CONF-760850--1

Interpretation of Neutron Activation Analysis Data of Ancient Silver

P. Meyers,[*] L. van Zelst,[*] and E. V. Sayre[**]

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I. Introduction

Whenever analytical studies on ancient metals are discussed, the claim is often made that metal analyses are of limited use because of remelting and the use of "scrap" metal. It is indeed true that elemental analyses of metal artifacts have provided relatively little information on metal sources, trade relations, ancient metal working traditions, for authentication, etc. The results of such analyses have been considerably less impressive than the sometimes spectacular results of analyses of ceramics, obsidian, flint, turquoise, sandstone, etc. The major reason for the difficulties in the interpretation of metal analyses is the fact that the elemental composition as it is in the material of the artifact now is considerably different from that of its source(s); smelting, purification, alloying and to a lesser extent corrosion have produced an almost entirely unrelated material. Other factors that have restricted the success of metal analyses are: inaccurate and insensitive analytical techniques, problems related to sampling, lack of comparative analytical data and incomplete publication of these data, limited cooperation between analyst and archaeologist/art historian.

Nevertheless the literature contains a number of publications where analytical data have been very helpful to the numismatist,

*The Metropolitan Museum of Art, New York.
**Brookhaven National Laboratory, Upton, and Museum of Fine Arts, Boston.

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art historian and archaeologist.

Analyses of ancient silver artifacts have in general been limited to the determination of the major components silver, copper, gold and sometimes lead. Except in those instances where the fineness of the silver was of interest, copper concentration levels appear to be of little use. Only gold concentration levels seem to be useful in distinguishing silver metal from different sources.

Our work on Sasanian silver and objects from related periods and geographic provenances will be used here to demonstrate that analytical data in combination with other properties can be used with reasonable success in establishing groups of objects of common geographic provenances, in providing information on the production, use and distribution of silver metal and on ancient metal working techniques.

II. Sampling and Analytical Techniques

The sampling method and analytical techniques used for the analysis of ancient silver have been described in detail (1, 2). It will suffice here to briefly summarize the experimental conditions.

Drilled samples from the interior of the metal, approximately 500 μg in weight, were irradiated together with silver metal standards with known impurity levels at a flux of 2.10^{14} n·cm^{-2}· sec^{-1} in the Brookhaven High Flux Beam Reactor. The irradiation time was 16 hours or 7 days depending on the half lives of the elements to be analyzed. After irradiation the silver metal samples were

dissolved and the matrix elements silver, gold and in some cases
copper, whose high levels of radioactivity interfered with an
accurate quantitative determination of other elements present in
trace quantities in the metal, were chemically separated from these
elements. Standard gamma ray spectrometry equipment was used
to record the gamma ray energy spectra. The concentration levels
of various elements in the ancient silver samples were determined
by comparison of the spectra of these samples with those of the
standards.

In addition to the major components silver, copper and gold,
of which the concentration levels were determined by normal in-
strumental neutron activation analysis, the following elements
could in most cases by determined quantitatively: sodium, potassium,
scandium, chromium, manganese, iron , nickel, cobalt, zinc,
arsenic, bromine, tin, antimony, selenium, iridium, and mercury.

Because of the small sample size it was investigated to
what extent the 500 μg samples were representative for the entire
object. This was achieved by multiple analyses of samples from
the same objects. It was found that only for the elements silver,
copper, gold, zinc, arsenic, tin, antimony, selenium and iridium,
the results were reasonably reproducible. Large variations were
observed in multiplicate analyses for all other elements.
Although knowledge of the concentration levels of these inhomo-
geneously distributed elements may still be of use, the dis-
cussion of the interpretation of analytical data will be restricted

to the elements copper, gold, zinc, arsenic, tin, antimony,
selenium and iridium.

III. Interpretation of Analytical Data

Before an attempt is made to interpret analytical data it
is most useful to consider the various factors that have or might
have contributed to the final elemental composition as it is
determined by the analyst. Almost certainly the sources of silver
during the Sasanian period as well as for preceding civilizations
in the Near East were argentiferous lead ores, mainly galena (PbS)
and cerussite ($PbCO_3$). Silver metal can be obtained from these
ores in a two step process: the ore is first smelted in a furnace
where, under proper oxidizing and reducing conditions, molten
lead containing most metallic impurities is collected at the bottom
of the furnace. The silver is then extracted from lead by cupel-
lation, i.e., the lead is oxidized by air during heating in a porous
vessel (cupel). Most of the less noble metals will also be oxidized
during this process. The lead oxide (litharge) is absorbed in
the porous materials in or near the bottom of the cupel, leaving
the silver metal behind. A certain amount of copper, for Sasanian
silver generally about 5%, was deliberately alloyed with the silver
thus obtained to increase its strength and malleability. (Cupel-
lation experiments by McKerrell (3) clearly indicate that after
cupellation copper concentration levels in silver are reduced to
less than 1 percent. Concentration levels higher than 1 percent,

therefore, are a result of addition of copper to the silver after the cupellation process).

Impurity concentrations in silver objects depend on:

(1) Initial concentration of each element, relative to the concentration of silver in the ore.

(2) Contamination by materials added during smelting and cupellation - i.e., fuel, flux.

(3) Evaporation of volatile metals or metal compounds during smelting, casting and annealing.

(4) Separation of less noble metals from silver during cupellation.

(5) Contamination (for some elements) by the addition of copper.

(6) Use of "scrap" silver, especially when obtained from different lead ores.

(7) Inhomogeneous distribution of the impurities in both the lead ore and the silver metal.

The elemental composition of silver objects is obviously a complicated function of many variables. All that can be predicted a priori is that the amount of noble, metals, such as gold and iridium, relative to silver will probably be the same in the silver as it was in the ore. If weight ratios of these elements to silver were relatively constant in single ore bodies and if they were to show significant variations from one ore body to another, noble metal concentrations would be most useful to distinguish silver obtained from lead ores of different geographic origins. Although direct evidence for this hypothesis is as yet not available,

previous analysis of silver coins, especially those by Kraay
and Emeleus (4) and by Gordus (5),(6) have shown that the concen-
tration of at least one element - gold - can be indicative of the
silver bearing ore used. As will be shown below, our work on
Sasanian silver strongly suggests that both gold and iridium
concentrations can be used for provenance studies.

At this moment we have analyzed approximately 170 objects,
mostly from museum collections. The majority of these objects are
Sasanian (Persia, 227-651 A.D.), others are from related near
eastern civilizations. In a first approximation only gold and
iridium concentrations were considered. The absolute concentra-
tions of gold and iridium were normalised to 95 percent silver, an
arbitrarily selected number representing the average silver content
in Sasanian objects. (The results for 63 objects, all from the
collection of the State Hermitage Museum in Leningrad, are represented
in Figure 1.) It was observed that a significant correlation
existed between gold and iridium concentrations and other charac-
teristics, such as style, iconography, shape, method of manufacture
and toolmarks. Based on this information a group of objects
was formed with such a large uniformity in gold and iridium
concentrations, in style and iconography that the assumption could
be made that all these objects were produced from silver from
one single source in a relatively restricted geographical area.
This large group (group 2 in figure 1) contained about 40 samples
and was used for a statistical study of the elements of interest.

In any statistical study of analytical data correlations between various elements can be highly informative. Table 1 shows the correlation matrix for the absolute concentrations of the elements determined in the 40 samples. Of interest are the significantly high correlation coefficients between copper and each of the elements zinc, tin, arsenic, antimony, and selenium, as well as the high correlation coefficients for most of the various combinations of the latter five elements. From this it can be concluded that each of these elements is introduced into the silver as an impurity of the copper. Their concentration levels in the silver are mainly determined by their concentration levels in the copper and the amount of copper that was added to the silver. A correlation diagram for copper and antimony is shown in Figure 2.

This observation virtually eliminates the possibility of using the elements zinc, tin, arsenic, antimony and selenium to differentiate between silver metal from different sources. It is worthwhile, however, to investigate to what extent these elements could provide information on the copper that was added to the silver. For that purpose all concentrations of zinc, tin, arsenic, antimony and selenium were normalized to 5 percent copper. The next step is to consider our test group of 40 samples and use the normalized zinc, tin, arsenic, antimony and selenium values of these samples to define a population in a 5 dimensional space. To this population we will compare a series of 42 individual samples, each of which is taken from objects that mostly do not belong

to our stylistically homogeneous group 2. If no relationship exists between
the geographic provenance of the objects and the normalized concentrations of
zinc, tin, arsenic, antimony and selenium, then we would expect the group of 42
individual samples to be statistically identical with group 2; . . ·
in other words: the 42 individual samples would populate the identical
space as the 40 samples of our test group. However, it was found
that a statistically significant fraction of the 42 samples, circa
50 percent, fell outside the 95 percent probability limits of
our test group. The conclusion must be that different geographic
origins to some extent are reflected in different normalized
concentration levels of zinc, tin, arsenic, antimony and selenium.
Figure 3 shows the results of a statistical comparison of the 42
samples to our test group. Each column gives the number of
samples which have a probability larger than 5 percent to belong
to the test group (indicated by yes) and the number of samples
with a probability less than 5 percent (indicated · by no).
The numbers in column "a" are based on normalized gold and iridium
values, column "b" on normalized zinc, tin, arsenic, antimony
and selenium values and column "c" on all seven elements. Figure
4 shows the distribution of the zinc and antimony values of our
test group. The solid line represents the 95 percent probability
limit. It is easily seen that a significant number of samples
fall outside this limit.

With the above information taken into account, the analytical

data have been examined. Applying multivariate statistics in combination with information on stylistic and pertinent physical characteristics, a number of groups could be formed, as shown in Figure 1. Samples in the overlapping areas of groups 1, 2 and 3 could in many cases be associated with one group only.

The best defined group is group 2. This group contains most of the objects considered to be from Sasanian Iran. Additional support for this grouping is found in the fact that all silver plates in this group (with one exception) have at the exterior of the plate an engraved or chased line, parallel to the rim at a distance of 2-3mm from the rim. Sometimes a similar line is seen on the outside of the footring. Plates that do not fall in group 2 do not have an exterior rim line (again with only one exception). Group 1 and group 3 are less well defined. All that can be said at this time is that they probably were produced east of Sasanian Iran. Group 4 is a stylistically homogeneous group of objects produced in central Asia.

Many analyses can not yet be grouped. These objects were probably produced from silver sources from which not enough objects have been analyzed to identify the sources.

A group of approximately 100 mostly Sasanian silver coins was analyzed in the hope that their elemental composition might provide further information on the use of silver. All coins were reasonably well dated; a certain number contained mint marks from which the mint city could be inferred. The gold and iridium

concentration ranges of 75 of these coins are indicated by the

shaded areas in Figure 1 (not indicated are non-Sasanian coins

and a small number of Sasanian coins with scattered gold values

less than 0.3% and a small group of coins with iridium values less

than 2 μg/g). It is immediately obvious that there is little

similarity between the composition of the Sasanian objects of

group 2 and any of the coins. Ninety-three percent of the coins

have distinctly different compositions from the group 2 objects.
                                      and
Most objects with gold iridium concentration levels matching

those of coins are not from Sasanian Iran so that their respective

silver metal sources are not likely to be the same. It appears,

therefore, that in Sasanian Iran different sources were used for

the production of silver metal for coins and for objects. With

a few exceptions (notably three of the earliest Sasanian silver

objects), all the typical objects from Sasanian Iran appear

to be manufactured from silver of one single source or source

area, while a number of sources (five or more) were used to produce

silver for coins. There is in general agreement among art historians

that the production and distribution of silver was a royal privilege

and that silver metal had a high intrinsic value. Our results

indeed confirm a strict control even to the extent of the use of

different sources for the production of silver metal for objects

and coins respectively. The results described above also indicate

that little or no remelting took place from coins into objects

or vice versa.

Besides information on provenance the analytical data provide
evidences of alloying and metalworking traditions. The concentra-
tion levels of zinc and tin relative to that of copper are in
general so low that the use of scrap metal (bronze or brass) in
the alloying of copper with silver appears to be unlikely.
Unalloyed copper, probably from a nearby copper mine, was used
in the alloying process. Most of the exceptions, in which relatively
high levels of zinc and or tin were found, occur in group 1.
A possible explanation is that copper was not easily available
in the area where the silver metal of group 1 was used and that
remolten bronze or brass objects were used instead.

It was investigated to what extent the parts of one object
were produced from the same or a different batch of silver or
even of silver from a different source. Many of the objects
studied consist of separate parts joined together; for example,
most of the plates have a foot that was fabricated as a separate
piece from the plate shell. Analyses of foot and plate shell
samples can indicate whether these parts are made from the same
or related silver. Agreement between the two pieces in the
concentration of all the elements would indicate a high probability
that they were formed from the same batch of silver. A marked
difference in the concentrations of copper, zinc, tin, arsenic,
antimony and selenium but agreement between gold and iridium
would be a good indication that the same source of silver was

used for the alloys of the 2 pieces but that the silver was prepared
in different batches. Total disagreement in composition, of
course, suggests silver from different sources. It was found
that among the objects for which comparative analyses for different
parts were available approximately 1/3 match in all
elements. These parts, therefore, appear to be from the same
batch of silver. Approximately 25% of the objects show matching
concentrations of gold and iridium but not of the less noble metals.
The separate parts of these objects, therefore, could have been
made of silver from a common ore source but not from a single
batch. In a surprisingly large number of the objects, 40-45%,
there is no match at all in the minor and trace elements.
Possible explanations for this distinction between the separate
pieces of these objects (usually the shells of plates and the
supporting feet) might be manufacturing tradition, that is, the
feet were produced separately as standard items for attachment
onto plates. It is also possible that feet were replaced in later
repairs.

After completion of the analysis program (a relatively
small number of objects still have to be analyzed) the research
will be concentrated on a study of argentiferous galena and
cerussite from the Near East to establish if any lead ore deposits
can be identified as the probable sources for Sasanian silver.
For that purpose noble metal concentration ratios and lead isotope
ratios will be used to characterize each lead ore sample. We hope

to be able to collect a large series of ore samples which will allow a systematic study of the possible ore sources used for the production of Sasanian silver.

Acknowledgement:

The authors express their gratitude to Prudence O. Harper, curator for the Ancient Near East Department of The Metropolitan Museum of Art, for her many valuable suggestions, her expert evaluation of the objects analyzed, and her continuous interest in this project.

The authors are also grateful to the following institutions for the cooperation received in the study and sampling of the objects in their collections: The State Hermitage Museum, Leningrad, U.S.S.R.; The British Museum, London, Great Britain, Le Musée du Louvre, Paris, France; The Freer Gallery of Art, Washington, D.C.; The Walters Art Gallery, Baltimore; The Cleveland Museum of Art; and the Cincinnati Art Museum.

Literature:

1) P. Meyers, L. van Zelst, E.V. Sayre, J. Radioanal. Chem.
   (1973) 16, 67-78.

2) P. Meyers. L. van Zelst, E.V. Sayre, "Major and Trace Elements
   in Sasanian Silver" in Archaeological Chemistry, Advances in
   Chemistry Series, Number 138, American Chemical Society,
   (1975) pp.22-23.

3) H. McKerrel and R.B.K. Stevenson, "Some Analyses of Anglo-Saxon
   and Associated Oriental Silver Coinage" in Methods of
   Chemical and Metallurgical Investigation of Ancient Coinage,
   Royal Numismatic Society Spec. Publ. 8, 195-210, London (1972).

4) C.M. Kraay and V.M. Emeleus, "The Composition of Greek Silver
   Coins: Analysis by Neutron Activation," Oxford University
   Press, Oxford, England, 1962.

5) A.A. Gordus "Neutron Activation Analysis of Coins and Coins-streaks,"
   in Methods of Chemical and Metallurgical Investigation
   of Ancient Coinage, Royal Numismatic Society Spec. Publ. 8,
   127-148, London (1972).

6) A. A. Gordus and Y. P. Gordus, "Neutron Activation Analysis of Gold
   Impurity Levels in Silver Coins and Art Objects," in Archaeological Chemistry,
   Advances in Chemistry Series, Number 138, American Chemical Society(1975)
   pp. 124-147.

	AG	CU	AU	IR	ZN	SN	AS	SB	SE
AG	1.0								
CU	-0.888	1.0							
AU	0.579	-0.494	1.0						
IR	-0.089	0.233	-0.212	1.0					
ZN	-0.333	0.418	-0.294	0.105	1.0				
SN	-0.490	0.622	-0.353	0.292	0.513	1.0			
AS	-0.556	0.712	-0.299	-0.105	0.488	0.535	1.0		
SB	-0.607	0.759	-0.380	0.210	0.537	0.665	0.845	1.0	
SE	-0.681	0.798	-0.214	-0.116	0.465	0.576	0.743	0.687	1.0

TABLE 1

Correlation matrix for the absolute concentration of
elements determined in 40 samples of group 2.

FIGURE CAPTIONS

Figure 1. Distribution of gold and iridium in 63 silver objects from the
collection of the State Hermitage Museum, Leningrad, U.S.S.R.
The shaded areas indicate analyses of Sasanian silver coins.

Figure 2. Correlation diagram for copper and antimony concentrations in
40 samples of group 2.

Figure 3. Statistical comparison of 42 samples to group 2. Column a) is
based on normalized gold and iridium concentrations only. The
probability to belong to group 2 is more than 5 percent for 18
samples (yes) and less than 5 percent for 24 samples (no).
Column b) shows the division in number of samples with probabilities
of more than 5 percent and less than 5 percent, respectively, based
on normalized zinc, tin, arsenic, antimony, and selenium values.
The numbers in column c) are based on all seven elements.

Figure 4. Distribution of normalized zinc and antimony values for 40 samples
from group 2 indicated by solid dots and 42 individual samples
indicated by other symbols. The solid line represents the
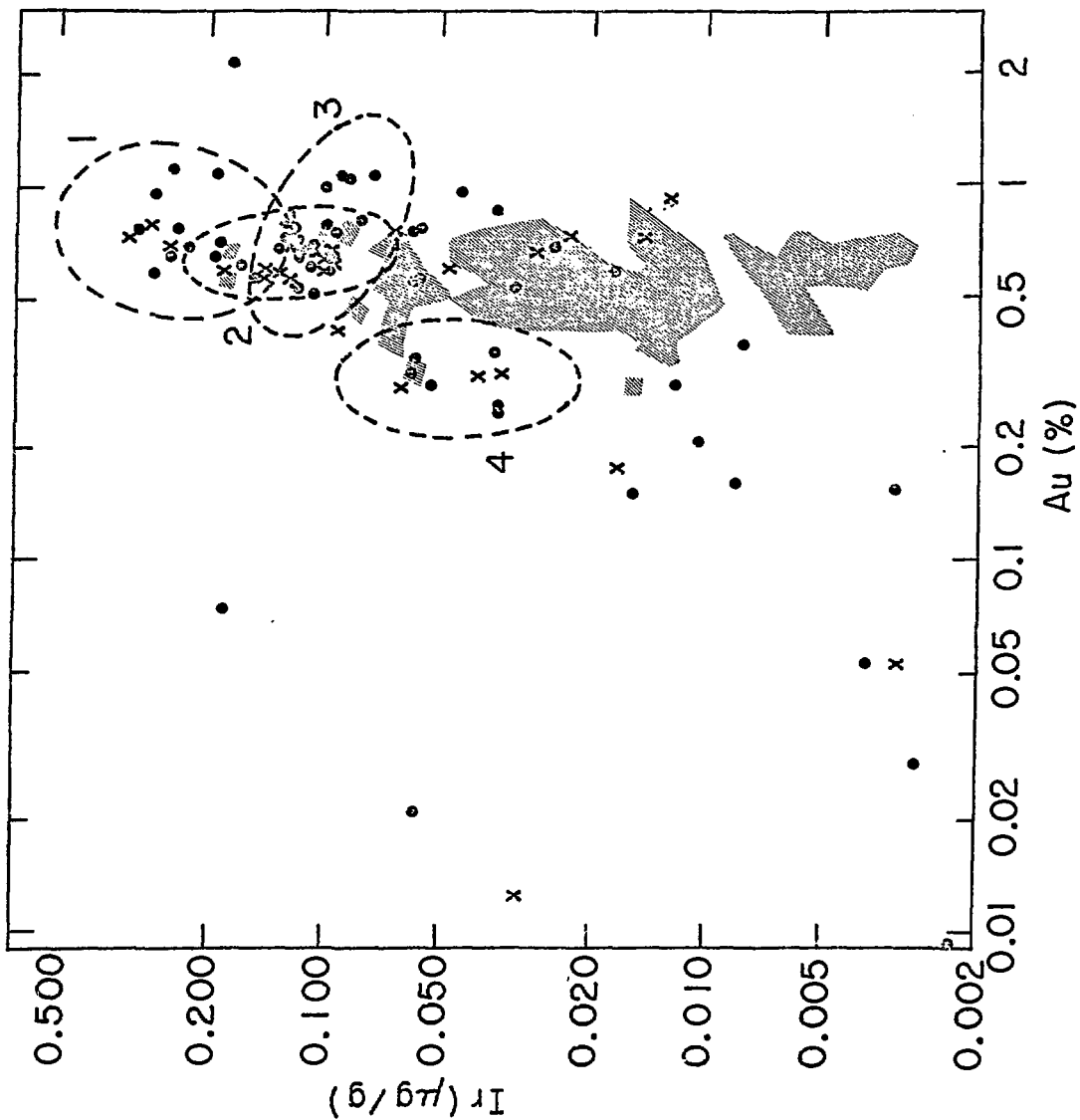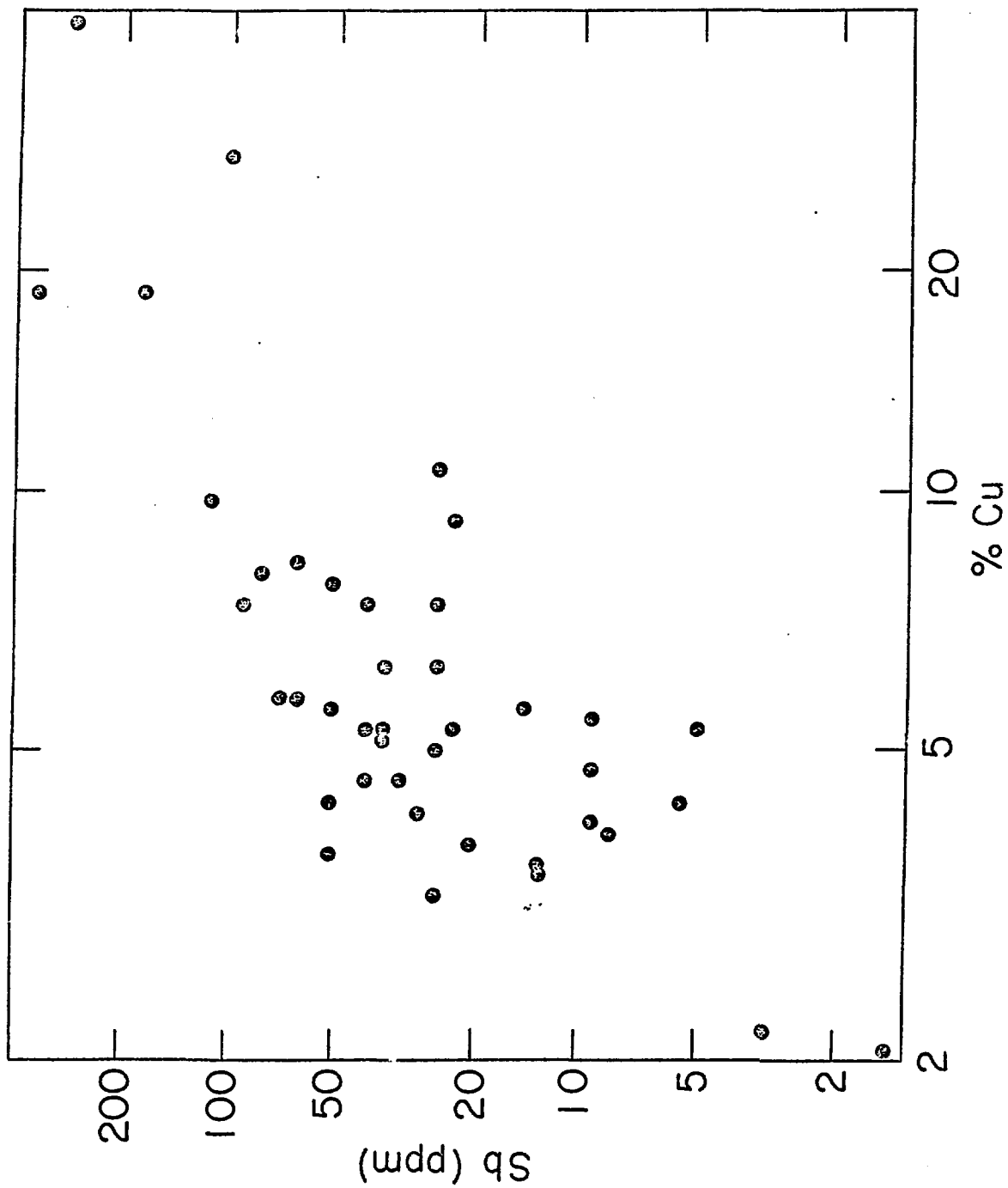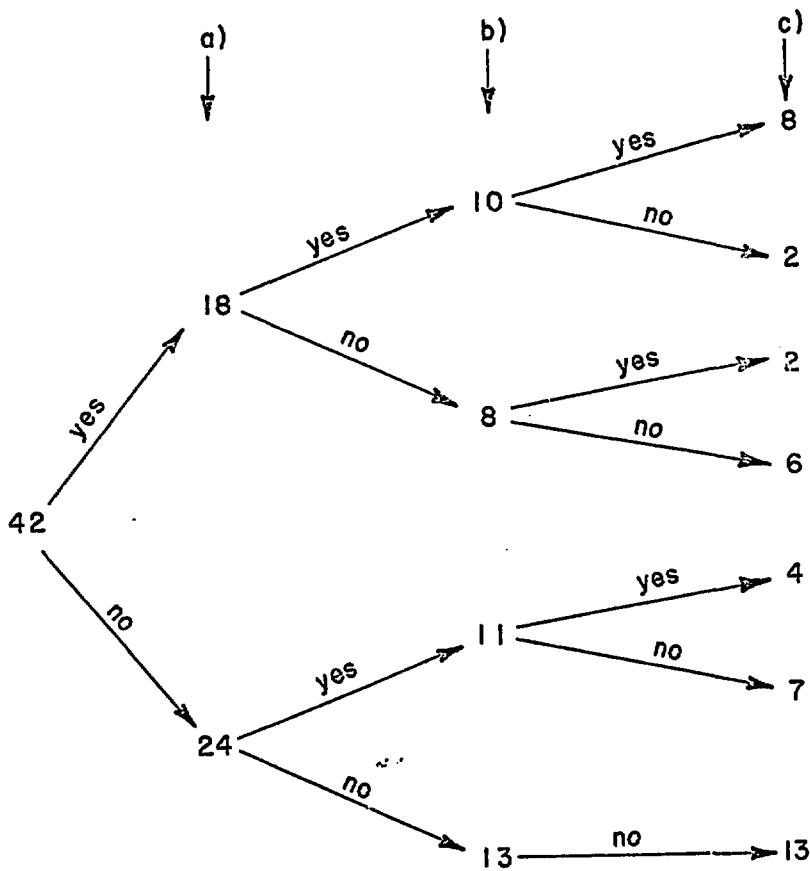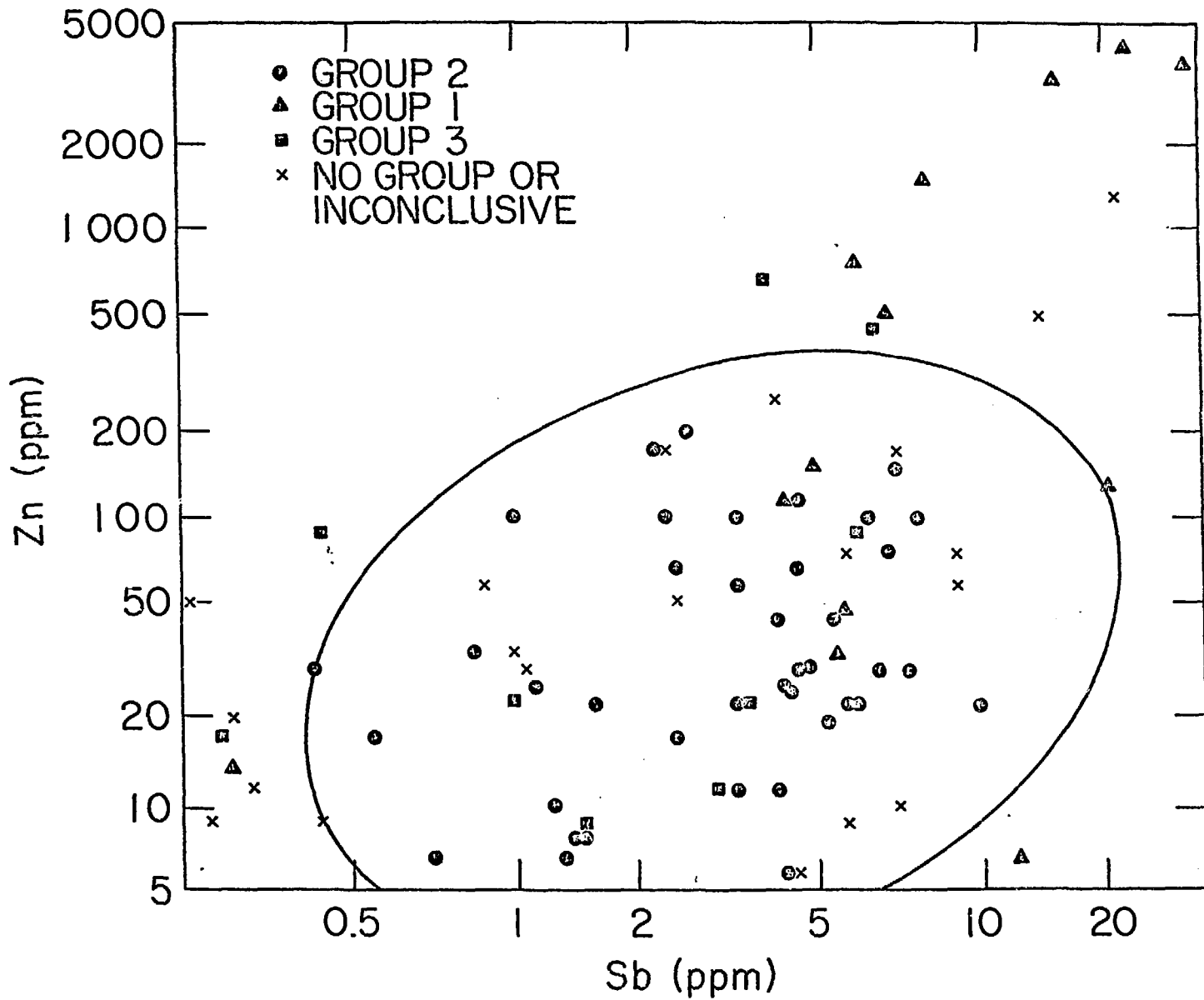95 percent probability limit.

Fig. 1

Fig. 2

a)   b)   c)

                                           yes   8
                              10
                                           no   2
              yes
        18
                              no   yes   2
                         8
42   no   no   6

                              11   yes   4
        24   yes   no   7
              no
                         13   no   13

Fig. 3

Fig. 4

GROUP 2
GROUP 1
GROUP 3
NO GROUP OR
INCONCLUSIVE

Zn (ppm)

Sb (ppm)