Study and Comparison of Coins by X-ray Diffraction (XRD);
Preliminary Findings

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**Introduction/Overview:**

The researchers subjected a number of modern, ancient, and historical coins to compositional and structural testing using X-ray fluorescence and X-ray diffraction techniques. The goal was to test the viability of X-ray diffraction as a tool for examining micro-structural characteristics of very old and often corroded coins that could shed light on ancient processes of production.

Two modern US pennies (one pre, the other post -1980) were used as testing controls. Comparatively reliable information on the composition and manufacture of these coins could be accessible through the US Mint.

![Image of coins](image)

*Fig 1: From left to right: Diocletian “Antoninianus” (Cyzicus mint), Maxentius “Follis” (Rome mint), 1698 Half Penny, GFAP Unknown, and 1975 US Penny.*

From a conservation perspective, XRD - a non-invasive technique - is an attractive alternative to other methods used for coin analysis which require that the artifact be probed or otherwise compromised in order access useful information. Sectioning or probing of artifacts have hitherto been necessary evil of the analysis of coins - particularly ancient coins - given the
Little has been done by way of the study of modern or ancient coinage using X-Ray Diffraction (XRD). The aim of this study is to explore the potential for the application of XRD to expanding our knowledge of coins. Each coin was subjected to at least two XRD scans. For each scan testing parameters such as: scan length, number of steps and depth of probe were adjusted. These adjustments were made in order to gain a thorough understanding of the crystallographic structure of the coins, it is hoped that with further study we can definitively correlate structural readings to what we know of the composition and/or manufacture of the coins.

The five coins discussed here were selected from the original sample because they illustrate the potential and pitfalls encountered during the course of this study. All interpretations related to coin composition and manufacture are preliminary. The issues discussed which relate to the practical aspects of the execution of the XRD scan (mounting techniques, probe and glancing angle settings etc.) are intended to aid those who would engage in similar study in the future.

**Background:**

**History of Coin Manufacture and Archaeometric Analysis:**

Previous archeometric analysis of Roman coins has focused primarily on issues of composition: bulk alloy constitution, trace impurity presence (including lead isotope analysis), and variation in the composition from surface to interior. This work has concentrated on sourcing the raw materials used at different mints over time, as well as investigating the re-melting of old coinage and manipulation of alloy composition to vary inherent value in the currency.¹ Such insight is used to track the wealth and expanse of the empire. This project seeks to extend this approach by not only examining composition, but atomic structure: investigating the metallic and oxide phases present by x-ray diffraction.

**X-ray Diffraction (XRD), and its Applications:**

X-ray diffraction analysis uses the interaction of x-rays with the atomic structure of a crystalline phase to deduce the arrangement of atoms within the lattice. X-rays are scattered by the atoms (primarily by electrons), and interfere with one another to form a unique pattern. Constructive interference results when certain geometric conditions are met as described by Bragg’s Law:

$$2d \sin \theta = n\lambda$$  \hspace{1cm} (1)

Where \(n\) is an integer, and the geometry is described by figure 1. X-rays are used to produce the diffraction pattern because their wavelength \(\lambda\) is typically the same order of magnitude (1-100 Å) as the spacing \(d\) between planes in the crystal.²

Powder diffraction (XRD) is a technique used to characterize the crystallographic structure, grain size, and preferred orientation in polycrystalline or powdered solid samples. In a diffractometer, radiation emanating from the x-ray tube is diffracted at the sample and recorded by the detector. One-dimensional diffraction patterns are generated by counting incident x-rays (intensity) as a function of Bragg angle. Each phase can be identified by a unique “fingerprint” of peak locations, which correspond directly to specific interplanar spacings. The location of these peaks can be solved for quantitatively based on the lattice parameters of the characteristic unit cell, but are more often developed experimentally using reference standards of known structure. The Research Associateship Program of the Joint Committee on Powder Diffraction International Centre for Diffraction Data (JCPDS-ICDD, now known as the ICDD) has developed many such reference patterns. All reference patterns used in this report are of

randomly oriented, polycrystalline samples of high purity and simple stoichiometry. Fig 3, below, shows the reference pattern for copper and cuprite.

![Diffraction Pattern (Reference) for Cu and Cu₂O](image)

Fig 3: Diffraction Pattern (Reference) for Cu and Cu₂O

The effect of alloying may be seen in the slight shifting of these peaks. For example, the addition of an atomic species with a larger atomic radius into solid-solution will result in an increase in interplanar spacing and corresponding decrease in 2θ (shift “left” in location of peak intensities). Also, the presence of minor phases and/or impurities is observed in the presence of minor peaks which do not correspond with the major phases being analyzed.

In addition to identifying the major metallic and oxide phases present, XRD also provides information about the orientation of the crystal. When a metal is shaped, the deformation mechanism may align the crystallographic orientation. This effect is known as texturing. Since the reference patterns used in this analysis are taken from randomly oriented polycrystalline samples, the relative height of peaks for a given phase in the coin may be compared with the random orientation to see if the metals have been textured. This may provide insight into the processes by which the coins were formed. A full texture analysis requires a 4-circle diffractometer. Fig 4, below, shows the experimental diffraction pattern from the 1975 Penny which exhibits texturing. The effect is particularly evident in the height of the second peak, which corresponds to the {200} family of planes and has almost twice the intensity of the randomly-oriented reference. This corresponds with the fact that the metal used to min
modern coins is rolled from an ingot, before being cut into discs and the design struck onto the surface. This rolling operation textures the metal.

1975 Penny (theta 2-theta, 1hr)

![Graph showing XRD pattern for 1975 Penny]

**Fig 4: Measured XRD Pattern for 1975 Penny**

It may also be possible to extract information about the grain size of the metallic phases by measuring broadness of peaks (though this effect is also coupled to residual stress in the lattice). Such insight can provide important clues as to the casting process, as well as additional heat treatment steps. It may also suggest alloy design not related to inherent coin value.

In order to interpret the diffraction patterns generated by XRD it is necessary to have a basic idea of what chemical constituents are in the specimen. There is some data available for typical compositions of these coin typologies in the literature. However, in this laboratory we opted to begin with a chemical analysis (by XRF) of the coins to determine the composition.

**Methods:**
**XRF**

Energy-dispersive X-ray Fluorescence (ED-XRF) was performed to get a general sense of the composition of the coins in order to aid in the analysis of the XRD data. An XRF “gun,” was used to perform these scans. Since the instrument was newly acquired by the laboratory, and of unknown tolerance and accuracy, a series of scans were performed on standards of known composition (see appendices 1a-c). Each coin was scanned several times to verify a consistent reading.

**XRD**

X-ray diffraction (XRD) analysis was carried out using a SIEMENS Diffraktometer D5000, at an accelerating voltage of 40kV and current of 35mA. The coins were mounted in putty on a three-pronged stage to insure that the surface of the face was properly aligned with the x-ray source and detector. All scans were completed over the range $20^\circ \leq 2\theta \leq 90^\circ$. Preliminary scans were performed over 1 hour, while 18hr scans were used to further refine complex patterns.

Two scan “types” were employed: theta-2theta and glancing angle. For what will be referred to as a “theta-2theta” type scan, the sample is rotated at a constant angular velocity whilst the detector rotates at double angular velocity around the sample. The diffraction angle ($2\theta$) is thus always equal to twice the glancing angle ($\theta$), and the motion of the stage and the detector is coupled. Alternatively, in what we will call a “glancing angle” scan, the sample remains at a fixed glancing angle, whilst the detector is allowed to rotate. Since the penetration depth of the x-ray is a function of the angle of incidence, fixing the stage at a low angle and only allowing the detector to rotate allows for a more “shallow” scan. This scan type is traditionally used when analyzing thin films to avoid penetration of x-rays into the substrate. It is used here to compare the “surface” of the coin, with the “interior.”
The Bruker DIFRAC$^+$ program was used to identify crystallographic species and to shift and scale the peaks of the known patterns to fit. The following ICCD$^3$ diffraction pattern card-files were used in the analysis: Copper (4-836), Cuprite-Cu2O (5-667), Silver (4-783), and Lead (4-686). Reference patterns were scaled by matching the height of the “primary” peak (the peak of highest intensity) of the reference pattern with the corresponding measured peak. Relative phase percentages were deduced by comparing the primary peak height of the various phases. Texturing was observed by comparing the relative peak intensities of the reference (randomly oriented polycrystal) with the corresponding peak intensities of the measured pattern. Since the primary peak intensities were forced to match, this effect is seen in a lack of agreement in the height of the secondary peaks.

**Results & Analysis:**

**XRF**

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$^3$ The Research Associateship program of the Joint Committee on Powder Diffraction International Centre for Diffraction Data (JCPDS-ICDD, now known as the ICDD).
The x-ray spectra generated by ED-XRF were interpreted by the analysis software\textsuperscript{4} and converted into parts-per-million (PPM), by weight, for 27 elements, including: Si, Al, Fe, Na, Mg, K, Ca, Ti, Mn, Cr, Cu, Ni, Pb, Sr, V, Zn, Ag, and Sn. Prior to commencing XRF testing on the coins, samples of known composition - from the National Institute for Standards and Technology (NIST) – were analyzed to test the accuracy and precision of the equipment\textsuperscript{5}.

Since coins are largely metallic in composition and other elemental data appears unreliable, only data for the six most common metallic elements are reported here (Table 1). Assuming a composition made entirely of these constituents, relative percentages were calculated (Table 2).

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
PPM (by weight) & Cu & Zn & Pb & Ag & Sn & Fe \\
\hline
Penny, 1975 & 4,461,974 & 150,400 & & & & 8,043 \\
Half-Penny, 1698 & 3,365,038 & & 16,764 & 682 & & 8,145 \\
Maxentius, Rome Mint & 1,062,887 & 3,285 & 81,868 & 12,439 & 33,689 & 3,831 \\
Diocletian Cyzicus Mint & 1,105,732 & 2,011 & 11,772 & 47,182 & 12,609 & 6,677 \\
GFAP Unknown & 879 & 21,556 & 8,413 & & & 401,568 \\
\hline
\end{tabular}
\caption{Parts-per-million of metallic constituents reported by analysis software.}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Relative Composition (%) & Cu & Zn & Pb & Ag & Sn & Fe \\
\hline
Penny, 2005 & 47.15 & 52.68 & 0.01 & & & 0.17 \\
Penny, 1975 & 96.57 & 3.26 & & & & 0.17 \\
Half-Penny, 1698 & 99.25 & & 0.49 & 0.02 & 0.24 \\
Maxentius, Rome Mint & 88.72 & 0.27 & 6.83 & 1.04 & 2.81 & 0.32 \\
Diocletian Cyzicus Mint & 93.23 & 0.17 & 0.99 & 3.98 & 1.06 & 0.56 \\
GFAP Unknown & 0.20 & 4.99 & 1.95 & & & 92.87 \\
\hline
\end{tabular}
\caption{Relative Composition of metallic constituents.}
\end{table}

\textsuperscript{4} We did not have access to the software package for interpreting alloy data. As a result, our reported values are assumed to be only comparatively significant and have been scaled.

\textsuperscript{5} NIST 2702 (Inorganics in Marine Sediment) and NIST 2781 (Domestic Sludge). See Appendix 1a and b for analysis of standards.
The assemblage is composed of a variety of copper-based alloys. The notable exception being the unidentified ‘coin’ from Greene Farm whose composition is predominantly ferrous.

In addition to copper the two oldest coins contained lead, silver, tin, zinc and iron. The most conspicuous contributions are the 7% lead content in the Maxentius Rome Mint, and 4% silver in the Diocletian Cyzicus Mint. Such alloying additions may be the result of impurities from processing or part of the alloy design. To address this question one would need information about sources of raw materials, common coin composition and known technological benefits of particular alloys. For example some elements may be the result of re-melting coins or diluting precious metals with base metals in antiquity to modify the inherent values of coins. In other cases, certain impurities in the ore may have been difficult to separate and remove. Alternatively, alloy additions may have been made intentionally to lower the melting temperature, or to make the final alloy more or less malleable.

The two modern US pennies are intended as standards, since they are of known composition and structure. Pre-1982 pennies are a single phase brass alloy 95 Cu: 5 Zn. XRF readings confirm an overwhelming predominance of copper although the Zn results were lower than values reported by the US Mint. Post-1982 pennies are composed of a pure zinc core plated in pure copper (total composition 2.5 Cu, 97.5 Zn). Experimental data indicates equivalent amounts of Cu and Zn. This suggests that the x-ray beam penetrates to the zinc core. Moreover, the depth to which the beam penetrates must be on the order of twice the thickness of copper plating.

The 1698 Half penny is almost entirely composed of copper with approximately 0.5% Pb. Cu and Pb have a very restricted mutual solubility in solid state (solubility of Pb in Cu does not exceed 0.09 atomic percent at 600°C). Thus the Pb is expected to be a second phase in the alloy (Appendix 3). Small concentrations of Fe and Sn form a solid solution with Cu, and result in a modification of the crystallographic structure.

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6 Presentation by Lisa Anderson Graduate Student, Joukowsky Institute for Archaeology and the Ancient World, Brown University.
7 www.usmint.gov
**XRD**

**Modern (1975) US Penny**

This coin was subjected to two one hour scans at theta-2-theta and on a glancing angle. The four major peaks present correspond to the known signature for copper (JCPDS 4-836). No second phase was identifiable although there is a broad peak at 2-theta=36 and a shoulder/suggestion of a peak at 2-theta = 42.

There is nominal peak shifting – by less than 0.005 in opposing directions on the scans. This exact cause of this effect is unknown. Phase diagram indicates high solubility of Zn in Cu. However, since Zn had Cu have the same atomic radius (approximately 135pm\(^9\)) we do not expect the addition of Zn atoms in solid solution to affect the crystallography. A possible explanation for this effect may be an alteration in the orientation of the coin for each test.

Copper peak at 2theta = 43.5 which corresponds to the \{111\} plane, was scaled to match the intensity of the corresponding measured peak. The other four measured peaks were compared to the scaled JCPDS reference peak (based on a randomly oriented polycrystal). In the theta-2theta reading the second peak is almost twice the intensity of the scaled reference peak. The third and fourth peaks are also slightly higher in intensity than expected. In the glancing angle test the second third and fourth peaks had a lower intensity than the reference peaks. This suggests:

1. Texturing throughout the material, likely from the rolling operation to produce the sheet metal (this is evident in the theta-2theta scan)\(^10\),
2. Re-orientation of the crystals on the surface as a result of striking (as seen in glancing scan).

**1698 Half Penny**

This coin was subjected to two one hour scans at theta-2-theta and on a glancing angle. The major peaks present correspond to the known signature for copper (JCPDS 4-836) and cuprite (JCPDS 5-667). In the glancing scan the primary cuprite peak has a higher intensity that

\(^10\)www.USMint.gov
the primary copper peak, the reverse is true in the theta-2theta scan. This is consistent with the observation that metals oxidize from the outside in.

Reference peaks showed good correspondence to measured peaks. Copper reference peaks were shift to the left by less than 1.002 percent. This shifting effect is likely a result of the Sn and Fe additives whose atomic radii, 145pm and 140pm respectively, are larger than that of Cu (135pm).

**Diocletian “Antoninianus” (Cyzicus mint)**

This coin was subjected to four one hour scans: 1 theta-2 theta and 3 at a glancing angle. The major peaks present correspond to the known signature for copper (JCPDS 4-836), cuprite (JCPDS 5-667), and silver (JCPDS 4-783). Cuprite peaks correspond well without shifting. Copper and Silver peaks were shifted in 3 of the 4 four scans, copper to left silver to the right; the sum of the shifts totaling a factor of approximately 0.004.

Interpretation of these results is difficult. Since total shift is consistently 0.004, discrepancies in the extent of shifting for either element may be attributed to a slight misalignment in the mount, as seen in the modern penny. In general the shifting phenomenon may be attributed to the effect of Sn in solid solution with either Cu, Ag, or both (see Appendix 3, Ag-Sn and Cu-Sn phase diagrams). Since Ag has an atomic radius of 160pm adding Sn would reduce the inter-planar spacing (2theta shift right) whereas addition of Sn to Cu would expand the lattice (shift left). Differentiating between a shift resulting from misalignment of the specimen, or from alloy additions is beyond the scope of this research.

Between the three glancing tests there is a discrepancy between the relative intensities of Cu and Ag. In tests 1 and 3 the primary silver peak at 2theta = 38.2 is roughly half the intensity of the primary Cu peak at 2thea = 43.5. In test 2, the Cu peak is half the intensity of the Ag peak. This surprising result suggests a local concentration of Ag which may be:

1. An enrichment effect as a result of a corrosion process.
2. Inhomogeneity in the melt

It can be assumed that all 3 scans were of different places on the coin since each time it was remounted the coin was randomly re-oriented (no consistency in testing the obverse vs.
reverse was maintained). This also suggests a need to sample in a number of different spots as the structure may vary across the specimen (composition, phase, texture etc.).

Finally comparing the glancing scans to the theta-2theta scan we see that the intensity of the Ag is approximately 3/4s that of the Cu.

Maxentius “Follis” (Rome mint)

This coin was subjected to several scans. One short (1 hr), theta 2theta scan and one long (18 hr), theta 2theta scan are presented here to demonstrate noise reduction and the potential benefits of longer scans. The long scan has a better signal to noise relationship, having more well-defined peaks which roughly correspond to those in the short scan but are more easily distinguishable.

The major peaks present correspond to the known signature for copper (JCPDS 4-836), cuprite (JCPDS 5-667), silver (JCPDS 4-783), and lead-tin oxide Pb2SnO4 (JCPDS 11-233). The overnight scan allowed us to tentatively identify the as yet unidentified peaks as lead tin oxide. While the matches are tentative the first 5 measured peaks correspond well with all the major peaks between 2theta =25 and 2theta = 35.

GFAP Unknown

This coin was subjected to several scans, with greatly varying result. Although there was consistently a major peak at 2theta = 27.5. The rest of the signature varied from very noisy (amorphous?) to starkly defined (textured?). In this case the long scan did not reliable clarify the location or relative intensity of peaks. Based on the XRF data we attempted to match alloys and oxide of Fe, as well as Zn and Pb without success.

Conclusion:

These preliminary studies did point to the potential for archaeologists and material scientists to gain valuable insight into the atomic structures of coins using advanced XRD techniques. In this research our use of XRD would have been greatly improved by the availability of more reliable compositional tests, though our XRF results were useful for
qualitative analysis and comparisons. We were also hindered by our inability to access a well documented history of some of the objects, particularly concerning their possible preservation using chemicals, this issues was compounded by the fact the we were uncertain of the depth of penetration of our diffraction beam.
**References Cited**


Presentation by Lisa Anderson Graduate Student, Joukowsky Institute for Archaeology and the Ancient World. Brown University.


www.usmint.gov

Appendix 1a: XRF Standards and Reference XRF Analysis

Appendix 1b: Correspondence with Dr. Murray

Appendix 1c: Raw XRF Data

Appendix 2: XRD Patterns with Reference Peaks

(see http://proteus.brown.edu/materialsscience/6108 for appendices 1a -2)

Appendix 3: Phase Diagrams
Cu-Pb Phase Diagram
Cu-Sn Phase Diagram

Ag-Sn Phase Diagram

From [44Ray].

Appendix 4: Artifact Inventory

“Old World” Coins\textsuperscript{11}:

* Diocletian (Roman emperor, r. 284-305 CE)
  1. Alexandria mint (Milne 4837, Year 3): JIAAW Tray F20, DF
  2. Cyzicus Mint (RIC VII p. 253, n. 306): JIAAW Tray 45, Row 4, Column 1

* Maxentius (Roman emperor, r. 306-312 CE)
  1. Rome mint (RIC VI p. 378 n. 210): JIAAW Tray 49, Row 4, Column 2
  2. Ostia mint (RIC VI p. 404 n. 35): JIAAW Tray 49, Row 5, Column 8
  3. Ticinum mint (RIC VI p. 295 n. 102): JIAAW Tray 49, Row 4, Column 5

"New World" Coins\textsuperscript{12}:

  1. Colonial era unidentified coin from Greene Farm (5182 GF791: K NO W4, L1, SW Q)
  2. 1698 Half Penny (courtesy of the Rhode Island Historical Society)
  3. Fugio Cent (courtesy of the Rhode Island Historical Society)
  4. Pine Tree Shilling (courtesy of the Rhode Island Historical Society)

Modern, “Reference” Coins:

  1. 1975 US penny
  2. 2005 US Penny

\textsuperscript{11} “Old World” coins courtesy of the Artemis A.W. and Martha Joukowsky Institute for Archaeology and the Ancient World (JIAAW).

\textsuperscript{12}“New World” coins courtesy of the Rhode Island Historical Preservation & Heritage Commission (RIHPHC)