Archaeometry 39, 2 (1997), 393–405. Printed in Great Britain

X-RAY FLUORESCENCE AND DENSITY MEASUREMENTS ON SURFACE-TREATED ROMAN SILVER COINS*

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Some 630 Roman silver coins excavated at Augusta Raurica *(Switzerland) have been analysed by non-destructive X-ray fluorescence and X-ray diffraction. Furthermore, the density and the weight have been determined. The measured average density of plated and massive depletion-silvered coins is lower than the density calculated from the chemical composition, whereas massive coins display equal values for both of the densities. Based on experimental X-ray investigations of modern silver (tempering, acid treatment, production of corrosion layers), the nature of corrosion products on silver, their impact on surface analysis, and aspects of wearing-off by circulation are briefly discussed.*

KEYWORDS: SWITZERLAND, *AUGUSTA RAURICA*, ROMAN, ENERGY-DISPERSIVE X-RAY FLUORESCENCE, NON-DESTRUCTIVE ANALYSIS, X-RAY DIFFRACTION, COINS, SILVER, CHEMICAL COMPOSITION, CORROSION, DENSITY, DEPLETION-SILVERING, PLATING, WEIGHT

INTRODUCTION

Coins have been surface-treated since the early days of minting until modern times. Surface treatment is intended to improve the fineness of an alloy at the visible surface. Two main methods of treatment exist, a physical and a chemical one. Whether coins are treated, and how, has technological and numismatic importance. The aim of this study is to examine non-destructive analytical methods and their ability to detect surface treatment.

Physical surface treatment

A planchet of, for example, copper, bronze or iron is covered with a thin layer of noble metal—silver or gold. Different procedures are reported, for example, plating *sensu stricto*, dipping into molten silver, soldering, fire gilding or silvering (La Niece 1993), fusion with fluxes (Peter 1990). In general, the striking takes place after the plating *sensu lato*.

According to the length of circulation and the cover thickness, the plating (having an estimated initial thickness of 0.05 to 0.1 mm; see below) wears off partially or entirely so that many physically treated coins are easily detected. If the cover remains intact, these plated coins are not identified easily by the naked eye. However, by destructive examination, like pinching the edge or breaking, a plated coin will be detected.

In theory, an effective non-destructive method of detection is the determination of the specific weight (density) which differs considerably from gold (19.3 g/cm^3) to copper (8.9 g/cm^3). Silver-plated coins are more difficult to detect, since the densities of silver (10.5 g/cm^3) and copper or bronze (8–8.9 g/cm^3) are much closer to each other. One has to bear in mind, also, that

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* Received 6 October 1995, accepted 22 July 1996.

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not only does the copper core reduce the overall density, but so does alloying gold or silver with copper. Hence, it is the surface composition and the density calculated from it versus the experimental, overall density which may give information on plating not evident macroscopically (Fig. 1).

One drawback of experimental density determination by Archimedes' Principle is a restricted accuracy due to bubbles sticking to the surface when dipping the coin into a liquid for buoyancy examination, and another is the porosity of certain coins. An experimental error as low as 0.25%-rel. in the case of, for example, a gold ingot contrasts with considerably larger errors when a plated coin is tested.

Chemical surface treatment

A massive alloy of restricted fineness can be visibly improved by chemical extraction of, for example, copper, from the region close to the surface. Although this process has sometimes been referred to as 'enrichment', surface 'gilding' or 'silvering', one should rather label it depletion-gilding/-silvering since it is not the noble metal that is being enriched, but copper which is being depleted. A thin, spongy layer remains which is condensed by the following striking process, thus improving the surface aspect. Long-term use (see below) as well as intense circulation may wear-off the treated layer. It may also be altered during burial because of corrosion processes. Certain aspects of depletion-silvering and their impact on non-destructive X-ray fluorescence analysis have already been discussed by Hall (1961).

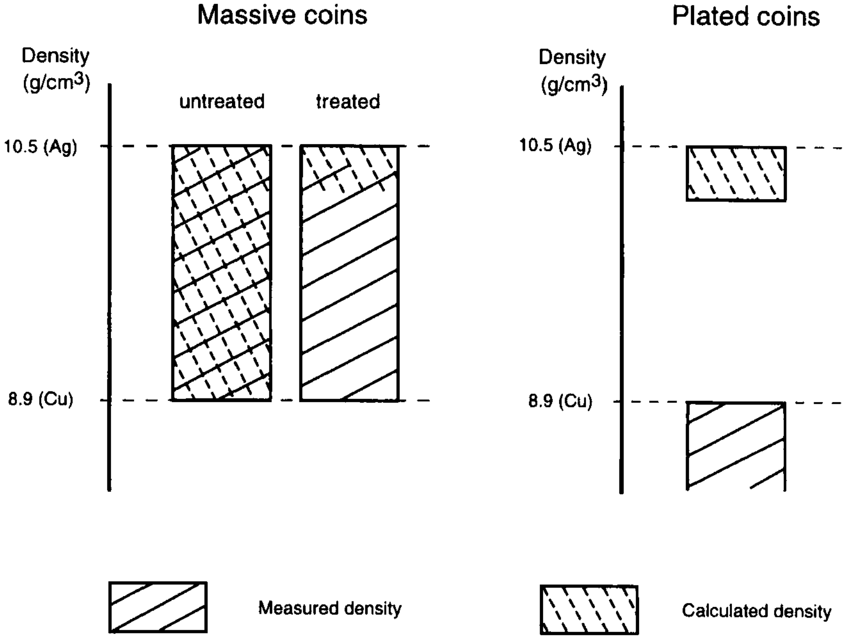


Figure 1 *Experimentally measured and calculated density of massive* (left) *and plated silver coins* (right), *schematic. For massive, homogeneous, untreated binary silver alloys, measured and calculated density is identical covering the range between pure silver and copper. Chemically treated silver alloys display a lower average measured density than the one calculated from the chemical composition of the treated surface. In the case of plated silver coins, a density gap exists between average measured density and calculated density from chemical composition of the plated surface.*

In general, chemical surface treatment hardly changes the average specific weight. Therefore, the experimentally measured density of an uncorroded, chemically treated silver coin corresponds with the average composition of the alloy, whereas the density derived from surface analysis displays a higher fineness (Fig. 1).

ANALYTICAL PROCEDURES

Non-destructive analysis was performed using energy-dispersive X-ray fluorescence spectrometry (ED-XRF), X-ray diffraction (XRD) and density determination as described by Naef (1984), Burkhardt *et al.* (1994), and Zwicky (1995).

RESULTS AND DISCUSSION

Experiments with modern silver alloys

Because all museal objects submitted for analysis had to be investigated in a strictly non-destructive way, certain partially destructive evaluations were executed using modern silver alloys (sterling silver, silver ingots, silver and copper coins).

Physical treatment As heavy elements like silver or gold display spectral X-rays of very different energy and, therefore, different penetrative power, one might conclude that massive and plated silver objects can easily be distinguished by comparing their K/L intensity-ratios (Stern 1995): the silver K-α line with its 22.2 KeV stems from depths of up to 0.15 mm or more, but the silver L-α line with its 3.0 KeV stems from several microns only. Hence, plated and massive coins could display—according to their silver percentage—similar Ag L-count rates, whereas the Ag-K lines should be lower in plated coins than in massive ones, provided the silver layer is thin enough and no corrosion layer covers the surface. A similar situation would be encountered with gold L-lines (9.7 KeV) and M-lines (2.1 KeV).

Measurements on the embossed surface and on the polished surface of the same silver objects show, however, a large count rate variation of the silver L-intensity (repeated analysis of different spots), but show a small variation of the corresponding K-lines so that the K/L-ratio changes strongly with surface morphology, even when no corrosion layer is present (Fig. 2).

The surface of silver objects contains not only chemical, but also mineralogical information: corrosion products can be identified, but also the ‘crystallinity’, that is, the shape of X-ray reflections as a function of crystalline ordering and strain. Cold worked metals display broad reflections with relatively large widths at half peak maximum, whereas, for example, tempered silver displays sharp reflections with small widths. Tempering experiments performed on modern silver alloys show a sudden change in half-width around 300 to 320 °C, which means that cold worked alloys display broad reflections (large width), but hot worked ones sharp reflections (small width). This phenomenon is essential in numismatics as far as cold versus hot striking is studied. All Roman silver coins studied so far display broad Ag-reflections indicating cold-working, that is, striking below a temperature of 300 °C.

Chemical treatment Chemical treatment has been carried out on commercially available sterling silver (Johnson-Matthey) and modern silver coins taken from circulation (Switzerland 1899–1969), using ammonia and acetic acid for the Swiss silver coins, and ammonia and tartaric acid with and without addition of salt in the case of sterling silver. The experiments were carried out step by step, followed by non-destructive analysis (X-ray fluorescence and X-ray diffraction).

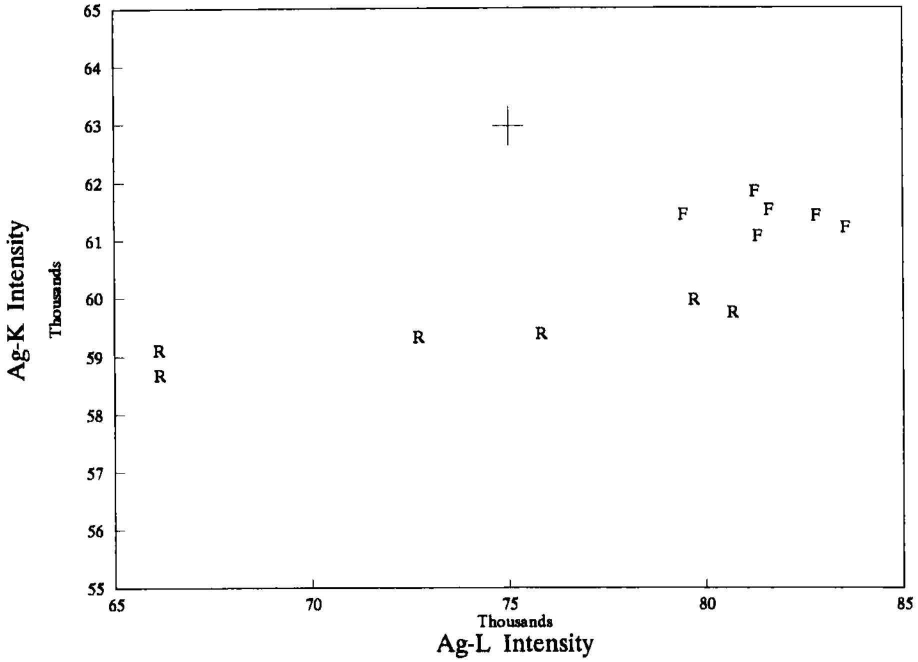


Figure 2 *The influence of surface morphology on spectral intensities of high and low energy Ag-lines.* (R)*: relief;* (F)*: flat;* cross*: statistical error-field, three sigma.*

Attacking a silver alloy with boiling ammonia or tartraric acid for one to 20 minutes did not significantly change the copper content found at the surface. Tempering at 700 °C in air, however, did raise the copper content by 54% in the average. Copper oxide, formed at an elevated temperature and identified by XRD as tenorite (CuO), was easily solved by ammonia (32% Cu decrease), tartaric acid (44% Cu decrease), or tartaric acid plus salt (60% Cu decrease). Hence, the treatment with tartaric acid plus salt seems to be most effective.

The corrosion layer on used Swiss silver coins generally contains kerargyrite (AgCl) and sometimes metallic Cu as its mineral main constituents, whereas tempered sterling silver displays mainly tenorite as well as metallic Ag. Rolled sterling silver initially contains (before tempering) metallic copper as well as silver, which was also fairly often encountered on the ancient silver coins examined.

In binary, massive, untreated Ag-Cu alloys (marked ‘U’ on Fig. 3) the spectral intensities for silver and copper K-α follow a close linear correlation, and correspond with the respective elemental concentrations, provided the compositional range is not too large (Fig. 3, solid line). If copper is oxidized at 700 °C forming a black layer of tenorite on the silver surface, the copper K intensity rises (marked ‘T’ on Fig. 3), but decreases after chemical attack (ammonia, tartaric acid, tartaric acid + salt; marked ‘C’ on Fig. 3), whereas the Ag-K intensity increases slightly only due to lower absorption by the remaining silver matrix.

Modern, massive silver coins (Swiss coins from 1899 to 1954, having a certified fineness of 83.5% Ag) display a specific correlation between age/time of circulation and copper analysed at the surface by ED-XRF (Fig. 4). The longer a coin circulates, the more the treated layer is worn off until the composition of the original core is encountered, which occurs in this case after

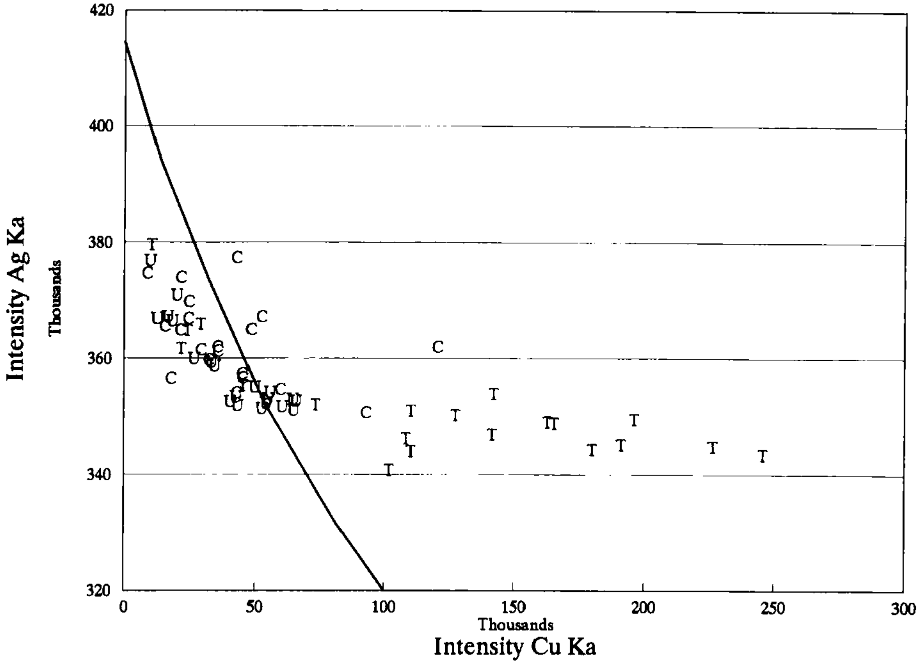


Figure 3 *Chemical composition of untreated, tempered and chemically treated Swiss silver coins, as expressed by their main components silver and copper (K-α intensities, ED-XRF).* (U): *untreated coins;* (T): *tempered coins;* (C): *chemically treated coins.*

roughly 50 to 80 years of circulation. The silver K-line intensities reach the values of the untreated core already after roughly 20 years of use due to the high penetrative power of the Ag-K spectral line.

Tempering and corrosion tend to enlarge the copper signal determined by non-destructive surface analysis while chemical treatment reduces this signal, the silver-K intensity remaining virtually constant. Hence, a non-destructive surface analysis should be based upon the silver determination alone, rather than upon the analysis of both silver and copper, if the fineness of the bulk composition is a target of analysis.

From metrics—diameter, and weight of new and old coins—it is possible to estimate the thickness of the depletion zone assuming that this zone is worn off in the case of the oldest specimens where Cu- and Ag-K intensities equal the values of the core. The results shown in Table 1 are consistent with earlier data on electrum coins (Das and Zonderhuis 1964).

Roman silver coins

Almost the entire museum collection of silver coins from *Augusta Raurica* (Switzerland) has been studied (Zwicky 1995); the coins originate from the excavations of *Augusta Raurica* and were kindly submitted for analysis by the Römermuseum Augst. In total, 630 coins (177 visibly plated, 453 presumably massive) from the Roman republic until the second half of the third century were analysed by strictly non-destructive methods. General aspects of the study will be published elsewhere; the following considerations are focused on surface treatment and its

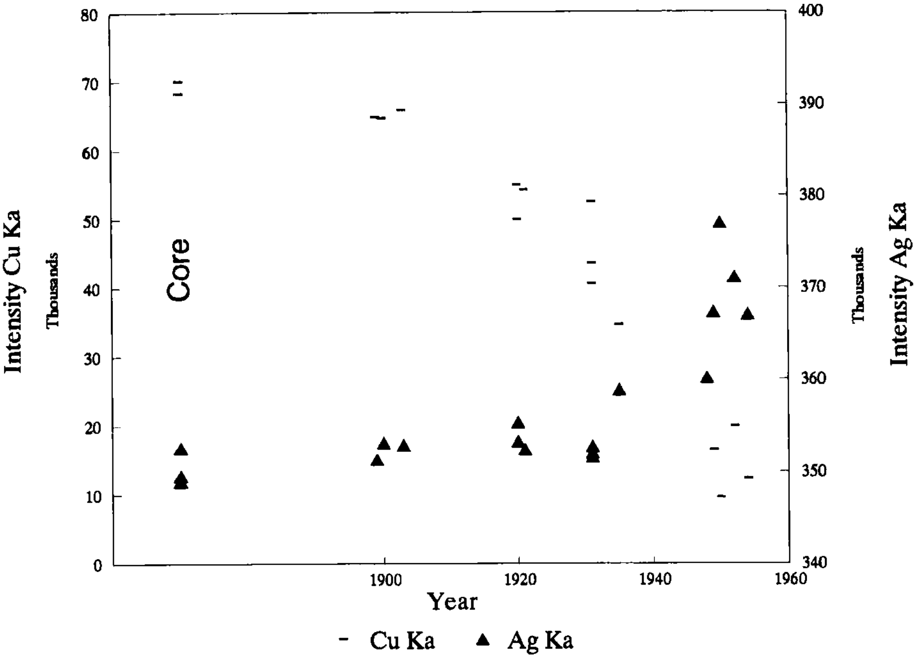


Figure 4 *Chemical analyses of circulated Swiss silver coins before cleaning, tempering or leaching. After approximately 50 to 80 years of circulation the copper K-intensity of originally depletion-silvered coins reaches—due to wearing-off—the values of the core* (above), *whereas silver K-α reaches minimum values after only 20 to 30 years because of the high energy of Ag-Kα.*

impact on non-destructive analysis. The silver content of the coins covers a range from *c.* 3 to 98%, whereas the copper content ranges from 0 to *c.* 90%.

Since it was concluded from experiments with modern silver that oxidation/corrosion has a strong influence on the copper concentration found in silver alloys, the Roman coins were first classified according to their grade of visible corrosion (classes 1 to 5), ranging from entirely fresh to strongly corroded, and split into two main groups, labelled 'uncorroded' (classes 1 and 2) and 'corroded' (classes 3 to 5). Each main group was again divided into massive and visibly plated coins. Hence, all evaluations were executed on four subgroups of obviously different size, which will be discussed separately (Table 2).

The actual weight of a coin is the result of the original value, the wearing-off by circulation, and corrosion processes; broken or otherwise damaged specimens also display today a reduced

Table 1 *Estimation of the thickness of the depletion zone*

Denomination (Swiss franc)	*Year*	*Thickness (microns)*
1/2 SFr	1950 versus 1900	28 (0.028 mm)
1 SFr	1952 versus 1899	29 (0.029 mm)
2 SFr	1948 versus 1903	17 (0.017 mm)

Table 2 *The analysed Roman silver coins*

Age group	*Period*	*Number of coins*			
		Uncorroded		*Corroded*	
		Massive	*Plated*	*Massive*	*Plated*
1	Roman republic (−27 BC)	26	3	35	9
2	Augustus-Vitellius (−AD 69)	10	5	15	10
3	Vespasianus-Nerva (−98)	19	7	14	28
4	Traianus-Hadrianus (−138)	22	5	22	24
5	Ant. Pius-Commodus (−192)	19	8	15	26
6	Sept. Sev.-Macrinus (−218)	38	5	28	19
7	Elagabalus-Max. Thrax (−238)	31	1	56	15
8	Pupienus-Volusianus (−253)	19	5	29	7
9	Valerianus-Max. Herc. (−289)	5	0	50	0
Total	630	189	39	264	138
	100%	30%	6%	42%	22%

weight. The original weight of a denomination like the denarius has undergone from its inauguration, at the end of the third century BC, to its end, some 500 years later around the middle of the third century AD, several changes, such as gradual degradation as well as sudden changes by law (e.g., the reform of Nero, AD 64). The highest observed weights in this study equal the average weight of coins from the Ashmolean and British Museum, published by Walker (1976, 1977, 1978 and 1980), but most are considerably lower due to fragmentation, wearing-off and possibly porous flans (Fig. 5). As a consequence, weight reductions by reforms are not easily detectable, nor is there necessarily a close correlation between pieces from a museum collection (representing a selection) and those originating from excavations (reflecting here the 'daily life' of the Roman province). Neither the averaged weight nor the fineness lend themselves to a direct correlation with changes of the monetary system, because of the large variations within the given coin groups, a fact which is often ignored in numismatic literature (e.g., Carson 1990).

The weight of a silver coin need not be correlated with its fineness/specific weight at all. Since the weight is easy to check, one might assume that degradation as a government-controlled act takes place by maintaining the weight and reducing the fineness. In fact, both decrease simultaneously (Fig. 6). Though the weight may scatter considerably due to circulation, damage, corrosion, and so on, there exists a definite correlation between the weight and the experimentally determined density and, therefore, with the fineness. Rather than keeping the weight constant, the coin size (diameter and volume) remains the same: by reducing the fineness, the weight drops automatically.

The measured density displays a large variation, larger than can be explained by the range between pure silver (10.5 g/cm^3) and copper (8.9 g/cm^3). Assuming an experimental error of ±0.05 g/cm^3 or less, a large number of massive, uncorroded silver coins are well outside the density range of silver alloys. Late specimens (time code 5 to 9) especially belong to the latter group, whereas early coins (time code 1 to 3) are, to a large extent, within the density range

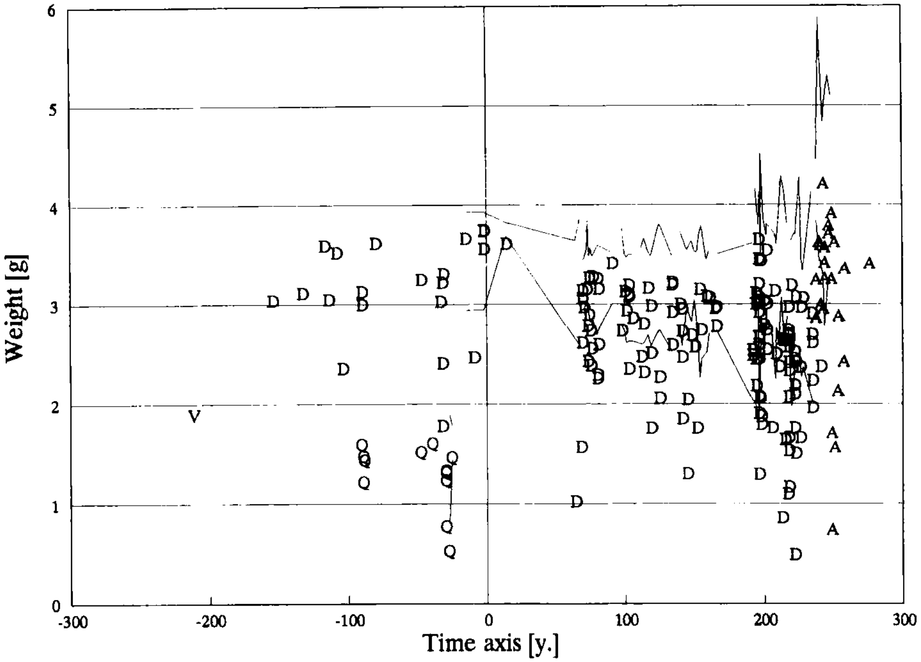


Figure 5 *The weight of massive, uncorroded silver denominations from* Augusta Raurica *((V): victoriate; (Q): quinarii; (D): denarii; (A): antoniniani) and from literature (Walker 1976, 1977, 1978 and 1980: solid lines, minimum and maximum values).*

(Figs. 7 (lower) and 8). One explanation is the prevalance of porosity in late coins with restricted fineness. This porosity is possibly induced by deteriorated manufacturing processes—if not intended in order to enlarge the minting output. Since all investigation of museum objects had to be carried out non-destructively, it was not possible to control the porosity by direct, invasive observation.

Homogeneous, uncorroded binary alloys of silver and copper display a correlation between the X-ray line intensities of silver and copper K-α, which may be calculated by using mass absorption coefficients of silver and copper (Fig. 3, solid line). A defined copper count rate belongs to each silver count rate/fineness. The correlation is linear, as long as small compositional ranges are considered, but bent over large ranges due to changing absorption of X-ray intensities in changing matrix. If copper is depleted or corroded (or if further chemical main components are present), deviations from this correlation line will occur. Statistically significant deviations to the left of the correlation line represent Cu-depleted alloys, those to the right, corroded (or tempered) alloys displaying copper oxide at the surface.

Although the effects of blanching and corrosion on the result of XRF analysis can be compensated for by using the Ag-K spectral line and estimating copper by difference, the influence of coin porosity on density determination and analysis in general still remains. The experimentally determined bulk density of a coin, and the density calculated from XRF surface analysis will be equal, if neither blanching nor plating or corrosion occurred (Fig. 7 (upper)). The density of plated coins (*P*) is necessarily higher than that of tin (7.3 g/cm^3): they plot above the

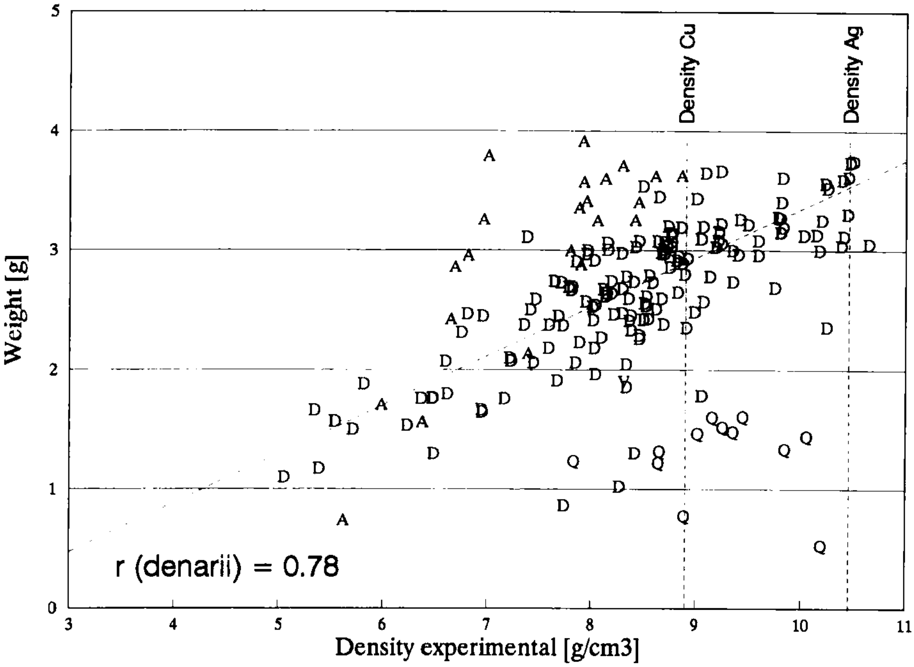


Figure 6 *Experimental (measured) bulk density and weight of massive, uncorroded silver coins from* Augusta Raurica *(*(V)*: victoriate;* (Q)*: quinarii;* (D)*: denarii;* (A)*: antoniniani). For each denomination a correlation exists between density and weight: both parameters drop, meaning that the volume and diameter were kept more or less constant with time, but the fineness deteriorated, and with it density and automatically the weight, too. Note that only a relatively small proportion of all coins has a density between 10.5 g/cm^3 and 8.9 g/cm^3 characteristic for binary Ag-Cu alloys.*

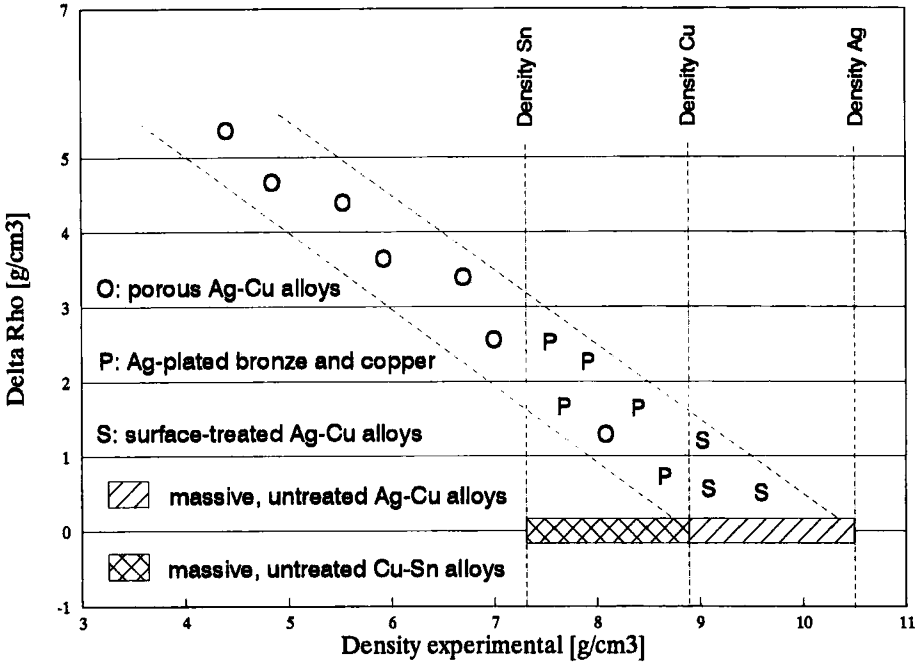
delta rho = 0 line. Surface-treated, massive silver-copper alloys (*S*) have to have a bulk density between 8.9 and 10.5 g/cm^3, whereas porous specimens may display widely scattering projection points (*0*). In fact, Roman silver coins from *Augusta Raurica* follow the predicted pattern closely (the numbers refer to age groups as defined in Table 2). Plated coins (Fig. 7 (lower)) plot in the expected field and to the left of it indicating a certain degree of porosity, possibly connected with the plating process. A portion of the uncorroded silver coins plot between the densities of silver and copper (Fig. 8 (upper)), but display in general a large delta rho as a result of surface treatment (blanching), whereas corroded coins have a generally lower delta rho due to wearing-off of the surface-enriched layer (Fig. 8 (lower)).

CONCLUSIONS

Experimentally measured density, and density calculated from average surface chemistry (ED-XRF), are

(1) equal in the case of massive Republican and early Imperial coins (time code 1 to 2), which were not chemically treated, that is, not depletion-silvered;

(2) different in the case of massive denominations from the late first to the third century (time code 3 to 9) due to chemical treatment before striking, the fineness of the not worn-off surface being higher than the silver content of the average coin as derived from measured density;



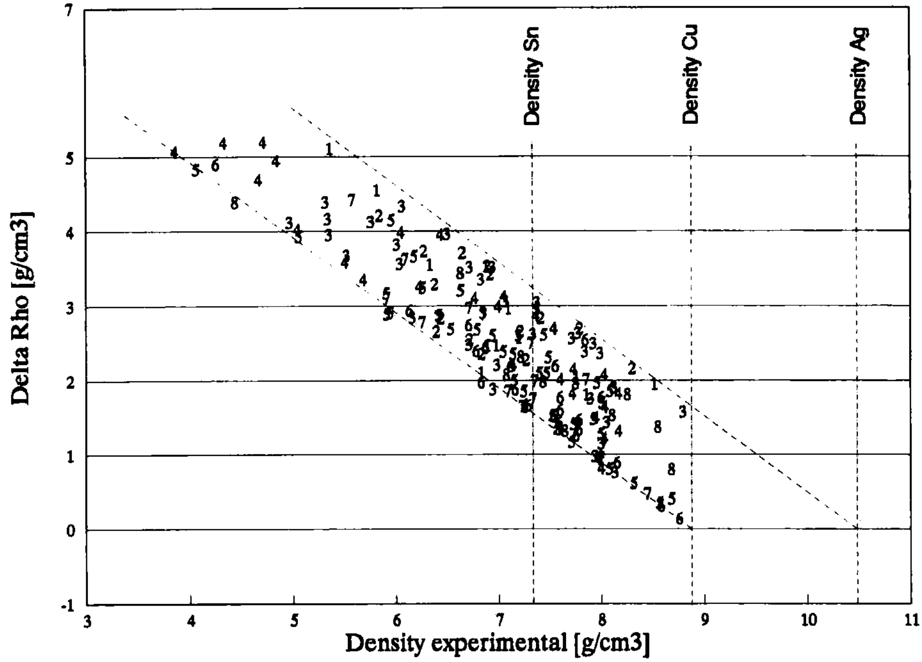


Figure 7 (upper) *Relation between the two non-destructive methods of coin analysis, experimentally determined bulk density and calculated density from XRF surface analysis (expressed as delta rho, i.e., density difference calculated minus experimentally determined bulk density).* (lower) *Plated coins: relation between the experimentally determined bulk density and the calculated density from XRF surface analysis (expressed as delta rho). The numbers indicate the age groups (Table 2).*

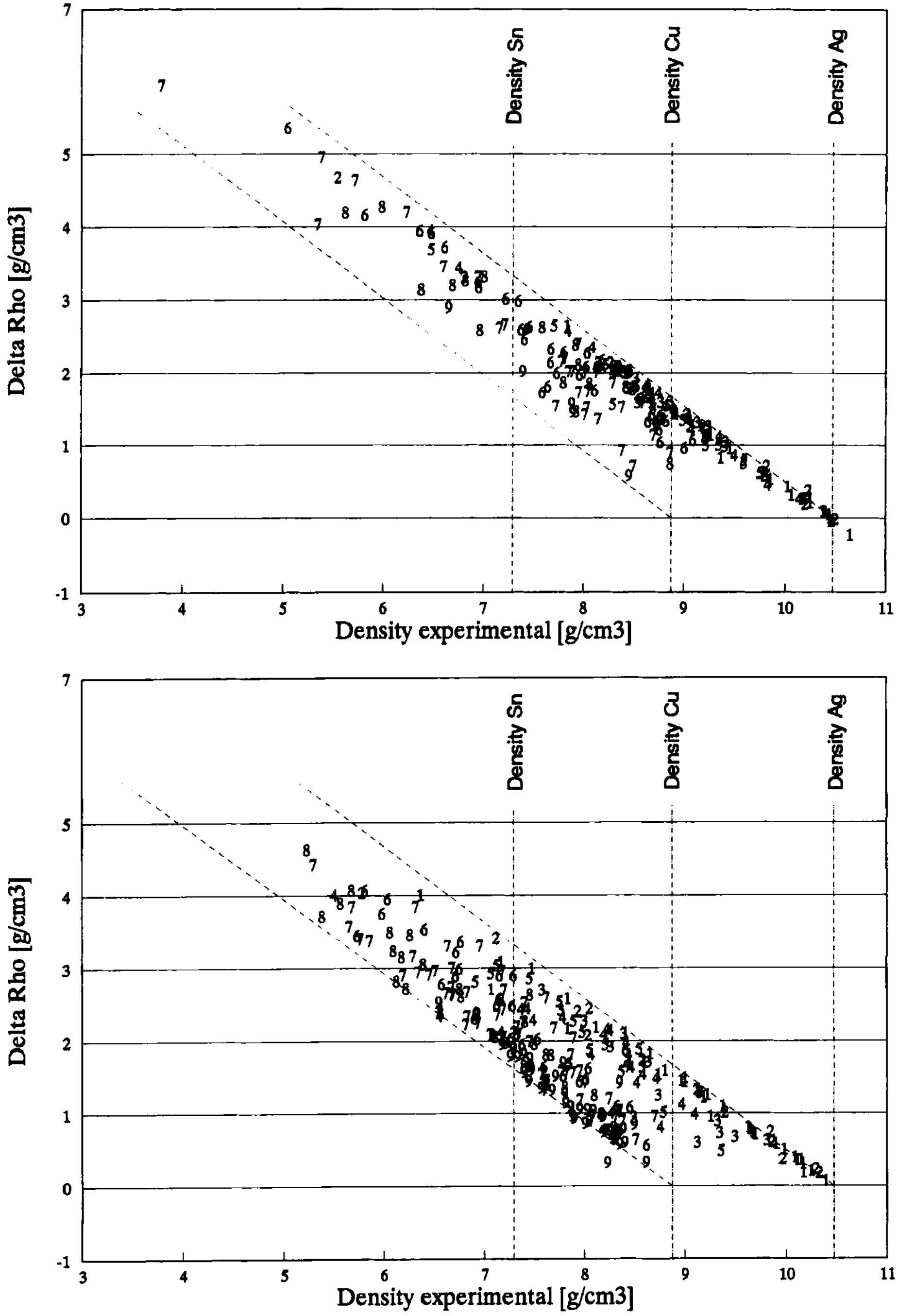


Figure 8 *Relation between the experimentally determined bulk density and the calculated density from XRF surface analysis (expressed as delta rho) for* (upper) *massive, uncorroded coins and* (lower) *massive, corroded coins. The numbers indicate the age groups (Table 2).*

(3) different in the case of plated coins, where the plating equals in general the fineness of contemporaneous massive coins, but the measured density is always below 9 g/cm^3.

Although the experimental, average density should be closely connected with the chemical composition, strong differences are observed in massive and plated coins of the late first to third centuries (time code 3 to 9), where the density is well below copper or bronze, probably due to high porosity of the flans. Whether this porosity is due to technical deterioration or was intended has to be elucidated by later, invasive studies. The analysed cores of plated coins consist of copper or bronze.

In analogy to results from experiments with modern silver it seems

(1) that depletion-silvering was a common practice and executed by first tempering and oxidizing the flan, then attacking it with organic acids like acetic or tartaric acid, with or without adding salt, before striking;

(2) that the thickness of this depleted layer is probably in the range of 20 to 30 microns, which are worn off by circulation in about 50 to 80 years on average;

(3) that corrosion/alteration starts with circulation by formation of kerargyrite ($AgCl$) at the coin surface, followed by oxidation and formation of cuprite (Cu_2O) and continuing during burial. These corrosion layers are sometimes so thick that not only the results of chemical analysis, but also of density measurement are obscured. Analytical investigations should, therefore, be executed preferably on uncorroded coins, when no cleaning is permitted. If the average fineness of a coin has to be estimated by non-destructive surface analysis, the silver K-α line intensity should be used for the assessment of silver and copper, as the silver intensity is much less affected by the chemical alteration of the coin than the copper intensity—the latter is in binary alloys easily calculated from the measured silver signal.

The intensity ratio of the high-energy Ag-K line over the Ag-L line in modern silver alloys is, theoretically, a clue to the presence of plating and layering, but with most ancient silver coins this ratio is strongly influenced by the impact of surface morphology and corrosion on the low-energy Ag-L lines. However, the Ag-K intensities of massive and plated uncorroded coins are clearly different: massive coins display Ag-K intensities which are significantly higher than those observed on plated coins. This effect is caused mainly by the missing silver mass when plated coins are investigated by surface analysis (ED-XRF). It is, therefore, definitely possible to distinguish between massive and plated coins, even when there is no visible evidence for plating.

ACKNOWLEDGEMENTS

The authors are indebted to the Swiss National Foundation (grants 21-32194.91 and 12-37534.93) for financial support, to the director of the Römermuseum Augst, Dr A. Furger, for his kind permission to use its rich numismatic collection, and to Professor H. G. Bachmann and the keeper of the numismatic department of the Römermusuem Augst, Dr M. Peter, for fruitful discussion and helpful comments.

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