF's issues they nevertheless ignored their own warnings and took Walker's figures as fact. They used these 'facts' to postulate new theories and those theories continue to proliferate. One tends to take for granted that scholars have done the appropriate basic research before they propose a new theory, especially when they are well-regarded. As a result of this confidence, other scholars will reiterate their theories or build upon them without questioning or checking the original sources. This is one of the main ways that Walker's incorrect data has affected the field. As an example, not once in Peter Temin's 2013 book *The Roman Market Economy*, does he mention or cite Walker. However, when discussing the pattern of coin debasement in the empire he cites Harl's *Coinage and the Roman Economy*.[21] Harl, as we know, derived his data from Walker. Temin thereby spreads Walker's incorrect data, likely without knowing that it is incorrect, and without crediting its true source. Readers of Temin, who are unlikely to trace this data back to

[20] K.W. Harl, *Coinage and the Roman Economy*, 130: the jump in silver fineness, according to Harl, would have taken place between Aemilian's coins of 253 and Valerian's coins of the same year. He cites Walker for coins of Aemilian at 35.5 percent, and then Tyler for coins of Valerian at 21.86 percent.
[21] P. Temin, *Roman Market Economy* (New Jersey, 2013) 149.

Harl and then to Walker, would almost certainly be unaware of the problems in the data and conclusions that they are reading.

An even better example to show the spread of theories based upon Walker's data can be found in Howgego's *Ancient History from Coins*. Here he states, as if a fact, that coin fineness was lower at the start of imperial reigns as a result of the pressure to produce more coins quickly.[22] As proof of this statement he cites Duncan-Jones' M*oney and Government in the Roman Economy*. As we saw above, Duncan-Jones developed this theory from Walker's data. No credit to, or warning against, Walker is given by Howgego here and as a result no reader would be aware of where this hypothesis came from. So far, this is not any worse than Duncan-Jones himself, but the problem is in fact far worse, since on only the previous page Howgego discusses the increasingly questioned accuracy of Walker's work. He assures the reader that due to the lack of allowances Walker made for surface enrichment and in light of chemical studies that have shown there to be much less variation amongst the coins than Walker implies, he will only be using Walker for the general pattern of debasement and therefore neither of these problems will be an issue for his analyses. He thus seems to have been unaware that Duncan-Jones based his hypothesis on Walker's annual silver standards. However that may be, what began as a theory by Duncan-Jones based on Walker is now taken as fact and spread in a new source that denies relying on Walker.

This leaves us with an unavoidable conclusion: future scholars will have to question every numismatic and economic hypothesis that could have possibly been derived from Walker's data. The sources of these hypotheses and claims will have to be tracked down and followed until the original supporting data has been found. This is especially important for older works that were

[22] C. Howgego, *Ancient History from Coins* (London, 2002) 119.

written before the problems of XRF analysis and surface enrichment were well known or understood, because such works may not provide any hint that their source material is in doubt. In such cases there is no red flag for readers to check the sources, but they need to know to do it regardless. Unfortunately, as we can see from Temin, whose book was published as recent as 2013, age is not always the best indicator for the possibility of hidden data. As earlier hypotheses are cited over and over again by later scholars, they become disassociated from their origins, which allows them to continue on even as the data on which they are based is called into question.

Future Uses for Walker

There are likely to be competing thoughts on whether or not Walker's work, and XRF in general, has a place in future scholarship. It could be easily argued that it does not. Once the inaccuracies are discounted there is little left of use, and almost all of it has been substantiated by other studies and analyses. However, seeing that Walker does cover a large period of time, much larger than any other published analyses, it could be more convenient to use Walker rather than several combined studies. In general, there are a few ways Walker can continue to be used in the future. First, as previously stated, his data reveals the general downward trend in silver fineness for the *denarius*, *antoninianus*, and *drachma* over the course of two and a half centuries. His data could be used simply to attest to the presence of debasement, or, expanding on that, what this debasement implies about the state of the economy over time (although these trends can also be tracked through visual observation of the coins by a skilled numismatist).

Along with the general debasement of silver, Walker's recordings of the weight of each coin can be of use. Decreasing the volume of a coin is another form of debasement. A smaller size overall means that less silver is needed for each coin. In this way, the weight of a coin

denomination tracked over time can say a great deal about the economy. Many authors have attempted to use Walker's weights alongside his silver fineness in order to make holistic theories about debasement patterns.[23] This is far too precise for the nature of his data for silver fineness, but his weights could be used in conjunction with silver fineness from other, more reliable, studies. It is worth noting that Walker includes 'corrected' weight averages alongside his data; these averages were arrived at by adding coin weights taken from similar specimens in the British Museum.[24] As Walker never identifies the coins he uses, how many coins he added, or what the individual weights of those coins are, there is good reason to avoid using these 'corrected' mean weights in the future. His weights prior to correction are listed as well. It should be noted, however, that with the widespread growth of on-line sale catalogues from dealers and auction houses around the world (consolidated by websites like CoinArchives.com and ACSearch.info) it is a very simple task for scholars to obtain weights for a huge number of coins throughout the Roman Empire, along with photos and descriptions of each.

Finally, Walker's data for the silver fineness for coins prior to the Neronian debasement in 64 are still useable. Since the fineness of these coins never dipped below ninety percent, they would not be subject to either the corrosion or silver blanching effects discussed in the previous chapter to the same degree as later debased coins. As we saw in Chapter Two, a comparison of Walker's data from Julio-Claudian coins with those from wet chemical analysis shows them to be quite accurate. At most Walker's data differs a little over one percent from the comparative wet chemical study from Butcher and Ponting. Furthermore, the standard deviation for Julio-Claudian coins before 64 never exceeds 1.02 in Walker's data.

[23] K.W. Harl, *Coinage and the Roman Economy 300 BC to AD 700,* 130 is one example.
[24] R. Walker, *Metrology of the Roman Silver Coinage* 1 (Oxford, 1976) 2.

In these ways Walker's work can still be used in the manner he intended. Apart from this, there is potential use for his research beyond his intentions. For instance, his data provides a great case study on the effects of corrosion and silver blanching. Walker's data, when compared with data from more reliable sources, displays the varying nature of corrosion amongst silver-copper coins. It also attests to the presence of silver blanching on the more debased coins. His data, combined with photos of coin cross-sections that display the visual difference between the corroded, silver blanched and unaffected areas of the coin, and data taken from more reliable sources, shows exactly how corrosion affects coins to varying levels and the presence of silver blanching. This is valuable information, but requires many secondary analyses. Overall, his work shows that surface enrichment remains a problem for gathering accurate data via surface-level analysis, and it makes a strong argument against the use of XRF in numismatics.

XRF in the Future

This leads us to the larger problem of whether or not XRF analysis in general has a place in the study of ancient coins. It is easy to understand how XRF became popular in this field. Its relative ease of use, e.g. no need for chemists, its portability, and its low cost made it accessible and understandable to the average scholar. In order to perform wet chemical studies most historians would require a third party to conduct their analyses, unless they had a background in chemistry. This not only adds to the cost and inaccessibility, but forces scholars to rely on someone else's work in order to complete their studies. And naturally, the allure of an analysis that one can conduct by oneself is great. Furthermore, as we saw in Chapter One, under the right conditions and in the right applications XRF has a high degree of accuracy. But most important of all, XRF is attractive to scholars because of its non-destructive nature. No historian is willing to destroy an

ancient artifact and even fewer museums or private collectors will allow their coins to be destroyed for the sake of study. The natural result is that scholars and donors insist on non-destructive analysis. But given the questionable results obtained from XRF it is difficult to continue justifying its use in future studies that involve silver-copper alloys.[25] While XRF does not have a place in the quantitative analysis of corroded or surface enriched coins – if the intended result is to discover the makeup of the coin at the time of minting – there are other ways it has potential in the field.

XRF could be used to study corrosion or surface enrichment. However, any real conclusions about such enrichment would also require an examination of the interior of the coin using a different method. If one were to drill an extremely small hole in the edge of a coin or cut a cross section, then more accurate results could be obtained from XRF from the interior of the coin. However, since this negates the most desirable aspect of XRF, its non-destructive nature, it is unlikely to be used much in such cases. Furthermore, XRF can still be used for coins that are not subject to corrosion, i.e. specifically those made of gold, or silver above ninety percent purity. Since the *aureus* was never debased in the same way the *denarius* or the *antoninianus* was, i.e. the size of the coin was decreased instead of the gold being alloyed with copper, it is not subject to corrosion in the same way. This means that XRF can be used on these coins with great accuracy. A 2018 study by Van Loon, et al. used synchrotron radiation (SR)[26] WD-XRF on four gold coins in order to map the trace platinum and use this information to determine the origin of the gold.[27]

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[25] This opinion is shared by Bartlett, Yoon and Pliego, who, in contrast to the prevailing attitude towards XRF of those who study the Roman economy and coinage, were so worried about the problems of surface enrichment and the corrosion of silver in Visigothic gold coins that they resorted to specific gravity analysis for all of their coins: P. Bartlett, D. Yoon, and R. Pliego, 'Weight, Fineness, and Debasement in Visigothic Tremisses from Theudis to Leovigild: New Evidence from the Hoards of Seville and Reccopolis,' *American Journal of Numismatics* 29 (2017) 149-211.

[26] Synchrotron radiation, like electromagnetic radiation, is caused by charged particles, but it differs from classical electromagnetic radiation because the particles are accelerated in a curve or orbit instead of a straight line.

[27] L. L. Van Loon, *et al.*, 'Rapid, Quantitative, and Non-Destructive SR-WD-XRF Mapping of Trace Platinum in Byzantine Roman Empire Gold Coins,' *Journal of Analytical Atomic Spectrometry* (2018) DOI: 10.1039/C8JA00227D.

The platinum level for three coins was determined by both SR-WD-XRF and spark ablation (SA) ICP-optical emission spectroscopy (OES) which showed a general consistency:[28] the results differed by -11 to 3 percent.[29] Furthermore, the removal of one side of each coin allowed them to analyze the true interior of the coin. Only one coin showed a higher platinum level from SR-WD-XRF than SA-ICP-OES, meaning SR-WD-XRF tends towards underreporting platinum instead of over reporting.

Perhaps the most potential for the future of XRF analysis is, as E.T. Hall proposed in his paper 'X-Ray Fluorescence Analysis Applied to Archaeology,' in a qualitative manner instead of a quantitative one.[30] As stated in Chapter One, XRF has the ability to identify any element whose atomic number is greater than twenty-two without the need for a vacuum.[31] This gives it the ability to examine nearly all inorganic compounds. This broad range includes all elements found in coins. Even if its quantitative readings are off by indeterminate amounts, XRF is still able to identify the elemental makeup of any coin, regardless of corrosion or surface enrichment, as long as the elements are present in quantities greater than 0.01 percent.[32] XRF can therefore be useful in identifying coins whose make-up is unknown as a result of either wear or corrosion, or for determining the source of bullion used in the coin by identifying the trace elements inside.

[28] Spark ablation is a method for converting solid samples into aerosol format. Optical emission spectroscopy is another name for atomic emission spectroscopy.
[29] This was also true of the initial study undertaken by some of these scholars which compared WD-XRF against SA-ICP-OES. These results differed from one percent higher to thirteen percent lower than SA-ICP-OES, with standard deviations ranging from two to three percent. M. Hinds, G. Bevan and R.W. Burgess, 'The Non-Destructive Determination of Pt in Ancient Roman Gold Coins by XRF Spectrometry,' *Journal of Analytical Atomic Spectrometry* (2014) 1799 and 1804.
[30] E.T. Hall, 'X-ray Fluorescent Analysis Applied to Archaeology,' *Archaeometry* 3 (1960) 33.
[31] Ibid. 32.
[32] Ibid.

Conclusions

In conclusion, while XRF is a highly reliable analytical method in other fields, it has many problems when used in numismatics. There are potential uses for XRF in future study, but not as a quantitative analysis for corroded or surface-enriched coins. Its use is justified by its low cost, ease of use, and the speed of analysis, but any analysis that produces inaccurate results ends up being a waste of time, money, resources, and corrupts any hypotheses or conclusions that are based upon them. In my opinion, based on the analysis presented above, with few exceptions, XRF is not useful in this field. Continued reliance on it could become a detriment to real progress.

Conclusion

The original purpose of this thesis was to evaluate the inflation of the third and fourth centuries in relation to the debasement of the silver coinage. It ended up being an evaluation of the results of David Richard Walker's XRF analysis and a comparison of those results against results from more reliable wet chemical analyses. In short, I ended up expanding upon the work started by Butcher and Ponting.[33] Since the 1990s, these scholars have raised the alarm about the potential errors in XRF analysis and demonstrated the difference between Walker's XRF results and the results obtained by wet chemical analysis, which has been proven to be a more accurate method. Unfortunately, their warnings were ignored or misunderstood. Scholars reading their work seemed to conclude that Walker's reported silver fineness was elevated, but that it was consistently elevated by the same amount. This assumption allowed scholars to continue using Walker's data, albeit with a small disclaimer and a nod to Butcher and Ponting.

In Chapter Two I sought to show that this assumption was incorrect. Indeed, the results I obtained from making thirty-four comparisons against Walker's data showed that his results are incredibly inconsistent. Walker's data is not a set amount higher than the true silver content, the amount it differs by varies from year to year and coin to coin. No pattern could be established. Furthermore, I demonstrated that the standard deviation across his samples is worryingly high. In over seventy-three percent of cases his standard deviation was higher than the standard deviation seen in wet chemical analyses. This meant that there was also no internal consistency, i.e. his data could not be compared against itself. Because of the variance in

[33] K. Butcher and M. Ponting. 'Rome and the East. Production of Roman Provincial Silver Coinage for Caesarea in Cappadocia under Vespasian, AD 69–79,' 63-77. See also K. Butcher and M. Ponting 'The Roman *Denarius* under the Julio-Claudian Emperors: Mints, Metallurgy and Technology,' 163-197.

corrosion, Walker's results showed coins that should have had the same silver fineness as being strikingly different from each other. All in all, the results I obtained in Chapter Two demonstrated that Walker's data could not be used as he intended and that other scholars should not have been using his data.

Given this information, it was important to examine how Walker's data had been used by scholars, and why this is a problem. Any hypothesis based upon incorrect data should be discarded. Many hypotheses have been made from Walker's incorrect XRF data. Unfortunately, they are not always obvious. As we saw in Chapter Three, not all works that include theories that build upon Walker's data give him credit. The process of tracking down other such conclusions by other scholars will be long and arduous, but it must be done. For numismatic analysis to advance, and for accurate hypotheses and conclusions on ancient coins to be developed, we need to cease using Walker's data and XRF in the manner that they have been so far. The potential problems with XRF are known, and the evidence against using Walker is available for anyone who makes the effort to check. Walker continues to be cited because he remains the 'best' option available for data on the imperial silver coinage. The argument for his work being the 'best' is simply that he has the most data from the most coins of any study of its kind. But it must be conceded that since the data has been proven to be inaccurate it cannot be qualified as the best option, or even an option, no matter how many coins were included in the study.

The willingness to continue using this data even as the problems with it become more widely recognized and understood creates further problems. New hypotheses are presented that are based upon evidence that is inaccurate, which leads to the spread of misinformation. We must now weed out the work that has been tainted by Walker's data. We need to be more

diligent with fact-checking the sources. We can no longer keep moving forward without first stepping back and fixing the problem. Instead of continuing to use Walker's research and XRF on surface-enriched coins, that time and energy needs to be put towards expanding more reliable data in order to start making real progress in this field.

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