CONF-700663--1

MASTER

Presented at the symposium on the "Application of
Scientific Methods in the Analysis of Works of Art"
Boston Museum of Fine Arts, June, 1970

Neutron Activation Analysis of Streaks from
Coins and Metallic Works of Art

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Introduction

The ore-refining techniques used in ancient and medieval times were relatively crude. As a result metalware and coins from these periods contain detectable amounts of various impurities. For example, gold, lead, antimony, arsenic, and frequently also zinc, tin, bismuth, and iron are usually associated with silver. Some of these impurities such as gold may have been contained in the original silver; others, such as antimony and arsenic, may arise principally as impurities in the copper used to alloy or debase the silver; the lead impurity, on the other hand, probably was mainly introduced during lead-cupellation processing of silver.

It appeared to us that it might be possible to use information on the level of impurities in silver coins and art objects to assist in the authentication and the identification of the region and period of manufacture of the art objects. Described in this report are studies we have performed of one of the impurities, gold, which seems to provide particularly useful information.

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Two non-destructive analysis methods were devised and perfected. Emphasis in both methods was on the speed of analysis since we wanted data for a large-enough number of coins and art objects to permit obtaining statistically relevant results. The bulk of the coins and art objects we have analysed by both methods are Near Eastern in origin and examples will be given mainly of data derived from Sasanian (Persia: 224-651 AD) and early Islamic coins and metalwork.

Howitzer Coin Analysis

This method of analysis has been described in detail in previous publications ¹⁻³. It consists of irradiating a coin for one minute in a low-intensity neutron source ^(Fig. 1) followed by a one minute analysis of the induced silver radioactivity. The activity in the coin is dissipated in 10-15 minutes and it is possible to perform repeat analyses thus improving the statistics. In using this method we have been able to determine the silver fineness of a coin to ± 1 to 1.5 % ¹⁻³.

We have analysed over 3500 ancient and medieval coins using this method of activation. Shown in Fig. 2 are silver fineness data for over 400 Sasanian coins. Alternating open and closed circles are used to assist in the visual correlation of the data with the ruling monarch issuing the coins. Those coins beginning with the reign of Kavad I have inscribed on them the year of issue and the data in Fig. 2 are arranged in accord with these dates. Prior to these analyses, many historians had assumed that, except for some obvious debased-looking issues of Shapur I, all other Sasanian drachms

were of better than 90% silver.

Streak Analysis Method

The oxidized surface of a coin or metallic art object and the non-tarnished portion in immediate contact with the corrosion layer generally have a composition quite different from that in the interior of the coin.^{4,5} This results from the fact that the more reactive elements such as copper are oxidized and lost from the surface more readily than the less reactive elements, silver and gold. Because of this surface-depletion effect it is necessary to be certain that samples are taken at a depth where the composition is that of the original coin. For extremely heavily corroded coins, or coins corroded throughout it is important to emphasize that no method of analysis, including destructive chemical analysis will yield composition data indicative of the original coin.

Our procedure involves first removing the corrosion layer on a tiny area on the edge of the coin or art object by stroking the edge with fine-grained emery paper. A few extra strokes with the emery paper removes about 0.01 inches of metal. A small, cleaned piece of roughened quartz tubing is then rubbed on the brightened area of the coin edge (Fig. 3) producing a streak on the quartz tubing weighing less than about 0.0001 gm. Usually one or two additional pieces of quartz are also streaked in the same spot and used for confirmatory analyses.

Usually 40 to 50 streaks from coins plus 5 streaks from alloys of known composition are individually sealed in polyethylene and ir-

rated together in a nuclear reactor for two hours at a neutron intensity of 3×10^{13} neutrons $\times$ $\text{cm}^{-2} \times \text{sec}^{-1}$. The irradiated streaks are then mounted separately on cards and analysed for their silver, gold, copper, zinc, arsenic, and antimony radioactivity. A multichannel pulse-height analyser coupled to a high-resolution Ge(Li) detector is used for the analysis. ^(Fig. 4) Since the streaks are not weighed the radioactivity levels in the streaks are compared with those in the standard-alloy streaks and the ratios: $\% \text{Cu}/\% \text{Ag}$, $\% \text{Au}/\% \text{Ag}$, $\% \text{Zn}/\% \text{Ag}$, $\% \text{Sb}/\% \text{Ag}$, and $\% \text{As}/\% \text{Ag}$ are calculated.

Published chemical analyses of ancient and medieval silver coins and art objects indicate that, in almost all cases, silver and copper account for over 95% of the metallic content. Some, having high copper contents may also have more than 1% tin or zinc. But in most cases the lead, gold, silver, and copper percentage sum is about 99%.

Our method of streak analysis does not permit us to determine tin or lead. Hence, we assume that the $\% \text{Ag} + \% \text{Cu} + \% \text{Zn} + \% \text{Ag} + \% \text{Sb} + \% \text{Au} = 100$. For almost all of the coins and art objects discussed below the $\% \text{Zn} + \% \text{As} + \% \text{Sb}$ is much less than 1%. Our approximation, therefore, reduces to: $\% \text{Ag} + \% \text{Cu} + \% \text{Au} = 100$ and data are reported here in two forms, $\% \text{Ag} + \% \text{Au}$ and $100 \times (\% \text{Au}/\% \text{Ag})$. This latter term, as is discussed below, is indicative of the $\% \text{Au}$ impurity in the silver.

It was apparent early in our studies that the gold being detected was associated almost entirely with the silver in a coin. For instance, data for 40 coins of Shapur I are arranged in decreasing order of the $\% \text{Ag}$ contents on the upper graph of Fig. 5. The lower graph of this figure illustrates that the gold-to-silver ratio for these coins is

quite constant irrespective of the amount of silver in the coin. What the data on the lower graph also suggest is that certain gold: silver ratios exist. There are data clusters at about 0.3, 0.4 to 0.5, 0.55, and 0.65. This must mean that as many as four separate sources of silver were being used by minters during the reign of Shapur I.

Apparently the ancient minters did not know that the silver they were using contained up to one-percent gold impurity and, therefore, did not attempt to remove it. Since gold and silver are chemically similar, the gold impurity level would not be changed appreciably in the silver refining process. As a result, the percent gold impurity level of silver in a coin is an indication of the level existing in the original silver ore. Of course, there was some reuse of old coins and if coins made from different silver sources are remelted together an averaging of gold levels would result. The composite data for a series of coins from a given period or even from a single mint during a given period will not necessarily show distinct levels but instead general clusterings. More randomness would be expected for those mint-cities that relied on a number of silver sources. Similarly, cities that were on principal trade-routes and might receive coins from other mints might then remelt these coins for their own use; these cities would have also issued coins that showed greater randomness in their gold levels. The most uniform levels of gold impurity would be expected for coins issued by small mint-cities adjacent to silver sources.

The data of Fig. 6 for coins from the reigns of six Sasanian kings indicate either that the same silver sources were not being exploited for prolonged periods of time or, if they were, that the gold levels changed as the mines were being worked. In any case, the coins from

each time-period tend to have separate overall gold-impurity patterns. In plotting this and other bar-graphs of gold levels we have chosen to use an arbitrarily-divided logarithmic scale. The listing in Table I indicates the gold-impurity ranges used in constructing these graphs.

The gold levels from over 1000 Sasanian coins are shown in Fig. 7. The latter years were characterized by the partial utilization of silver having relatively low gold levels.

Of interest in Fig. 7 are the data given by open squares. These all correspond to modern fakes. Some modern fake silver coins can be even more readily identified since they contain less than 0.001% gold impurity which is characteristic of modern highly-refined silver.

The fact that the gold is associated with the silver as an impurity means that the analysed gold content should be added to that of the silver content in determining the intended silver fineness of a coin. In addition, lead, which probably remains from the silver-ore refining process, should also be included in calculating the intended fineness.

Caley, in 1957, published a series of chemical analyses of eight Umayyad dirhems⁶. His data are given in Table II as the top row of values for each coin. Also given are his % Ag + Au + Pb data which we have taken as the intended silver fineness. The second row contains his data normalized for % Ag + Cu + Au = 100%, which is the equation we use here for reporting our data. It is important to note that the adjusted % Ag + Au values are generally within 0.1 to 0.2% of the experimentally observed intended silver fineness. Thus, our method of reporting the data, even though we do not detect lead or tin or iron, results in data which very closely approximate the answer to the question being asked: "What did the ancient minter intend as the fineness of the coin?" Our data for the silver content

using the streak method will generally be a few percent higher than the actual silver content as is seen by the comparison of the two sets of % Ag values for each coin in Table II. We also observe this small difference when comparing the streak % Ag with the actual % Ag as found by the Howitzer method.

Umayyad Dirhems

Shown in Fig. 8 are the gold-impurity data for Umayyad dirhems issued at 17 mints during the nine year period: AH 90-98/798-717 AD. The mint locations are shown in Fig. 9. It is clear from Fig. 8 that a number of silver sources were being used during this period. One silver source, used mainly for coins issued at Hamadhan, Mahi, and al Taimara, had about 0.05 to 0.20% gold. Another source, used mainly by Wasit, but also by Sabur, Ardashir-Khurra, and Darabjird, had about 0.6 to 0.8% gold impurity. Sijistan used silver with about 0.8 to 1.0% gold whereas Harat, Abrashar, Sarakhs, and to some extent Merv relied heavily on silver with about 1.0 to 1.3% gold. The occasional points in the range of 0.3 to 0.4% gold in Fig. 8 could be the result of silver mixtures or could represent the occasional use of silver from yet another source. This latter hypothesis is a distinct possibility since a large number of later-dated Islamic coins have this level of gold impurity. Because of the distance from Abrashar, and the small use of silver having about 1% gold at Rayy, it would appear that the silver used at Arminiya having about 0.9 to 1.2% gold is from a separate source. Perhaps part of the silver used at Dimishk derives from the same source being utilized by Arminiya.

Data such as those given in Fig. 8 can be used in a variety of ways.

1. In some cases, the location of particular mint-cities may be

unknown. For instance, Walker⁷ states that the mint-city of Mahi may be either a city near Merv or a city near Hamadhan. The data of Fig. 8 clearly indicate that the latter is the correct choice.

2. Knowledge of the number and types of silver being used in manufacturing coins in a given city might indicate the degree of importance of that city as a trade center.

3. By determining which mints use which types of silver it is possible to approximate the locations of silver sources and to suggest the silver trade-route patterns. For example, a silver source must have existed in the vicinity of Hamadhan-Mahi-al Taimara.

4. As we have discussed elsewhere³, the gold-impurity data can assist in deciphering some of the Sasanian mint-names which are inscribed in the ancient script: Pehlevi.

5. The gold-impurity levels found in silver art objects can be compared with the levels found in coins to suggest periods or regions of manufacture of the art objects.

6. When an art object is clearly of a design indicative of a given period and region of manufacture, yet has a grossly different gold level (generally lower) compared with authentic coins of the same period and region, this observation can frequently be taken as evidence that the art object is a modern forgery.

7. Similarly, modern fakes of ancient coins can frequently be detected by their having gold levels different from those of authentic coins.

Sasanian Art Objects

The largest collection of silver Sasanian-style art objects is in the Hermitage museum, Leningrad. We have been able to obtain streaks from their entire collection as well as from Sasanian-styled silver art housed in other major museums and in certain private

collections throughout the world.

In examining data from these objects it is first necessary to consider which of the objects might be incorrectly attributed to the Sasanian period and which might be fake. The Sasanian coin analysis data can aid in this task since the silver used by the Sasanian metalworker most probably was derived from the same mines as the silver used in minting coins. The data of Fig. 7 indicate that, except for the first two reigns, Ardashir I and Shapur I (224-272 AD), over 90% of the Sasanian coins have between 0.50 and 1.00% gold impurity. Therefore, we would also expect most of the Sasanian silver art to have gold levels in this range.

The gold-impurity level data from the Sasanian labeled museum objects are given in Fig. 10 and the data from objects in private collections are given in Fig. 11. In both figures the graphs are plotted using the log ranges defined in Table I.

Of the 122 museum objects labeled Sasanian, 28 have gold-impurity levels less than 0.56% (ranges 1-18). Of these, 23 are either modern fakes or of a design and style that some art historians would identify as non-Sasanian. Included in the former group is a 19th century copy⁸ of the Bahram V plate which is part of the Oxus treasure in the British Museum. Of the 73 objects in ranges 19 and 20 only one may be fake and six may be misattributed. Of the 21 objects in ranges 21 and 22, 11 might be non-Sasanian. Seven of the 10 objects in these two highest ranges that are probably Sasanian have gold levels less than 0.95%. This range of 0.56 to 0.95% gold therefore includes 73 of the 81 objects that many art historians would label Sasanian. This is in good agreement with the distributions found for Sasanian coins.

The comparison between the gold levels in art objects and in coins can be illustrated by examining the data for museum objects

which portray a Sasanian king. For example, two plates from the Hermitage⁹ with Shapur II as well as the large head of Shapur II at the Metropolitan Museum of Art in New York have gold levels of 0.95, 0.69, and 0.67%, respectively. This fits very well with the data of Fig. 6 for this monarch. A Hermitage plate with Peroz¹⁰ has 0.77% gold impurity; another Peroz plate at the Metropolitan Museum of Art has 0.84% gold. Both are in agreement with the data for Peroz coins.

There are a few exceptions, however. The most notable is another Hermitage plate¹¹ with Shapur II having only 0.18% gold impurity--clearly outside the range for this king. This plate, for which there is no reason to question its authenticity, must have been constructed in a non-Sasanian geographical region or, perhaps more likely, must have been made in a later, perhaps post-Sasanian period.

When examining the data for samples taken from 115 privately owned Sasanian-style art objects there emerges a different pattern of gold levels as is seen in Fig. 11. Of the 74 objects having less than 0.56% gold, 72 are probably modern fakes and two may be misattributed. Of the 41 objects in ranges 19-22 a total of 34 are possibly authentic including the 21 plain oval bowls, three are probably fake, and four are probably misattributed.

It is also possible to examine the objects in terms of the % Ag + Au data as shown in Figs. 12 and 13. As is seen in Fig. 12, most of the museum objects have % Ag + Au values greater than 93.5% whereas the privately owned objects, most of which are probably modern fakes, generally are made of more debased silver.

The museum objects that may be misattributed can now be examined

in relation to data for gold, silver, and other elements from Parthian and Islamic coins and from these comparisons it is possible to suggest periods and regions of manufacture.

The complete data for over 400 silver art objects including Sasanian, Greco-Bactrian, Hellenistic, Achaemenid, Parthian, Islamic, and Central Asian objects will be published separately.

Acknowledgements

None of these studies would have been possible without the willing cooperation of curators at the Hermitage Museum, Tehran Archaeological Museum, Istituto Italiano de Medio e Estremo Oriente (Rome), Bibliothèque Nationale (Paris), Louvre, British Museum, Ashmolean Museum, Metropolitan, Boston, and Cleveland Museums of Fine Art, and the Freer Gallery, as well as numerous private collectors. Financial support for the development of these analysis techniques was received from the University of Michigan-Memorial Phoenix Project and from the U.S. Atomic Energy Commission, Division of Research. This is publication C00-912-24.

Table I. Logarithmic gold-impurity
ranges used in constructing
bar-graphs.

% Gold	Range	% Gold	Range
0.011	1	0.114	12
0.014	2	0.142	13
0.018	3	0.180	14
0.023	4	0.225	15
0.029	5	0.288	16
0.036	6	0.360	17
0.045	7	0.450	18
0.057	8	0.567	19
0.072	9	0.715	20
0.090	10	0.900	21
0.114	11	1.140	22

Table 11. Original and adjusted chemical analysis data of E. Caley.*

Umayyad Mint	Date AH	% Ag	% Cu	% Au	% Pb	% Sn	% Fe	Total	% Ag + Au + Pb	% Ag + Au
Wasit	AH-85	91.49	6.16	0.62	1.58	0.05	0.05	99.95	93.69	
		93.10	6.27	0.63	--	--	--	100.00		93.73
Darabjird	AH-92	92.73	4.25	0.66	1.85	0.12	0.18	99.79	95.24	
		94.97	4.35	0.68	--	--	--	100.00		95.65
Kirman	AH-95	94.15	3.56	0.67	1.48	0.10	0.10	100.06	96.30	
		95.70	3.62	0.68	--	--	--	100.00		96.38
al-Basra	AH-100	91.17	6.36	0.42	1.63	0.10	0.09	99.77	93.22	
		93.08	6.49	0.43	--	--	--	100.00		93.51
Dimishk	AH-100	95.58	2.24	1.35	0.68	0.07	0.07	99.99	97.61	
		96.38	2.26	1.36	--	--	--	100.00		97.74
Ifriqiyyah	AH-112	98.06	0.84	0.70	0.42	0.10	0.05	100.17	99.18	
		98.45	0.85	0.70	--	--	--	100.00		99.15
al Andalus	AH-118	94.21	3.96	0.60	1.10	0.05	0.06	99.98	95.91	
		95.48	4.01	0.61	--	--	--	100.00		95.99
Wasit	AH-124	98.46	0.23	0.06	1.10	0.01	0.04	99.90	99.62	
		99.70	0.23	0.06	--	--	--	100.00		99.77

*Am. Num. Soc. Museum Notes, VII, 211 (1957).

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10. Ref. 9, fig. 143.
11. Ref. 9, fig. 138.

Figure Captions

1. A student is inserting into the neutron Howitzer a cartridge containing the coin which will be irradiated.
2. Silver contents of Sasanian coins as determined by the Howitzer irradiation method of analysis.
3. Method of streaking a coin.
4. Gamma-spectra analysis using the multichannel pulse-height analyser.
5. Silver content and gold-impurity levels for 40 coins of Shapur I arranged in order of decreasing silver fineness.
6. Gold-impurity level data for coins issued by six Sasanian kings. Logarithmic ranges used in preparing graphs are given in Table I.
7. Gold-impurity level data for over 1000 Sasanian coins. Open squares are data for modern fake Sasanian coins.
8. Gold-impurity level data for Umayyad coins from 17 mints each for the period AH 90-98/708-717 AD.
9. Location of Umayyad mint-cities listed in Fig. 8.
10. Distribution of gold-impurity levels for Sasanian-style silver art objects in museum collections. Refer to Table I for log ranges. Cross-shaded data points are for plain oval bowls.
11. Distribution graph similar to Fig. 10 but for Sasanian-style objects in private collections.
12. Distribution of % Ag + Au data for Sasanian-style silver art objects in museum collections. Refer to Table I for log ranges. Cross-shaded data points are for plain oval bowls. Note X 10 scale used between 60 and 90% and X 60 scale below 60%.
13. Distribution graph similar to Fig. 12 but for Sasanian-style objects in private collections.

Reigns of Sasanian Kings

DRACHMS OF SHAPUR I
240-272 A.D.

% GOLD IMPURITY IN SILVER

MUSEUM OBJECTS

Log Gold Impurity Range

PRIVATE COLLECTIONS

MUSEUM OBJECTS

PRIVATE COLLECTIONS