

NEUTRON ACTIVATION ANALYSIS ON ANCIENT GREEK SILVER COINS AND RELATED MATERIALS

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66 archaic Greek silver coins have been analyzed for the minor elements Cu, Au, Bi and Pb, and for the trace elements Na, Mn, Co, Ni, As, Sn, Sb and Ir. Instrumental neutron activation has been used for the determination of Cu and Au and atomic absorption spectroscopy for Pb and Bi. The trace elements could be detected only after a separation of the interfering matrix activities by an extraction with a diethyl-dithio-carbamate complex. The homogeneity of Au and Cu in the coins and the significance of the trace elements are discussed. The statistical evaluation of the analytical data reveals distinct groups for coins of some provenances.

Introduction

The Institute started activities in the field of archaeometry in 1974. One major project concerns the chemical and isotopic composition of archaic Greek silver coins, lead ores and slags from mainland Greece, the Aegean Islands and Asia Minor. Objectives of this investigation are to trace back the provenance of the silver, as well as its parent ores (mostly galena = PbS), and the technological parameters of silver smelting and refining. The results at this stage of work reveal that the combination of chemical and lead isotope studies of coins and ores appears to be a promising approach to those problems.

Lead ores and slags of old and ancient workings in Asia Minor, North-East Greece (mainly Macedonia) and the Aegean Islands have been collected on two expeditions by two of the authors (Prof. W. GENTNER and Priv.-Doz. Dr. O. MÜLLER) and Priv.-Doz. Dr. G. A. WAGNER and mining geologist A. HAIDMANN. Most of the coins (113) under investigation belong to the hoard of Asyut (Egypt), which was buried about 475 B.C. and has recently been described in the monograph of PRICE and WAGGONER.¹ A brief outline on the significance of this hoard as written by those authors is given here. "In spring or summer of 1969 Egyptian workmen came by

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chance upon a hoard of about 900 silver coins, but it was not until 1970 when the first coins from this find were actually seen that its significance and importance were appreciated. Although it was then thought to have come from the Delta region, it is now fairly certain that it was from Middle Egypt, and the name of Asyut, a town 200 miles south of Cairo – the ancient Lykopolis – has been linked with it . . . The size of the Asyut hoard is linked with a great variety of coinage of mainland Greece, the islands and of Asia Minor, and it is this variety that is so important for the numismatist and historian in attempting to work out the chronology of the coins presented".¹

The restrictions not to damage the precious and often irreplaceable objects limit the type of applicable analytical method. Therefore, non-destructive methods such as X-ray fluorescence or non-destructive activation analysis were mostly applied in previous investigations. In silver coins, only silver and the minor constituents, copper and gold, and in ores manganese, antimony, copper and sometimes silver, can be determined by non-destructive neutron activation analysis. Therefore radiochemical methods have to be applied to obtain the trace element contents which are of great importance in the context of this work. However, this requires sample-taking of several milligrams. This was possible in our work because most of the ancient coins were damaged in the past by notches, and are, therefore, of low numismatic value.

We refer also to the extensive monograph *Methods of chemical and metallurgical investigation of ancient coinage*¹⁷ and to the work on archaic Greek coinage by KRAAY and EMELEUS.² Our paper deals with the analytical techniques applied to coins and gives a brief discussion of the analytical results so far obtained.

Experimental

Coin analysis

After activating a silver coin with thermal neutrons, radioactivities of all trace elements are superimposed by the main activities of ^{110m}Ag , ^{64}Cu and ^{198}Au . Therefore, a separation of the interfering matrix elements is necessary. Probably for this reason, most published work on ancient coins gives only concentrations for Ag, Cu and Au (e.g. Ref.²). To our knowledge, only MEYERS et al.³ published a method which enabled them to achieve the separation of the interfering matrix elements by stepwise ion exchange of radioactive Ag, Au and Cu ions with excess inactive AgI and CuI, respectively. Although this method yields good results, its performance is somewhat complicated. A simple solvent extraction of Ag, Cu and Au with a suitable metal diethyl-dithiocarbamate complex (DDC) appeared to us to be more promising. WYTENBACH and BAJO^{4,5} carried out intensive studies with

Table 1
 Fraction of element (%) in the aqueous phase after
 extraction with $\text{Bi}(\text{DDC})_3$

| Cu | Ag | Au | Na | Mn | Co | Ni | As | Sn | Sb | Ir |
|------|-------|------|-----|-----|-----|-----|-----|-----|-----|-----|
| <0.1 | <0.05 | <0.3 | >90 | >85 | >80 | >80 | >80 | >70 | >80 | >80 |

these complexes and they proposed the extraction of the elements concerned by means of bismuth diethyl-dithiocarbamate. Besides a successful application to biological material,⁴ no extraction in multi-ionic systems had yet been verified. Our work shows that the DDC method is very suitable to achieve selective extractions in one step in a multi-ionic system (see Table 1). The details and results of our application are described in a previous publication.⁶ Since then, the fraction of tin in the aqueous phase must be corrected to 70% compared to 30% published earlier.

As a matter of fact, there are interesting elements which cannot be determined by NAA, because they either activate very poorly (Pb) or they do not emit γ -radiation (Bi). Therefore we determined the concentrations of these elements and Cu by atomic absorption spectroscopy. Cu was useful for a cross-check between both methods. As a standard sample we have used thin shavings of a coin (so-called reference coin in Fig. 1) in which trace elements are relatively abundant. Trace and minor element contents of this coin have been determined in replicates by calibration with chemical standard solutions. The detailed scheme of coin analysis is shown in Fig. 1.

Gamma-spectra measurements

For measurements and evaluation of γ -spectra as indicated in Fig. 1 a PDP 11/40-system is mainly used. It consists of a 28k-central processor with a fast printer, a 9-track magtape unit, a calcomp-plotter, a tectronix display- and keyboard in conjunction with an interface to a fast Laben-ADC (4 nsec/event), usual amplifier and preamplifier and a 64 cm³ Ge(Li) well-detector, SAIP. Furthermore, we can use an 81 cm³ Ge(Li) solid detector of ORTEC which is usually connected to a 28k ND4 420 processor with magtape unit. The energy resolution is about 2.7 keV for the well-type and 2.1 keV for the solid-type detector (for the 1332.4 keV line of ⁶⁰Co). To both systems is connected a pulser for correction of random coincidence losses.

Measurements are carried out by means of commercial software programs. Evaluation of the data can be done in two ways. Firstly, the γ -spectra stored on magtapes may be evaluated off-line on a CDC 3300 with the multi-purpose program JANE.⁸

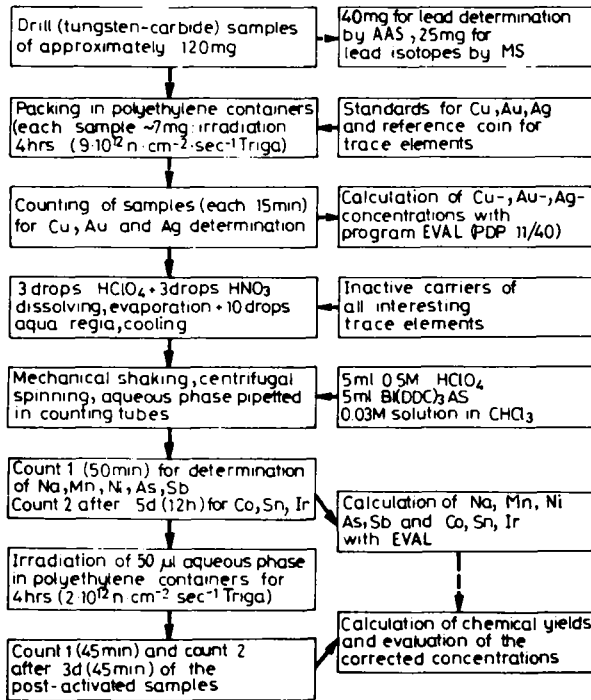


Fig. 1. Scheme of coin analyses

Secondly, and more convenient, evaluation is done online with the PDP 11/40-system. The DEC-company provides a program GASPAN/ISOID which is, in fact, a PDP 11/40-adaption of the program (GASPAN/ISOID published by BARNES.⁹ This PDP 11/40-GASPAN/ISOID has two major inconveniences. Firstly, it uses an input which is very impractical and hard to handle for a non-programming technician. Secondly, it stops with the integration of the peak areas. Thus, the input routines have been changed in two parts. The first part concerns the parameters which describe equipment features (resolution, calibration). These need not be changed with every run. The second part deals with spectra parameters (decay times, weights, etc.) which have to be changed with every run. All necessary programs are integrated in a batch stream (EVAL), which, once started, asks all questions in clear text. Furthermore, the program QUANT (integrated in the batch stream as well) has been added. It provides all calculations for transformation of the integrated peak areas to properly corrected activities (as described in Ref.⁹), and finally, it compares standards and samples to evaluate the concentrations of the nuclides desired. Comparisons with pro-

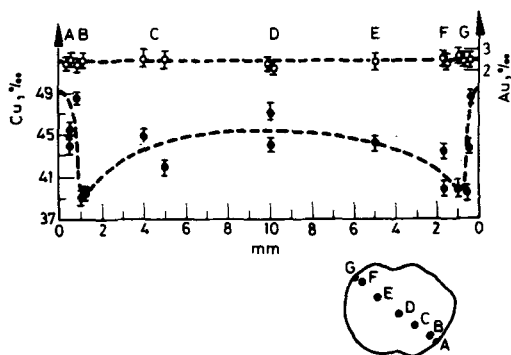


Fig. 2. Cu and Au distribution in areas A to G of coin MPI No. 14 (Athens 2nd B.C.) by instrumental neutron activation. \circ – Au-contents; \bullet – Cu-contents of 1 mg samples

grams of other institutes revealed favourable results for our EVAL system,* which is similar to JANE (version 1), as compared by PETRI.¹⁰ Since the ND-evaluation programs are too imprecise for quantitative analysis of complex spectra, a conversion program is used to read ND-produced tapes on the PDP 11/40, so as to evaluate these data with EVAL as well.

Results and discussion

Homogeneity of coin composition

The knowledge about the distribution of elements considered in a coin is very important in deciding which sampling technique provides the most representative sample of a coin. MEYERS et al.³ compare two techniques: one is drilling with small tungsten carbide drills and the other one is the rubbing-off of a clean coin surface with roughened quartz tubes. The weights of these samples vary between 200–1000 μg and 50–200 μg , respectively. The authors' findings are that rubbed samples give enlarged (about 30%) gold contents and depleted (about 35%) copper ones. Since some of our objects are of low numismatic value, we had the chance to cut some coins in horizontal and vertical sections so as to allow us more detailed profile analyses.

Small drill samples (tungsten carbide drill) of 1 mg from the rim to the centre of the horizontal section have been analysed by instrumental neutron activation analysis. The copper and gold values found are shown in Fig. 2. Gold is very evenly distributed and, within the error limits, homogeneous. However, the copper varies distinctly.

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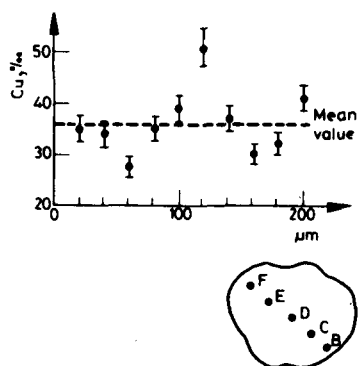


Fig. 3. Cu distribution in central area D of coin MPI No. 14 by microprobe analysis

In this coin (No. 14) there are high copper concentrations on the surface, followed by lower concentrations just below (about 1 mm) and medium concentrations in depths of more than about 2 mm, but even then the contents are rather inhomogeneous. To find out if this fact is confirmed for small ranges, electron microprobe analyses within one sample-taking point (area D) have been carried out. As Fig. 3 shows, inhomogeneities are also large in this range.

The profile analyses have been applied to several other coins. In Table 2 the results for “surface” and “body” analysis are summarised. Surface is defined as a sample taken from depths between cleaned surface and about 1.5 mm (so far, No. 14 “surface” includes areas A, B, F and G in Fig. 2). Of all 5 coins investigated the copper contents are depleted (4 cases) or similar (1 case) on the surface. The gold

Table 2
Comparison of “surface” and “body” analysis of some coins for copper and gold

| Coin MPI-No. | 14 | 19 | 31 | 32 | 33 |
|--------------|--------------------|--------------------|--------------------|---------------------|--------------------|
| Cu surface | 41.4 ± 8.3 (7) | 0.29 ± 0.01 (2) | 0.26 ± 0.15 (2) | 0.27 ± 0.09 (2) | 0.30 ± 0.08 (2) |
| Cu body | 43.1 ± 3.1 (10) | 0.39 ± 0.23 (4) | 0.48 ± 0.15 (3) | 0.43 ± 0.3 (3) | 0.29 ± 0.08 (3) |
| Au surface | 2.4 ± 0.05 (7) | 0.23 ± 0.02 (2) | 0.45 ± 0.04 (2) | 0.02 ± 0.007 (2) | 0.18 ± 0.03 (2) |
| Au body | 2.4 ± 0.05 (10) | 0.22 ± 0.01 (5) | 0.36 ± 0.25 (3) | 0.02 ± 0.01 (3) | 0.19 ± 0.02 (3) |

In parentheses the number of analyses is given.

content is similar (4 cases) or may be enriched (1 case) on the surface. From these and the above described findings, it is quite evident that a representative sample of a coin is best taken from a point towards the centre and if this is not possible at least from a depth greater than 2 mm (to avoid surface effects), and the weight should be at least 5 mg (to overcome small range inhomogeneities).

Analytical results and interpretation

About 150 coins are at our disposal. So far we have analysed 66 coins; their provenances and analytical results are shown in Table 3. All coins have been analysed in duplicate. As a reference coin (see last paragraph of coin analysis chapter) No. 14 has been chosen. In each analytical run duplicate samples of this reference coin have been included so as to have a check for reproducibility. Thus a variance s^2 of 30 duplicate determinations could be calculated; the standard deviations for each element are listed in Table 3. They can be considered as the precision of the analytical results of the trace elements. The minor elements, gold, copper and lead, have been determined against standard chemical solutions. These duplicate analyses give precisions equal to or less than 5%.

The precisions for the trace elements vary between 11% for nickel, and 50% for tin. The different values can be explained generally by their individual counting statistics (e.g. a few hundred counts in 15 hours for cobalt) and spectrum complexity (background, Compton edges, etc.). Inhomogeneities in the coins could cause larger standard deviations as well. Although these precisions may not be considered as particularly good, one has to be aware of the range of the analytical results (some orders of magnitude) with which we are dealing. In this context the precisions achieved are satisfactory.

Regarding the usefulness of the various elements, the following comments can be given:

(1) In quite a number of coins we can only calculate detection limits for cobalt and iridium. Therefore we cannot use these values for interpretation. Considering the iridium concentrations above detection limits only, no correlation to gold could be found. So far, we cannot find any understandable pattern in the iridium variation.

(2) Sodium seems to be distributed randomly. This must be expected since we are dealing with base metal ores. Manganese will be oxidized easily during the smelting process of the ore, so it will be removed effectively into the slag, independent of the initial concentrations. Preliminary analyses of Laurion ores¹¹ show manganese contents of about 100 to 500 ppm, whereas most coins have values of less than 0.1 ppm. For these reasons sodium and manganese do not appear to be very informative.

Table 3
Analytical results of 66 ancient Greek coins

| | MPI-No. | Content, ppm | | | | | | | | | | Content, % | | | |
|----------|---------|--------------|-------|------|-----|-------|-----|-------|--------|------|-------|------------|-------|--|--|
| | | Na | Mn | Co | Ni | As | Sn | Sb | Ir | Bi | Au | Cu | Pb | | |
| Cyprus | 103 | 7.3 | 0.060 | <0.2 | <10 | <0.04 | <3 | <0.03 | <0.01 | - | 0.28 | 0.02 | 0.077 | | |
| Lesbos | 117 | - | - | - | - | - | - | - | - | - | 0.36 | 0.76 | 1.18 | | |
| Lycia | 108 | 0.8 | 0.070 | <0.1 | 55 | 3.0 | <3 | 0.74 | <0.01 | - | 0.21 | 0.82 | 0.69 | | |
| | 107 | - | - | - | - | - | - | - | - | - | 0.023 | 0.93 | 0.26 | | |
| Dankle | 99 | 7.9 | 0.014 | 0.7 | 59 | 0.26 | <10 | 1.2 | <0.01 | 0.09 | 0.082 | 0.85 | 0.26 | | |
| | 100 | 1.2 | 0.004 | 0.7 | 63 | <0.05 | <29 | 4.4 | <0.01 | 0.27 | 0.31 | 0.76 | 0.65 | | |
| | 109 | 27 | 0.060 | 0.65 | 209 | 3.4 | <3 | 1.7 | <0.02 | 0.20 | 0.51 | 3.26 | 0.068 | | |
| | 143 | 4 | 0.015 | 1.3 | 193 | 2.5 | 300 | 5.7 | 0.036 | - | 0.25 | 3.18 | 0.90 | | |
| Sigloj | 93 | - | - | - | - | - | - | - | - | - | 0.15 | 1.71 | 0.63 | | |
| | 94 | 0.4 | 0.035 | 0.16 | 216 | 8.5 | 170 | 6.1 | 0.35 | - | 0.35 | 2.30 | 0.44 | | |
| | 95 | 0.5 | 0.010 | 70 | 153 | 0.70 | 20 | 2.7 | 0.012 | - | 0.16 | 2.63 | 0.92 | | |
| Acanthus | 90 | 0.3 | 0.085 | 1.0 | <4 | 0.65 | 41 | 5.8 | 0.010 | - | 0.14 | 0.014 | 0.78 | | |
| | 91 | 0.8 | 0.020 | 0.40 | <15 | 2.8 | <40 | 42 | <0.035 | - | 0.050 | 0.014 | 0.77 | | |
| | 92 | 0.3 | 0.008 | 0.70 | <11 | 0.45 | <40 | 6.9 | <0.035 | - | 0.17 | 0.016 | 0.13 | | |
| Thasos | 83 | 0.2 | 0.40 | 1.52 | 83 | 2.4 | 440 | 2.2 | <0.004 | 0.04 | 0.017 | 1.23 | 1.07 | | |
| | 84 | 0.2 | 0.006 | <0.1 | 31 | 3.4 | 160 | 6.5 | <0.004 | 0.12 | 0.060 | 0.74 | 1.11 | | |
| | 85 | 13 | 0.06 | <0.2 | <10 | 0.74 | 33 | 2.1 | <0.007 | - | 0.067 | 0.75 | 1.67 | | |
| | 86 | 1.7 | 0.030 | 1.5 | 59 | 0.38 | 340 | 10 | <0.007 | 0.36 | 0.39 | 1.35 | 1.47 | | |
| Samos | 74 | 1.2 | 0.010 | 1.3 | <4 | 0.63 | 6 | 0.20 | <0.004 | - | 0.035 | 0.046 | 0.75 | | |
| | 75 | 3.5 | 0.014 | 0.93 | <4 | 0.60 | 23 | 1.6 | <0.01 | - | 0.15 | 0.067 | 0.61 | | |

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|-----------|----|------|-------|------|-----|-------|------|-------|--------|------|------|--------|--------|------|
| Samos | 76 | - | - | - | - | - | - | - | - | - | - | 0.015 | 3.31 | 0.70 |
| | 77 | - | - | - | - | - | - | - | - | - | - | 0.040 | 0.071 | 0.91 |
| | 78 | - | - | - | - | - | - | - | - | - | - | 0.011 | 0.073 | 0.73 |
| Orrescioi | 68 | 1.6 | 0.009 | 0.30 | <7 | <0.05 | <2 | 31 | <0.004 | - | - | 0.0084 | 0.043 | 1.96 |
| | 69 | 0.1 | 1.3 | 4.0 | <10 | <0.8 | 5 | 29 | 0.002 | - | - | 0.0076 | 0.037 | 2.31 |
| | 70 | 8.6 | 0.025 | <0.8 | <1 | <0.08 | <24 | 13 | <0.01 | - | - | 0.0088 | 0.034 | 2.20 |
| | 71 | 0.1 | 0.014 | 1.0 | <6 | 0.15 | <0.2 | 5.0 | <0.004 | - | - | 0.0044 | 0.030 | 1.58 |
| | 72 | 0.4 | 0.006 | 1.6 | <5 | 0.22 | <4 | 4.8 | <0.004 | - | - | 0.0041 | 0.0033 | 1.84 |
| | 73 | 0.2 | 0.003 | <0.4 | <10 | 0.022 | <6 | 18 | <0.01 | - | - | 0.0046 | 0.047 | 2.66 |
| Malus | 30 | - | - | - | - | - | - | - | - | - | - | 0.45 | 3.41 | 0.77 |
| | 79 | - | - | - | - | - | - | - | - | - | - | 0.025 | 0.040 | 0.77 |
| | 80 | 64 | 0.019 | <0.5 | <7 | 0.39 | 9.0 | 0.07 | <0.004 | - | - | 0.028 | 0.051 | 1.02 |
| | 81 | 2.5 | 0.033 | <0.6 | 35 | 0.38 | 900 | 1.4 | 0.028 | - | - | 0.32 | 0.59 | 1.21 |
| | 82 | 0.01 | 0.005 | 0.36 | <10 | 0.15 | 0.4 | 0.22 | 0.025 | - | - | 0.091 | 0.051 | 0.21 |
| Athens | 14 | 0.1 | 0.006 | 1.2 | 270 | 0.77 | 40 | 1.1 | 0.32 | - | - | 0.24 | 4.31 | 1.93 |
| | 17 | 0.2 | 0.018 | 0.65 | 148 | 2.5 | 20 | 30 | <0.01 | - | - | 0.38 | 2.59 | 1.18 |
| | 19 | 0.1 | 0.17 | 0.5 | <10 | 0.076 | 7 | <0.03 | <0.01 | - | - | 0.022 | 0.039 | 0.55 |
| | 31 | 0.3 | 1.7 | <0.2 | <10 | 0.33 | <2 | 4.6 | <0.004 | - | - | 0.036 | 0.048 | 2.39 |
| | 32 | 0.06 | 0.001 | <0.2 | 2 | 0.030 | 4 | 0.64 | <0.01 | - | - | 0.0020 | 0.043 | 2.01 |
| | 33 | 0.4 | 0.008 | <0.2 | <10 | <0.08 | <2 | 1.6 | <0.01 | - | - | 0.019 | 0.029 | 2.48 |
| | 34 | 38 | 0.015 | <0.2 | <26 | 0.090 | 3 | 0.02 | <0.007 | 0.08 | 0.08 | 0.032 | 0.048 | 0.78 |
| | 35 | 39 | 0.016 | 0.46 | <26 | 0.30 | 5 | 0.24 | 0.005 | 0.12 | 0.12 | 0.019 | 0.28 | 0.82 |
| | 36 | 1.2 | 0.50 | 1.0 | <4 | 0.043 | <1 | 0.89 | 0.004 | 0.06 | 0.06 | 0.0016 | 0.032 | 2.03 |
| | 37 | 0.4 | 0.33 | 0.50 | <12 | 0.14 | 9 | 2.9 | <0.004 | 0.23 | 0.23 | 0.021 | 0.032 | 1.95 |
| | 38 | 0.2 | 0.007 | 1.36 | <5 | 2.8 | 2 | 5.3 | <0.01 | 0.09 | 0.09 | 0.038 | 0.091 | 2.11 |
| | 39 | 12 | 0.010 | 1.73 | <12 | 0.21 | 2 | 0.04 | <0.007 | 0.09 | 0.09 | 0.047 | 0.024 | 0.49 |
| | 40 | 1.4 | 1.5 | <0.2 | <12 | 0.42 | 10 | 0.96 | <0.004 | 0.07 | 0.07 | 0.043 | 0.036 | 2.99 |
| | 41 | 4.4 | 0.004 | <0.3 | 34 | 0.28 | <4 | 0.29 | <0.008 | - | - | 0.051 | 0.045 | 0.51 |

Table 3 (cont.)

| MPI-No. | Content, ppm | | | | | | | | | | Content, % | | | | |
|---------|--------------|------|-------|------|-----|-------|-----|------|--------|------|------------|-------|-------|--|--|
| | Na | Mn | Co | Ni | As | Sn | Sb | Ir | Bi | Au | Cu | Pb | | | |
| Corinth | 5 | 1.6 | 0.010 | 1.1 | 92 | 1.4 | 15 | 9.2 | <0.007 | 0.25 | 0.026 | 1.53 | 0.41 | | |
| | 6 | 0.3 | 0.060 | 2.7 | <6 | 0.53 | 15 | 0.02 | 0.007 | 0.05 | 0.026 | 0.62 | 0.31 | | |
| | 7 | 0.1 | 0.012 | 1.3 | <5 | 0.22 | 2 | 0.03 | <0.005 | 0.06 | 0.028 | 0.053 | 0.43 | | |
| | 25 | 0.05 | 0.020 | 1.6 | 17 | 0.27 | 19 | 0.30 | <0.007 | 0.37 | 0.26 | 0.32 | 0.48 | | |
| | 26 | 0.1 | 0.013 | 0.70 | <4 | 0.63 | <3 | 0.08 | <0.007 | 0.16 | 0.041 | 0.038 | 0.57 | | |
| | 27 | 0.06 | 0.006 | 0.80 | 34 | 0.067 | 20 | 0.07 | 0.070 | 0.10 | 0.13 | 1.73 | 0.36 | | |
| | 105 | 0.3 | 0.010 | 0.80 | 32 | 2.2 | 10 | 5.7 | 0.001 | - | 0.13 | 2.51 | 1.13 | | |
| | 106 | 0.03 | 0.76 | 0.30 | 140 | 2.2 | 0.4 | 1.8 | <0.02 | - | 0.14 | 1.87 | 0.47 | | |
| | 144 | 0.3 | 0.24 | 1.2 | 405 | 25.7 | 500 | 8.4 | 0.05 | - | 0.39 | 7.08 | 0.58 | | |
| Aegina | W1 | 0.09 | 0.004 | <0.1 | 199 | 0.048 | 17 | 1.3 | <0.01 | 0.31 | 0.027 | 1.97 | 0.58 | | |
| | W2 | 0.4 | 0.036 | <0.1 | 6.7 | 0.11 | 60 | 0.19 | <0.01 | 0.24 | 0.40 | 0.23 | 0.041 | | |
| | W24 | 1.4 | 1.4 | 1.2 | <10 | 0.24 | <3 | 0.04 | 0.003 | 0.10 | 0.016 | 0.015 | 1.02 | | |
| | W23 | 0.1 | 0.009 | 0.98 | 89 | 0.30 | <3 | 1.6 | <0.02 | 0.29 | 0.26 | 1.34 | 0.22 | | |
| | W27 | 0.2 | 0.013 | 0.70 | 206 | 6.9 | 5 | 1.9 | <0.01 | 0.50 | 0.084 | 2.58 | 1.36 | | |
| | W160 | 0.5 | 0.007 | 3.42 | 190 | 17.5 | 7 | 1.0 | 0.005 | 0.20 | 0.028 | 3.00 | 0.26 | | |
| | 424 | 0.6 | 0.12 | <0.2 | 21 | 0.77 | 40 | 0.30 | <0.004 | 0.18 | 1.58 | 0.81 | 0.051 | | |
| | 425 | 0.3 | 0.006 | 1.4 | 55 | 0.083 | <1 | 0.13 | <0.007 | 0.22 | 0.012 | 0.83 | 0.26 | | |
| | 431 | 0.08 | 0.017 | 0.98 | 10 | 0.014 | 50 | 0.03 | <0.01 | 0.03 | 0.14 | 0.24 | 0.14 | | |
| | | 30 | 35 | 25 | 11 | 16 | 50 | 19 | 30 | | | | | | |

$$\frac{\Sigma(x_1 - x_2)^2}{2n} \text{ in per cent}$$

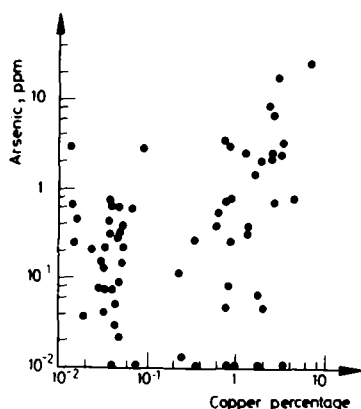


Fig. 4. Cu and As relations in 66 ancient Greek coins

(3) Arsenic which forms rather volatile compounds is removed to a large extent during the whole smelting process. Antimony shows a tendency to be enriched in the cupellation slag, as preliminary analyses on litharge of Laurion revealed. Variations in these elements seem to depend more upon the technological parameters than on initial concentrations. Compared to pure galena from Laurion the arsenic and antimony are depleted in the Athenian coins by a factor of some 10 000. Antimony has been discovered as metallic droplets within slags.^{1,2} Once metallic it should not be difficult to obtain antimony in argentiferous lead from where it would probably be removed during the cupellation process.

As reported by MCKERRELL and STEVENSON^{1,3} tin and copper were very readily removed during their cupellation experiments, but it is still possible that the contents of tin and copper in coins are not solely determined by the process but by initial concentrations as well. A large number of metallic copper grains up to $10\ \mu\text{m}$ were detected in polished sections of Laurion litharge. It was also detected in preliminary microprobe analyses in the oxidized phase.^{1,2} MCKERRELL and STEVENSON^{1,3} claim that copper is easily reduced to the 0.5–0.2 per cent level. However, in many coins we find copper concentrations up to 7%. Fig. 4 shows a plot of the arsenic and copper concentrations of all coins. There are two distinct groups: the first one with copper values up to 0.1% and arsenic up to 1 ppm, and a second one with copper concentrations up to 7% and arsenic up to 20 ppm. Since it is known that arsenic is often a trace in copper, it could mean arsenic containing copper has been added to the coins of the second group where arsenic is distinctly enlarged.

Furthermore, strong positive correlation is observed between copper and nickel which is probably due to mineral assemblage in parent ores. However, it means too that nickel provides no additional information about the coins.

(4) Lead probably is the best indicator for the effectiveness of the technological process, whereas gold, as a noble metal, should survive with its initial amount. Indeed, the silver-gold ratios in pure galena from Laurion are not very different from those of the Athenian coins. MCKERRELL and STEVENSON¹³ point out too that bismuth may partially survive, and may stay in the silver.

Summarizing the above discussion, one could try to put the useful elements in a certain order: Pb, Sn, Sb, Cu, Bi, Au. Lead would be a pure technological indicator and at the other end of the scale we would have a pure parent ore indicator (Au). To decide on the character of the elements inbetween, more analytical work will be done on slags and ores of ancient working sites.

In a previous publication¹⁴ we discussed the lead, antimony, tin, copper and gold contents of coins from Athens, Aegina and Thasos in detail. It could be demonstrated that these elements are very useful in distinguishing coins of different provenances. Since then more coins have been analysed and an outline of the actual findings is given here. For statistical evaluation of such multiparameter problems, one feasible tool is the application of an average link cluster analysis (ALCA). Principally, an ALCA evaluates similarity groups [clusters based upon the normalized parameters (analytical data)]. A detailed description of the method and the program used is given elsewhere.¹⁵ In Table 4 the results of an ALCA for coins of different provenances are given.

The ALCA-clusters formed are evaluated on the assumption that the Athenian coins form one cluster. This criterion is reasonable because the variation in the abundances of the elements concerned (Pb, Sb, Sn, Cu, Au)* is small in the Athenian coins. The clusters of Table 4 shall be interpreted briefly:

(a) Coins of Athens, Orrescioi, Acanthus and Thasos form rather uniform clusters which can be distinguished easily from each other except for Orrescioi and Athens.

(b) Corinthian, Aeginetic and Sicilic coins fall into different clusters. Coins of these provenances cannot be distinguished within each cluster, except for the Aeginetic coins in cluster II and IV.

At this point it is interesting to compare ALCA clusters with groups based upon lead isotope data of the same coins. The few coins so far analysed and discussed by CHAMBERLAIN and GALE⁷ form groups which reasonably correspond with our

*Bismuth has not been included because an insufficient number of coins have as yet been analysed. However, first results reveal that ALCA clusters when bismuth is also considered do not alter significantly.

Table 4
ALCA-clusters considering Pb, Sb, Sn, Cu, Au concentrations

| | I | II | III | IV | V | VI | VII |
|-----------|----|----|-----|----|---|----|-----|
| Athens | 11 | | | | | | |
| Acanthus | | | 3 | | | | |
| Orrescioi | 6 | | | | | | |
| Thasos | | | | | | 4 | |
| Corinth | 2 | | | | 3 | 1 | 3 |
| Aegina | 1 | 1 | | 2 | 1 | | 4 |
| Dankle | | | | | 1 | 1 | 2 |

ALCA-clusters for Athens and Aegina, but not for Thasos. Lead isotopes certainly are indicators for the parent ores, whereas considering the above discussion about the usefulness of the elements concerned, the following can be said about the meaning of the ALCA-clusters. Uniformity could indicate that the silver of the coins concerned came from the same source. This is known for the Athenian coins to be the lead ore deposits of Laurion. However, uniformity could also mean that the technological process was not changed much during the time period of the coins considered. Different clusters for coins of the same provenance could suggest different silver sources. In this context the overlapping of some groups of Aegina, Corinth and Dankle (Sicily) in several clusters could well mean that coins of these provenances were made from silver of the same (but from cluster to cluster different) source. This means, e.g. the coins of Corinth,⁽³⁾ Aegina⁽¹⁾ and Dankle⁽¹⁾ in cluster V could have the same silver source, which should be different from a source for the coins in cluster VII (3 Corinth, 4 Aegina and 2 Dankle).

To discuss and better understand all implications and meanings, more analytical work on coins, slags and ores is needed, and it is our intention to publish a more detailed discussion of our findings in the future in *Archaeometry*. However, concluding, we would like to say that the results so far obtained encourage us to carry out further studies in this field, and we hope to obtain answers of interest to archaeologists, historians and numismatists.

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