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SOLUBILITY STUDIES ON LIQUID AND SOLID METALS

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The idea of using a liquid metal in a high current antiproton target has gained favour in recent months, particularly because it does not suffer from many of the fatigué phenomena associated with solid metal targets. However, a factor of fundamental importance with liquid targets is the solubility of the container material in the liquid. Studies have therefore been carried out using the ISOLDE target development laboratory and the CERN scanning electron microscope in order to find a suitable combination of liquid metal target with metal containers. Such investigations are necessary because of the lack of information on liquid metal effects on other metals except for alkali metals and mercury.

1. CHOICE OF LIQUID METAL

Liquid gold is by far the best liquid metal, from the point of view of antiproton production and reabsorption, in that its $A^{1/3}/\rho$ is not much worse than that of solid iridium. However gold has a melting point of 1063°C and it seems reasonable to choose a binary alloy of gold which has a lower melting point. Suitable ones appear to be with germanium (12% by weight and a melting point of 450°C) and with silicon (6%) or indium (20%). In order to minimize the number of compatibility tests necessary and because of material availability, it was decided, at least initially, to confine studies to the Au-Ge eutectic mixture and investigate the solubility of UTA6V titanium alloy, pure tungsten, niobium, yttrium, molybdenum and chromium. Simple boat structures were made of these materials, sufficient to contain several grams of the liquid metal alloy.

2. SOLUBILITY DATA

An idea of the expected contamination of the Au-Ge can be found from a study of the various solid metal solubilities in gold given in literature on binary alloy systems. These are shown graphically in Fig. 1 as a function of temperature and it is seen that, for the materials quoted in the previous section, tungsten and molybdenum are strong candidates for the containment of the alloy, without producing contamination. Conversely titanium is known to have a high solubility in gold. The analogous results for silver are given in Fig. 2.

3. EXPERIMENTAL ARRANGEMENT

A vacuum coating unit at ISOLDE was used for the testing. It had the capability of creating a vacuum $\leq 10^{-6}$ torr and the facility of heating the boats by AC current (< 1000 A) up to any desired temperature, for indefinite periods of time. Temperature $> 700^{\circ}\text{C}$ could be monitored using a disappearing filament optical pyrometer, through an optical window. On completion of the high temperature runs, each complete boat/liquid metal sample was analysed on the CERN scanning electron microscope, which by observation of the characteristic K.L X ray lines, could measure the percentage weight of any element, over the sample cross-section.

4. RESULTS

4.1 Au-Ge eutectic alloy in titanium alloy UTA6V

This titanium alloy is very much favoured as an enclosing container because of the ease whereby it might be electron eroded and welded. A design of container based upon the idea of miniaturizing the lithium lens structure could easily be envisaged. However, when the Au-Ge alloy was heated to 450°C in a boat of this material, and after the expected melting of the alloy, there was a rapid (2-5 minutes) resolidification. Subsequent extra heating failed to reliquify the alloy even at temperatures of $1000-1100^{\circ}\text{C}$. The results of the SEM study are given in Figure 3 as a graph of percentage weight of each relevant constituent,

as a function of distance across a cross section of the sample. It is clearly seen that titanium has migrated significantly, up to a distance of 0,6 mm into the ingot, attaining a maximum weight percentage of 25%. The region of marked penetration is shown as x in Fig. 3.

Two other interesting features are that there appears to be a high concentration of gold immediately next to the titanium surface, and also the overall level of germanium appears to be higher than as originally added to the gold (overall the weight percentage of Ge was only 12.3%) although it must be stated that there is a large statistical fluctuation in this particular S.E.M. measurement.

Region Y of the sample, corresponded to Au-Ge alloy which was added to the original after contamination, and there appears to be a retarding effect of titanium diffusion into this part of the ingot.

4.2 Au-Ge in pure tungsten

This system was run for 3 1/2 days at a mean temperature of 600°C and, although both melting and metal creep were observed, no apparent tungsten erosion was visible at the end of this period. The S.E.M. results are shown in Fig. 4, where it is clearly seen that no diffusion of tungsten atoms into the alloy had occurred. The narrowness of the physical width of the tungsten region was due to the sampling width of the S.E.M. being comparable to the boat thickness. The presence of alloy on both sides of the tungsten was due to alloy creeping over the sides of the boat, forming a globule beneath.

An interesting additional feature of the S.E.M. results is that there appears to be a migration effect of the germanium towards the hot tungsten metal with of course the opposite effect for the gold. It should be noted that the weight percentage of Ge was 15,6% in the bulk alloy and this level is only approached well away from the alloy-boat interface. If this is a genuine effect then there is a lowering of the alloy melting point as the interface distance is increased. The sharp discontinuity occurring between the tungsten and gold-germanium alloy is very clearly shown in Plate 1 taken at a magnification of 320.

4.3 Au-Ge in yttrium

The results obtained for this combination are interestingly different to the two previous examples and are presented in Fig. 5. The most evident point is that there is both a migration of yttrium atoms into the gold-germanium alloy (% saturation $\approx 14\%$) and a reverse migration of gold only, into the yttrium (% saturation $\approx 21\%$), but with no significant penetration of germanium. However, it is clear that there is contamination of the alloy by the yttrium which does not appear to decrease in magnitude away from the boat/alloy interface. Furthermore the net migration of the Au-Ge in the alloy appears less than in the previous example.

The magnitude of the penetration of gold into the base metal is pessimistic in that, all samples for S.E.M. analysis, were coated with a thin gold layer, prior to study. The effect of this is to give a residual gold X ray response which has been estimated to be 2-3%. Consequently any gold penetration of this magnitude can be assumed to be zero.

4.4 Au-Ge in molybdenum

Molybdenum belongs to the same chemical family as tungsten and the favourable results obtained for the latter material, together with quoted low solubilities of Mo in Au, led one to expect good results from the test. The S.E.M. results are shown in Fig. 6, and reveal that there is no detectable penetration of Mo into the gold and only a small penetration ($< 5\%$) of Au into Mo. These results were confirmed by a second test of longer duration (3 1/2 days instead of 6 hours), where the maximum gold penetration, after correction, was found to be only 3%.

4.5 Au-Ge in niobium

These results, presented in Fig. 7 are interesting in that niobium produced the highest degree of alloy contamination, seen in these tests. After a very short time the alloy resolidified in a similar way to the titanium test and upon examination after 31 hours, there was 53% weight contamination of the alloy, the remainder being approximately equal weights of gold and germanium, indicating

a drastic migration effect of gold, since the original alloy was composed of 88% of this material.

4.6 Au-Ge in zirconium

This system, the results of which are given in Fig. 8, was interesting in that, aside from migration (18%) of zirconium into the alloy, there was evidence of agglomeration of the gold and germanium into distinct zones, as indicated by the oscillating behaviour of the weight percentages, near the Zr interface.

4.7 Au-Ge in tantalum

This system was investigated primarily because tantalum belongs to the same chemical family as niobium and therefore interest was generated as to whether there was similar behaviour in the two materials. The results for tantalum are presented in Fig. 9, where it is seen that there is no migration of the tantalum into the alloy. The overall behaviour was in fact totally dissimilar to that of niobium, shown in Fig. 7, where the alloy was very heavily contaminated by the base metal.

4.8 Au-Ge in chromium

The pure chromium, used in this run, was observed to be very brittle, consequently both runs with this material, were made with small chromium plates placed in a tungsten boat, with nodules of the Au-Ge alloy placed on top. Two runs with the temperature maintained respectively at 550-600° and 850° were made and the results for the lower temperature are presented in Fig. 10.

At the lower temperature there are three characteristic features:

1. a severe fragmentation of the chromium at the surface
2. a concentration of the germanium at the surface between the chromium and the alloy, producing a low concentration of this constituent elsewhere, which presumably causes the alloy melting point to approach that of gold itself, and

3. a migration of (4.4 ± 0.2) % of chromium into the alloy.

A closer inspection of one surface of the chromium, taken with 10 μm steps rather than the 33 μm ones of the previous run, revealed a distinct layered structure at the surface consisting in order of

a) pure chromium, b) 64% chromium - 16% gold - 90% germanium, c) 95% gold, d) 68% chromium - 24% germanium, followed finally by the relatively stable Au-Ge alloy, with chromium fragments imbedded therein.

An overall view at low magnification is shown in Plate 2, where the break-up of the two chromium surfaces is clearly seen. The layered structure at the surface of the chromium is shown in the high magnification view in plate 3.

The effect of increasing the run temperature to 850°C was dramatic in that the chromium was completely broken into small pieces, as shown in plate 4. Clearly chromium is totally unsuitable if the target temperature is maintained above 600°.

4.9 Au-20% In in chromium

This system was investigated, to eliminate the possibility that the Ge was responsible for the effects mentioned in the previous test. The results obtained are given in Fig. 11, and clearly show that the chromium has dispersed into the alloy, there being no distinct zones of high concentration of chromium, as occurred in the previous test. The low overall level of indium is due to evaporation of the metal during the 6 hours of the run at 650°. The results clearly indicate that chromium would not make a good containing material for any gold alloy.

4.10 Ag-20% In in chromium

The startling difference between Au and Ag is shown in this example, the results of which are given in Fig. 12. The silver indium alloy was run for the same length of time and at the same temperature (650°C) as the previous test, and yet no detectable break up of the chromium could be detected. Furthermore there was no migration of the chromium into the alloy. This

therefore suggests that a middle order density target made from silver with perhaps indium could survive if enclosed in chromium, whereas gold would definitely not.

A summary of the migration behaviour is given in Table 1 for all materials tested. As stated previously, any level of migration of the gold from the eutectic alloy into the boat material, of less than 2% can be considered as zero, due to the gold layer required to be deposited on all S.E.M. samples.

5. CONCLUSIONS

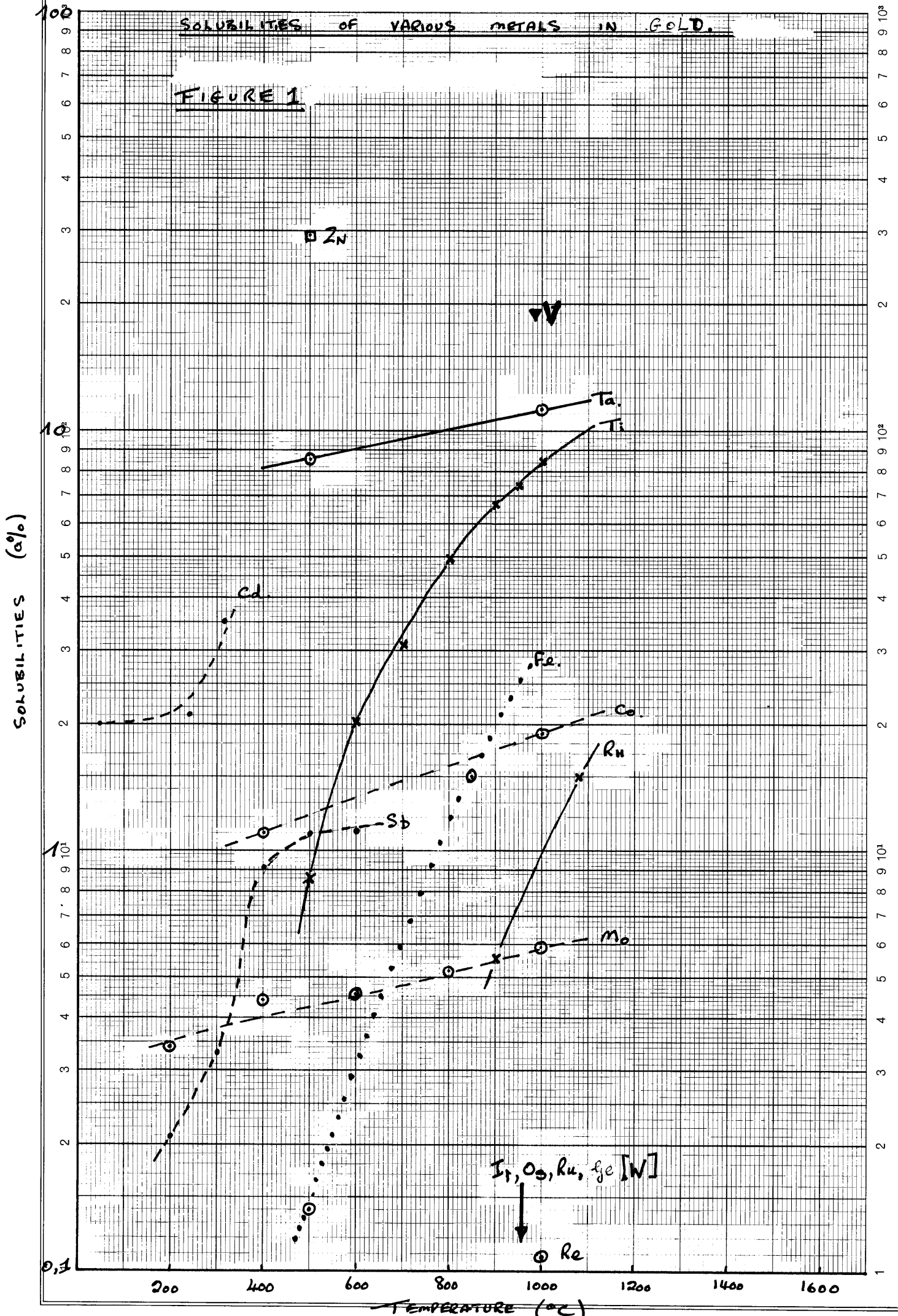
1. The most important consideration, from a metallurgical viewpoint, regarding the containment of a liquid metal target, is the possible contamination of the liquid by the surroundings. Such a phenomenon will occur far more quickly than serious erosion and subsequent failure of the container itself.
2. Several conclusions may be reached about the containment of 88%Au - 12%Ge eutectic alloy (melting point ~ 450°C).
 - a. untreated titanium alloys cannot possibly be used as a containment material, since sufficient titanium dissolved so that, within a few seconds or minutes, the melting point of the liquid metal was raised by several hundred °C.
 - b. The chemical family of elements, group VIA, appear to be the best candidates for enclosing gold alloys. Tungsten was excellent in this respect and molybdenum was almost as good, these being only a small diffusion of gold into the metal, this direction being far less serious than the reverse.
 - c. Chromium was a disappointment from the point of view of gold alloys, breaking into fragments at 600°C and dispersing into the alloy at higher temperature. However with silver alloys chromium showed much better performance and could be considered for the containment of liquid alloys which could be a good target for high

intensity PS beam, provided that the fragility of pure chromium is overcome by suitable alloying, as for example in chromel.

- d. Tantalum somewhat surprisingly behaved well although the literature suggested a high solubility in gold.
 - e. Niobium, yttrium and zirconium all displayed high mutual solubility, as summarized in Table 1. All are therefore unsuitable as container materials.
3. Other liquid alloys, based upon gold, could also be considered where it is known that the other constituent is a) effective from the point of view of antiproton production and b) inert in the container. Several candidates are i) 70% Au-30%Hg ($T_{\text{melt}} = 570^\circ$), ii) 50% Au-50% Hg (400°C), iii) 70% Au-30%Pb (640°), iv) 60% Au-40% Bi (630°C) and finally 60% Au-40% Tl (600°C). In general these alloys suffer from the disadvantage of having melting points about 200°C higher than those involving gold with germanium, indium or silicon. This could lead to an enhancement of the erosion and contamination effects.

SOLUBILITIES OF VARIOUS METALS IN GOLD.

FIGURE 1



SOLUBILITIES OF VARIOUS METALS IN SILVER

FIGURE 2

SOLUBILITIES (A%)

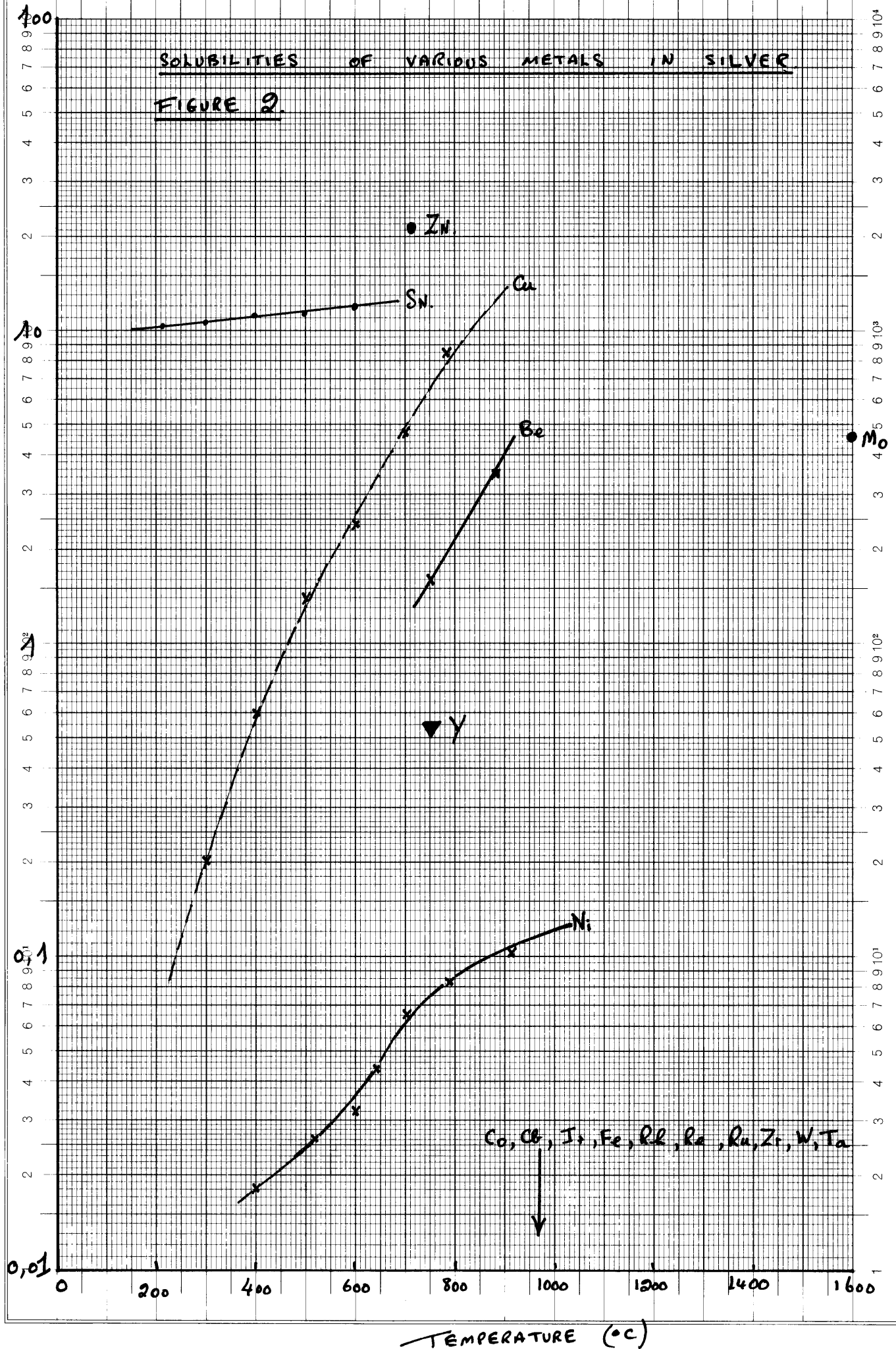


FIGURE 3 DISTRIBUTION OF TITANIUM, GOLD AND GERMANIUM FROM S.E.M. STUDY OF AU-GE EUTECTIC ALLOY

EDGE OF
TITANIUM BOAT.

EXTENT OF
FIRST INGOT
OF AU-GE
ALLOY.

(REGION Y)

SECOND DEPOSITION OF AU-GE ALLOY.

ORIGINAL ALLOY 87.7% Au - 12.3% Ge
EXPOSE TIME = SEVERAL MINUTES.
MELTING POINT 450°C.
NO WEIGHT LOSS DURING RUN. (<0.1%)

TITANIUM.

GOLD.

GERMANIUM.

WEIGHT PERCENTAGE. (%)

POSITION OF ANALYSIS (x 5 x 10⁻² mm)

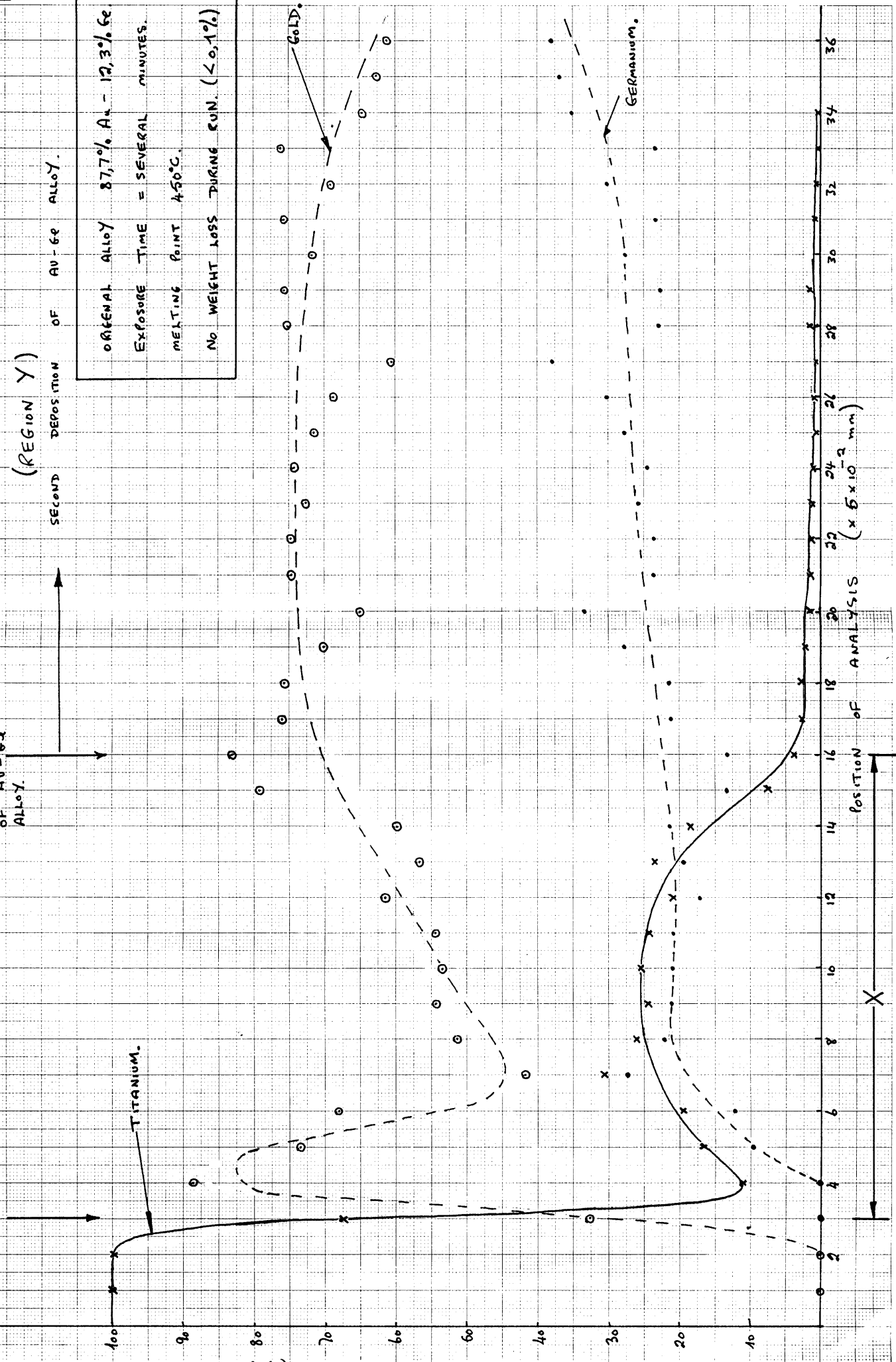
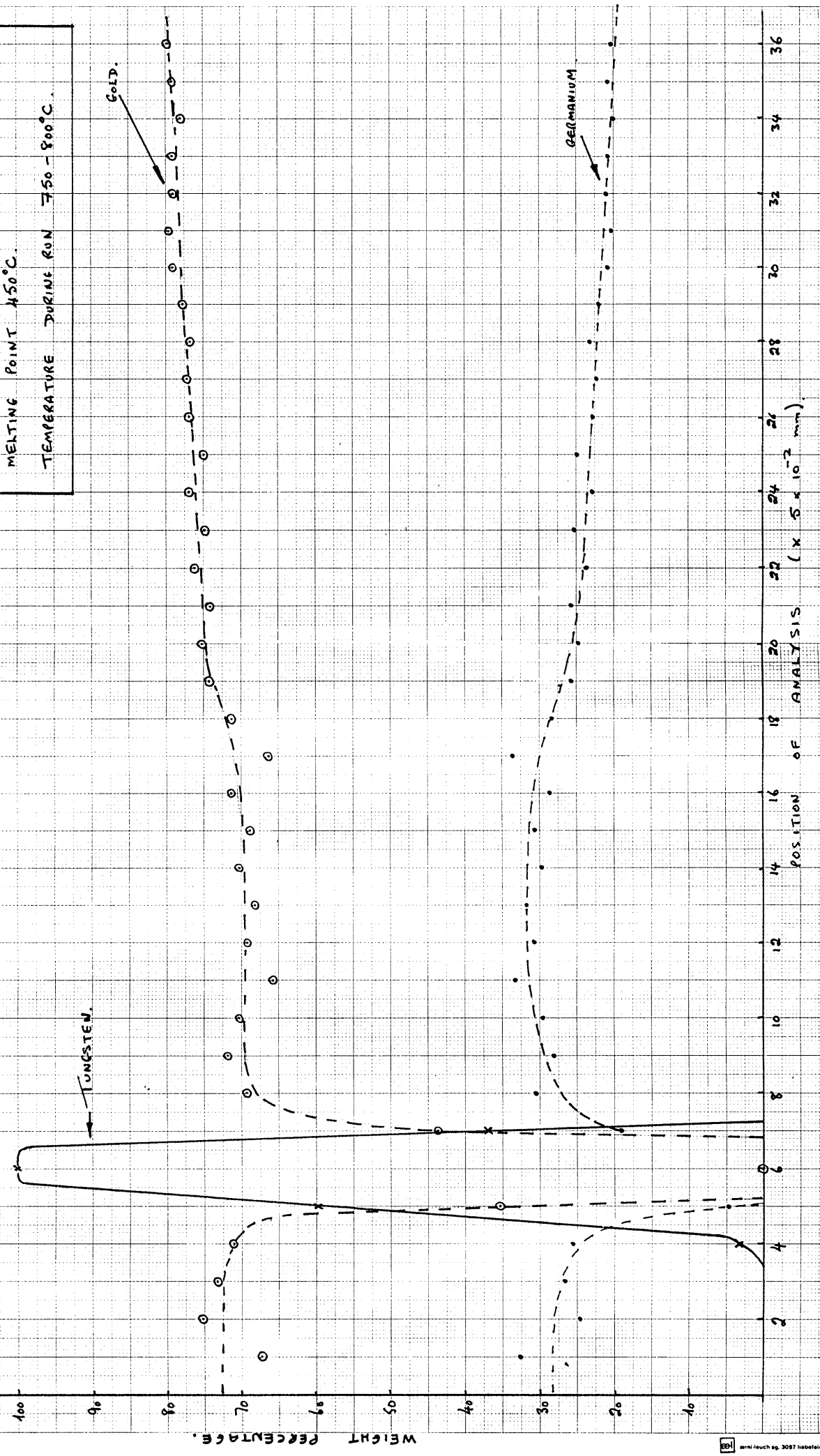


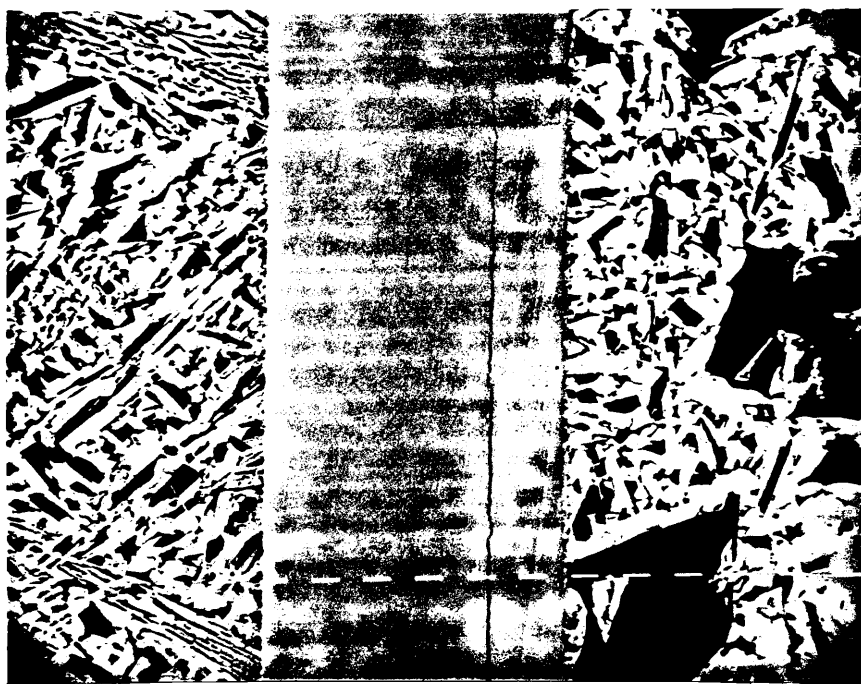
FIGURE 4. DISTRIBUTION OF TUNGSTEN, GOLD AND GERMANIUM FROM S.E.M. STUDY OF Au-Fe EUTECTIC ALLOY IN TUNGSTEN BOAT

ORIGINAL ALLOY 84.4% Au - 15.6% Fe.
 EXPOSURE TIME = SEVERAL DAYS. (3±).
 MELTING POINT 450°C.
 TEMPERATURE DURING RUN 750-800°C.

ORIGINAL BOAT THICKNESS



Au/Ge in Tungsten boat



Au-Ge

W

Au-Ge

x 320

Dark phase - almost pure Ge

Light phase - almost pure Au

FIGURE 5. DISTRIBUTION OF YTTRIUM, GOLD & GERMANIUM FROM S.E.M. STUDY OF Au-Ge EUTECTIC ALLOY IN YTTRIUM BOAT.

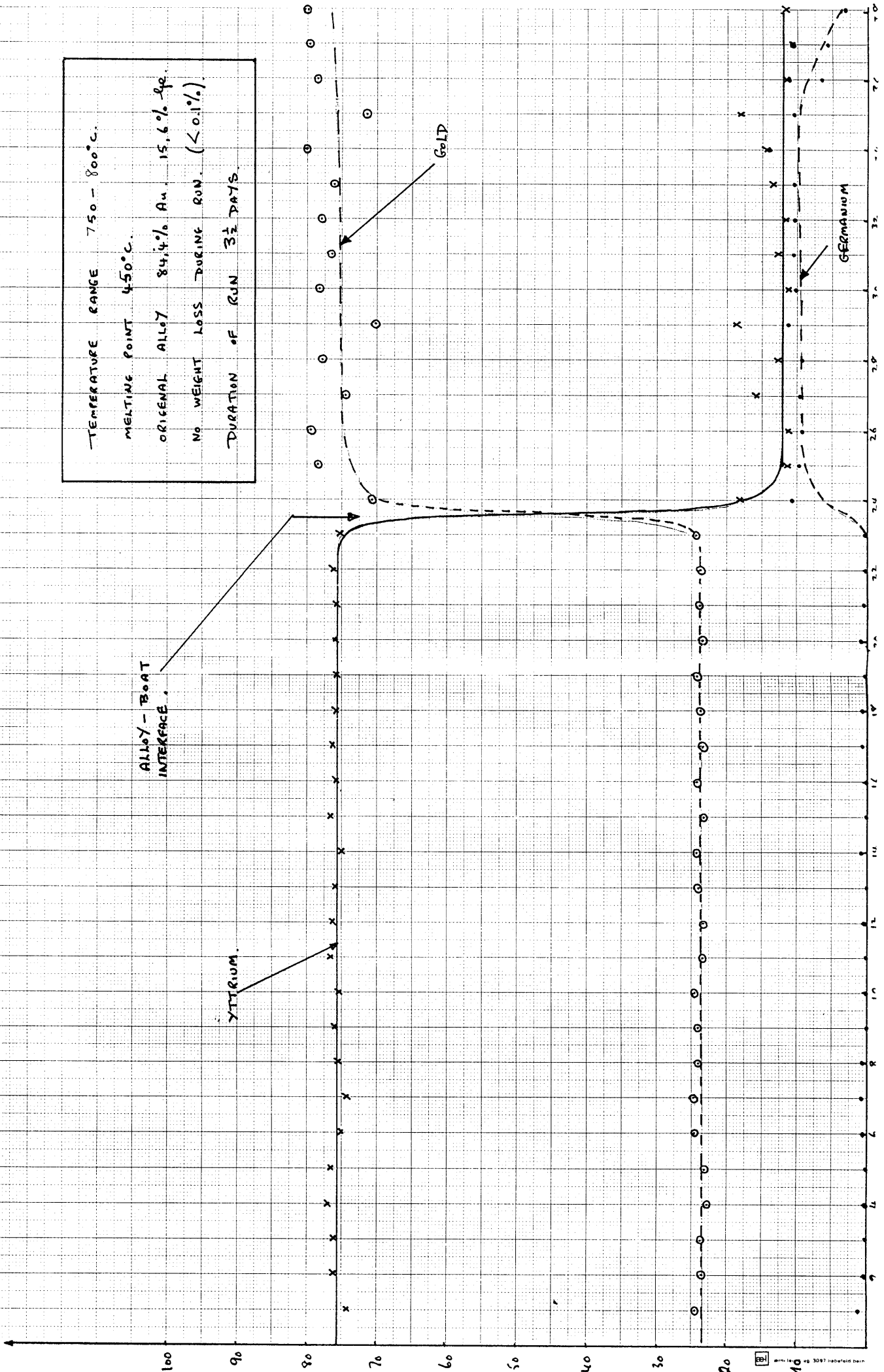


FIGURE 6.

DISTRIBUTION OF MOLYBDENUM, GOLD & GERMANIUM

FROM S.I.E.M. STUDY OF AU-GE EUTECTIC ALLOY IN

MOLYBDENUM BEAT

SCAN 1

ORIGINAL ALLOY 12.2% Au
87.8% Au
EXPOSURE TIME 6 HOURS.
NO WEIGHT LOSS DURING RUN
RUN TEMPERATURE 750°C.

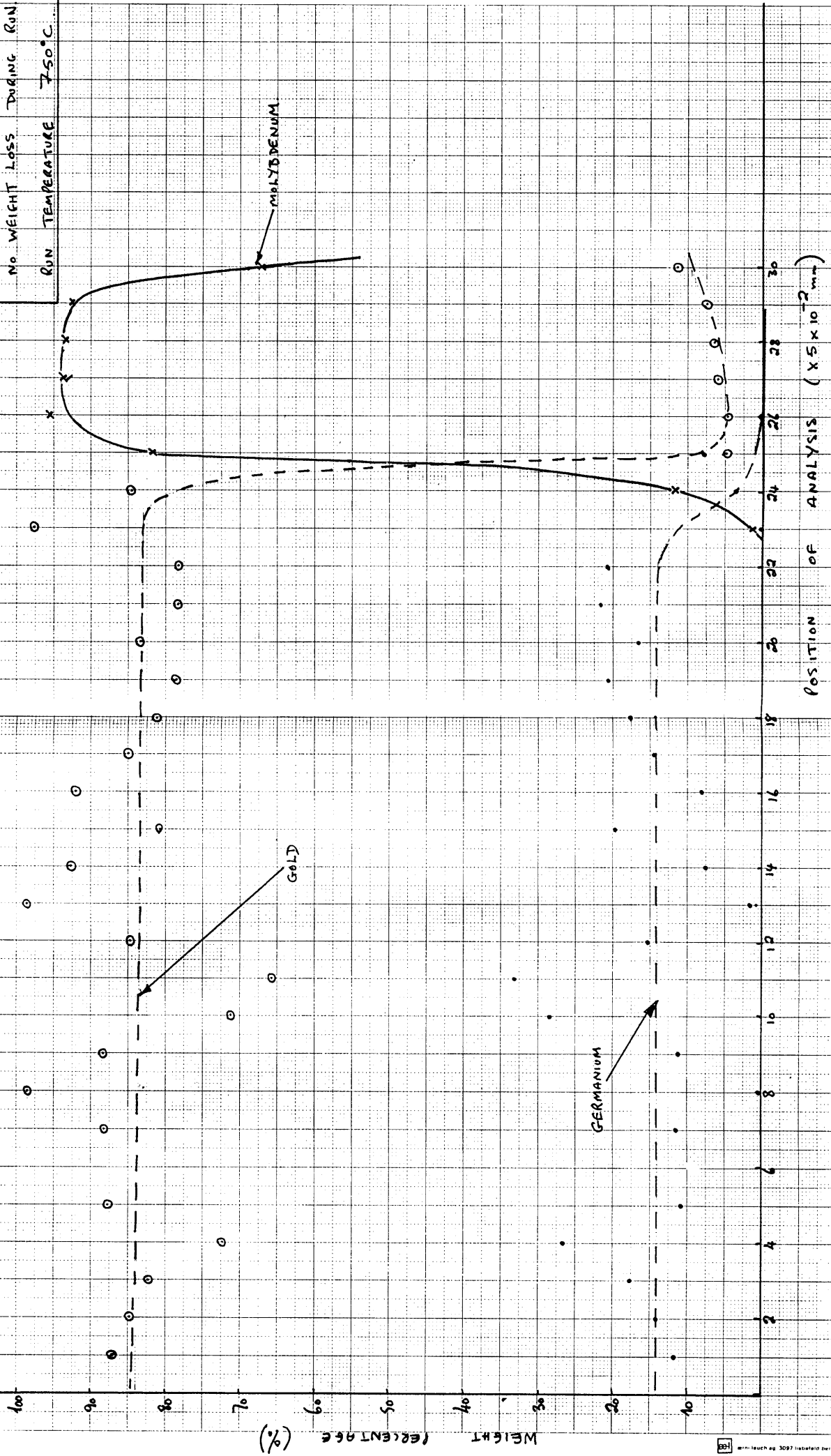


FIGURE 7. DISTRIBUTION OF NIOBIUM, GOLD & GERMANIUM FROM S.E.M. STUDY OF Au-6E EUTECTIC ALLOY IN NIOBIUM FOAT.

ORIGINAL ALLOY 87.8% Au - 12.2% Nb.
 EXPOSURE TIME 31 HOURS.
 RUN TEMPERATURE 700°C.
 NO WEIGHT LOSS DURING RUN.

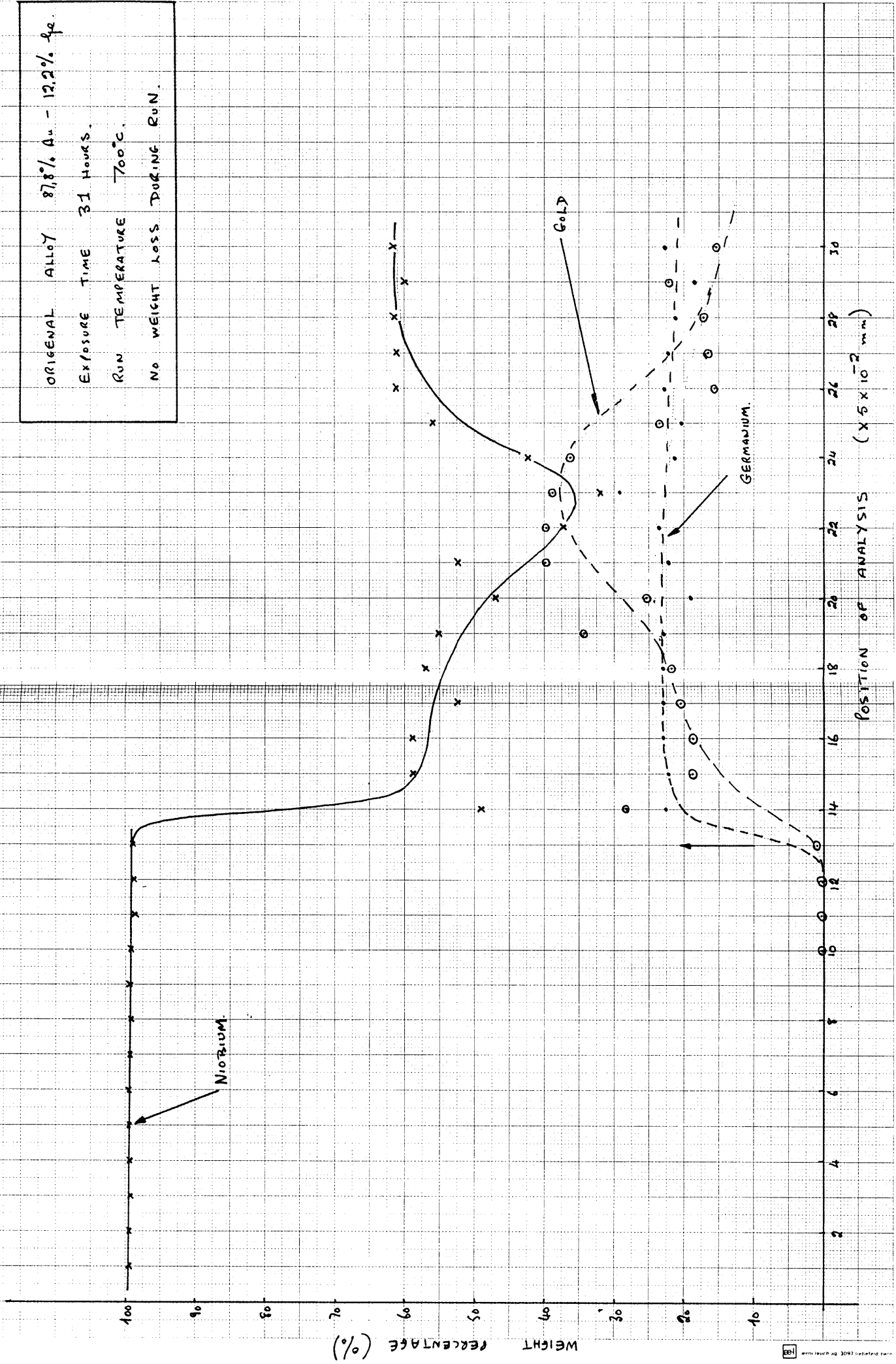


FIGURE 8. DISTRIBUTION OF ZIRCONIUM, GOLD & GERMANIUM FROM S.E.M. STUDY OF AU-GO EUTECTIC ALLOY IN ZIRCONIUM FOAT.

ORIGINAL ALLOY 87.8% Au - 12.2% Ge.
 EXPOSURE TIME 4 1/2 HOURS.
 1% WEIGHT LOSS DURING RUN.
 TEMPERATURE DURING RUN 850°C.

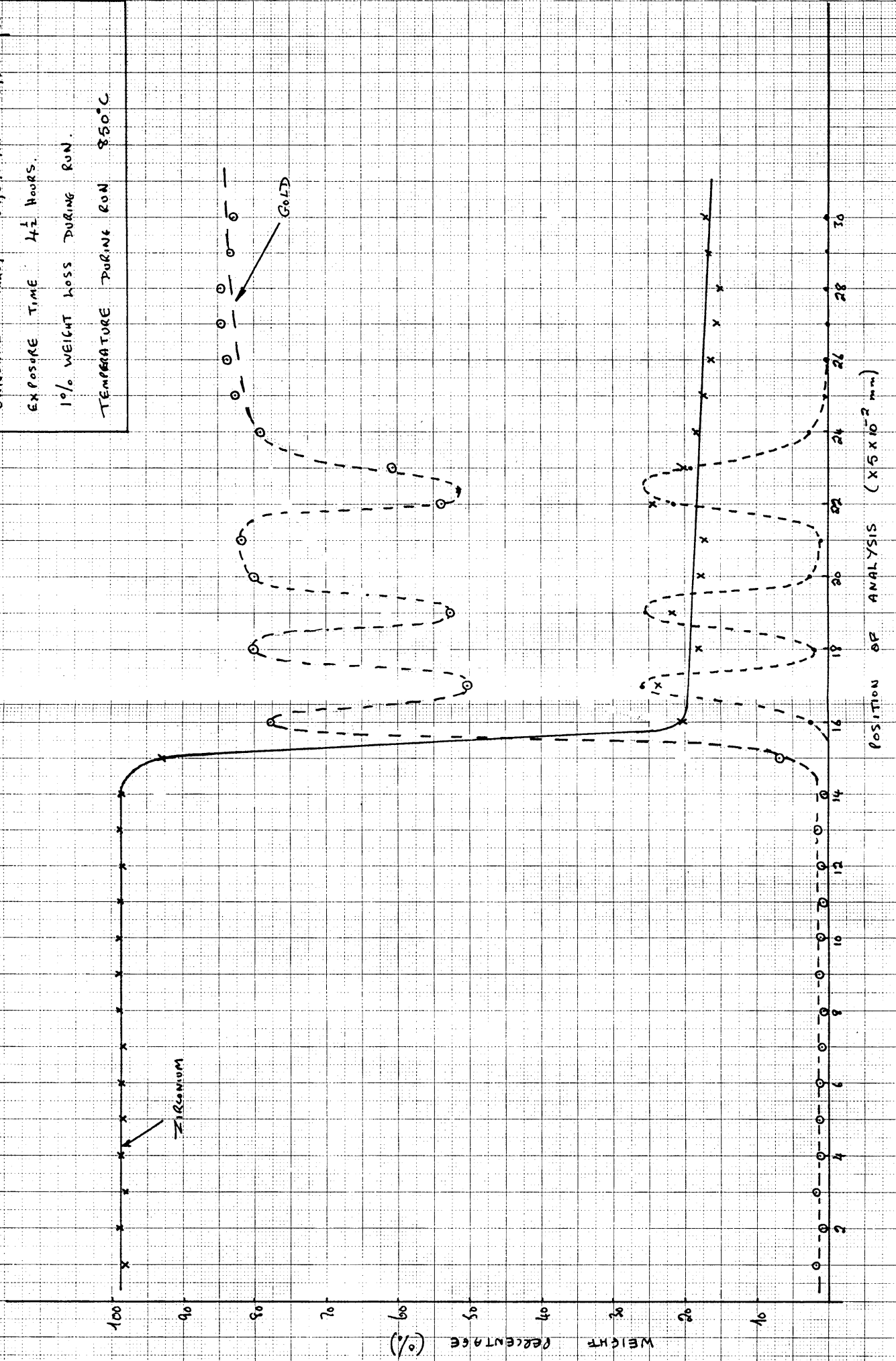
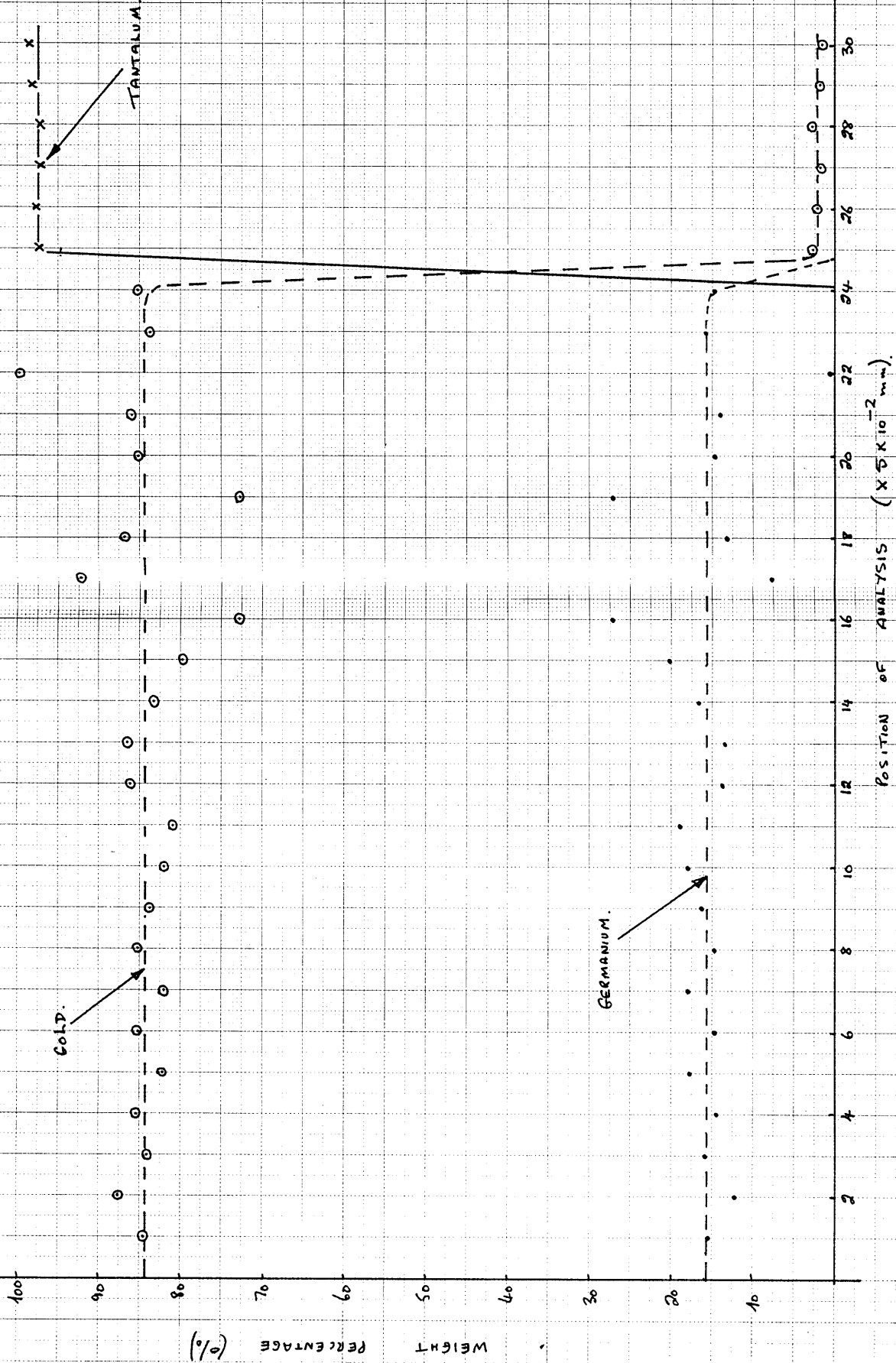


FIGURE 9. DISTRIBUTION OF TANTALUM, GOLD & GERMANIUM FROM S.E.M. STUDY OF Au-6e EUTECTIC ALLOY IN TANTALUM BOAT.

BOAT



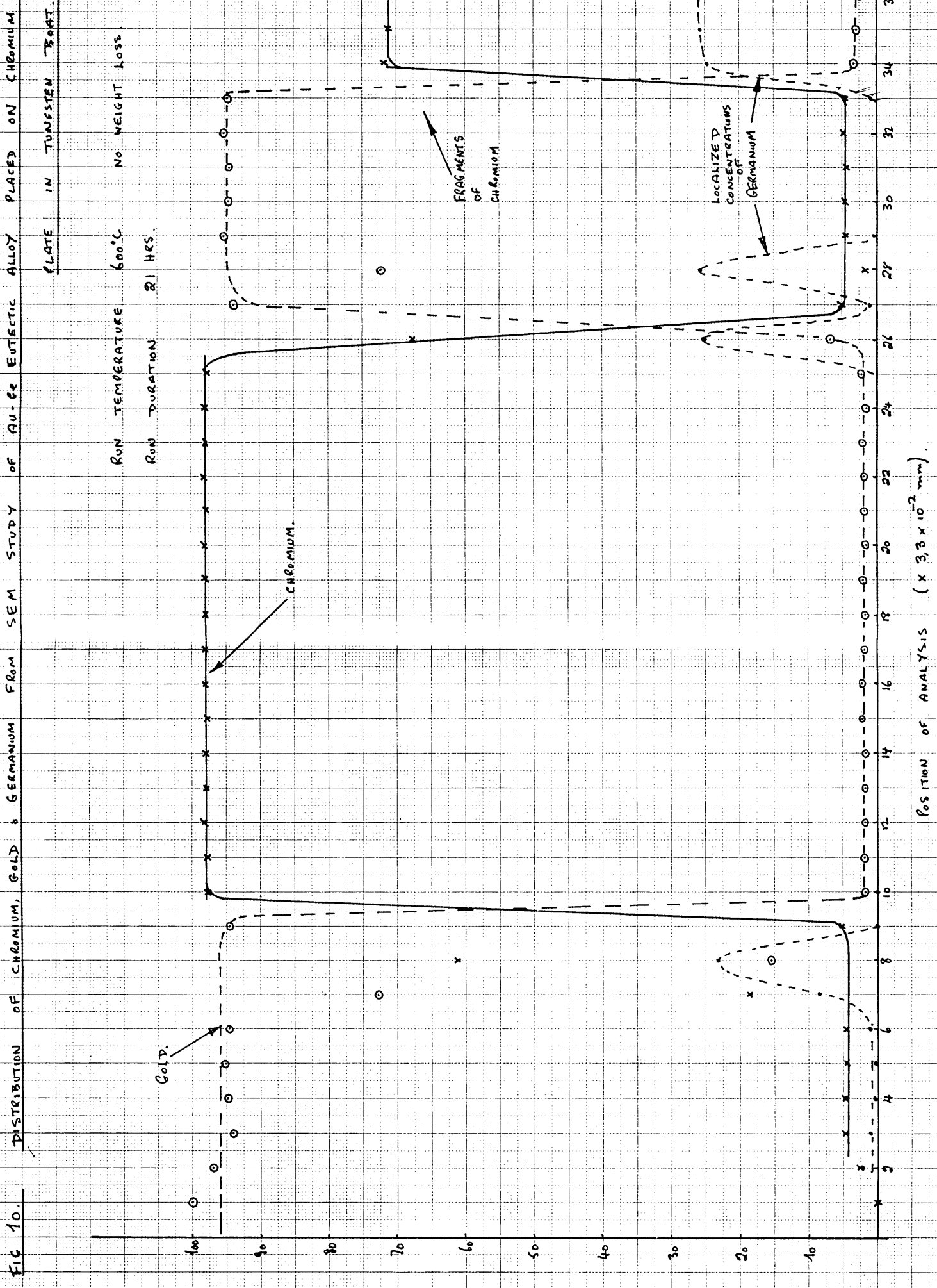
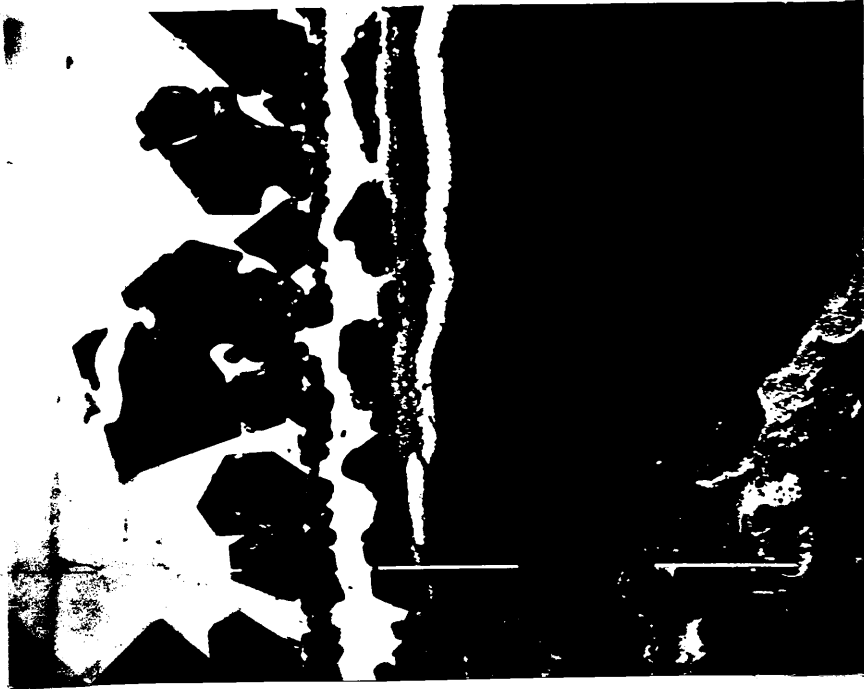


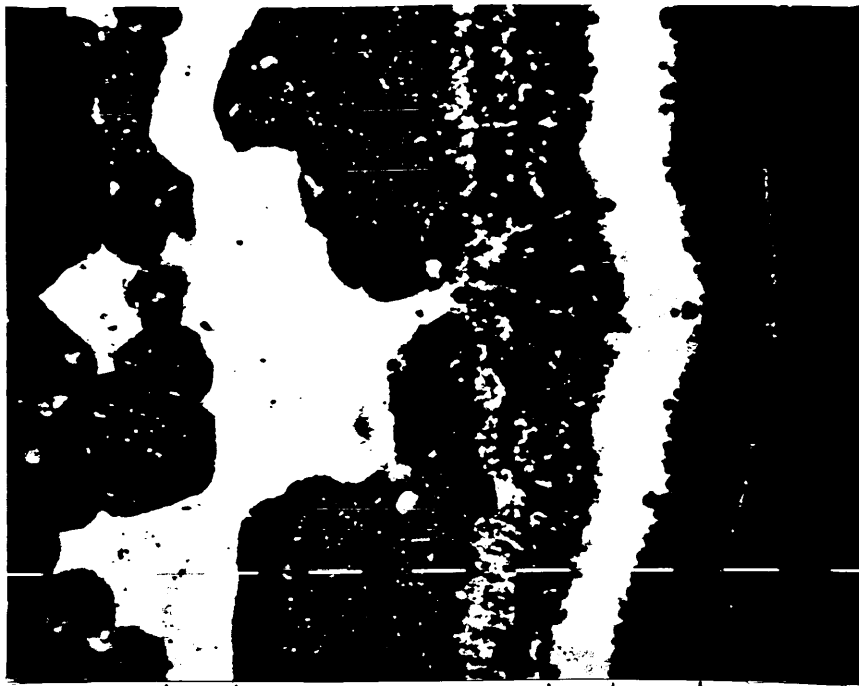
FIG 10.

POSITION OF ANALYSIS (x 3.3 x 10² mm).



X 160

X 640



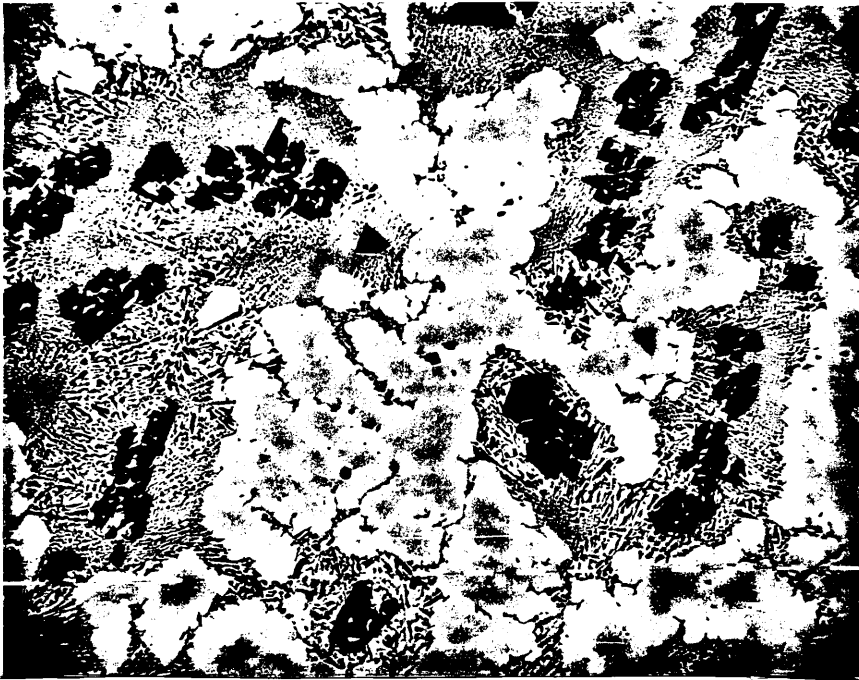
25% Ge 75% Cr

5% Cr 95% Au

5% Cr 95% Au

25% Ge 75% Cr

100% Cr



Dark phase - composed of approx. 25% Ge 75% Cr

White dendⁱtes - composed of approx. 5% Cr 95% Au

Third phase - composed of approx. 15% Ge 85% Au

FIGURE 11 DISTRIBUTION OF GOLD, INDIUM & CHROMIUM
FROM S.E.M. STUDY OF GOLD-INDIUM (20%) ALLOY
PLACED IN TUNGSTEN BOAT OVER CHROMIUM PLATE

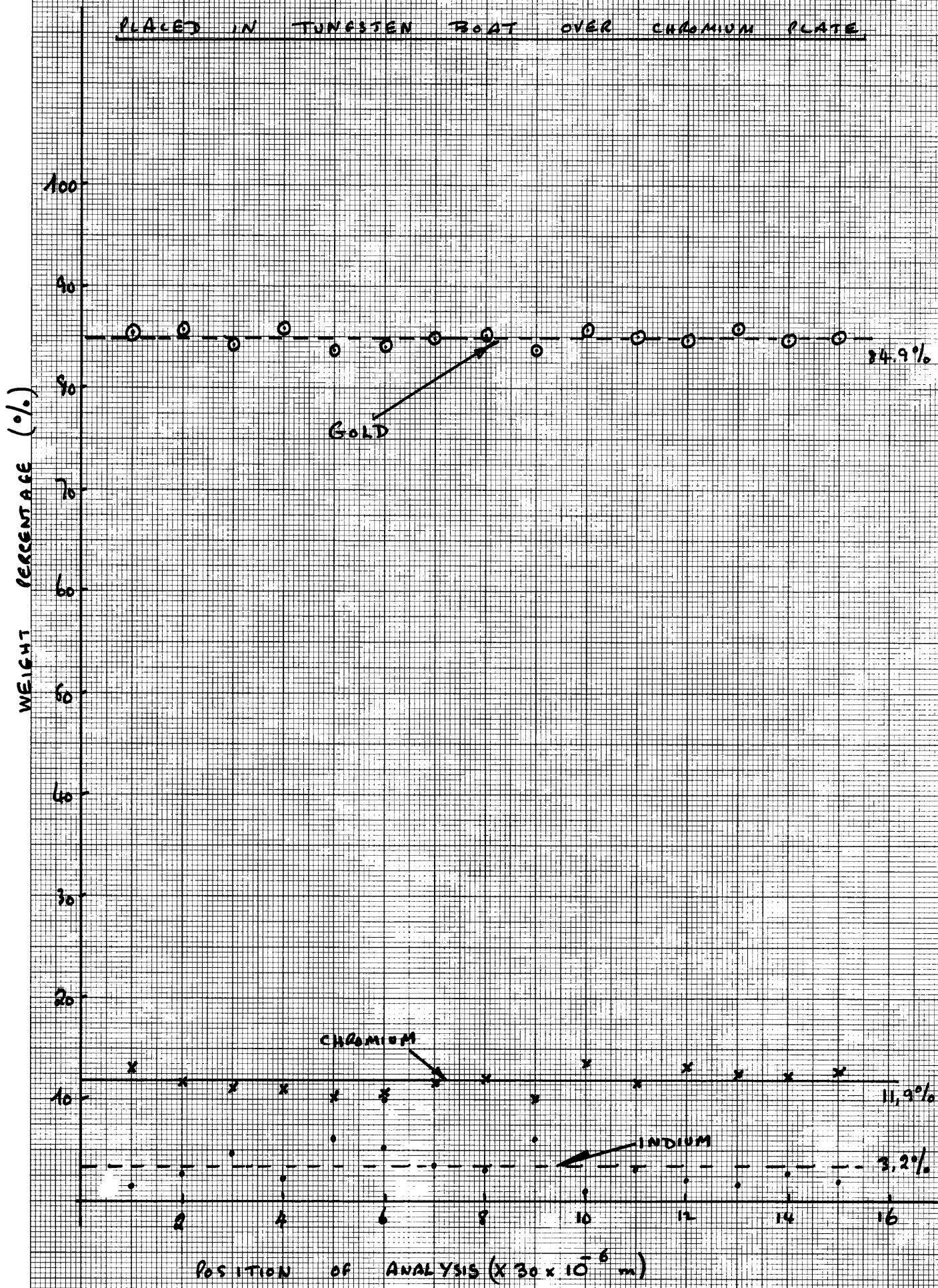
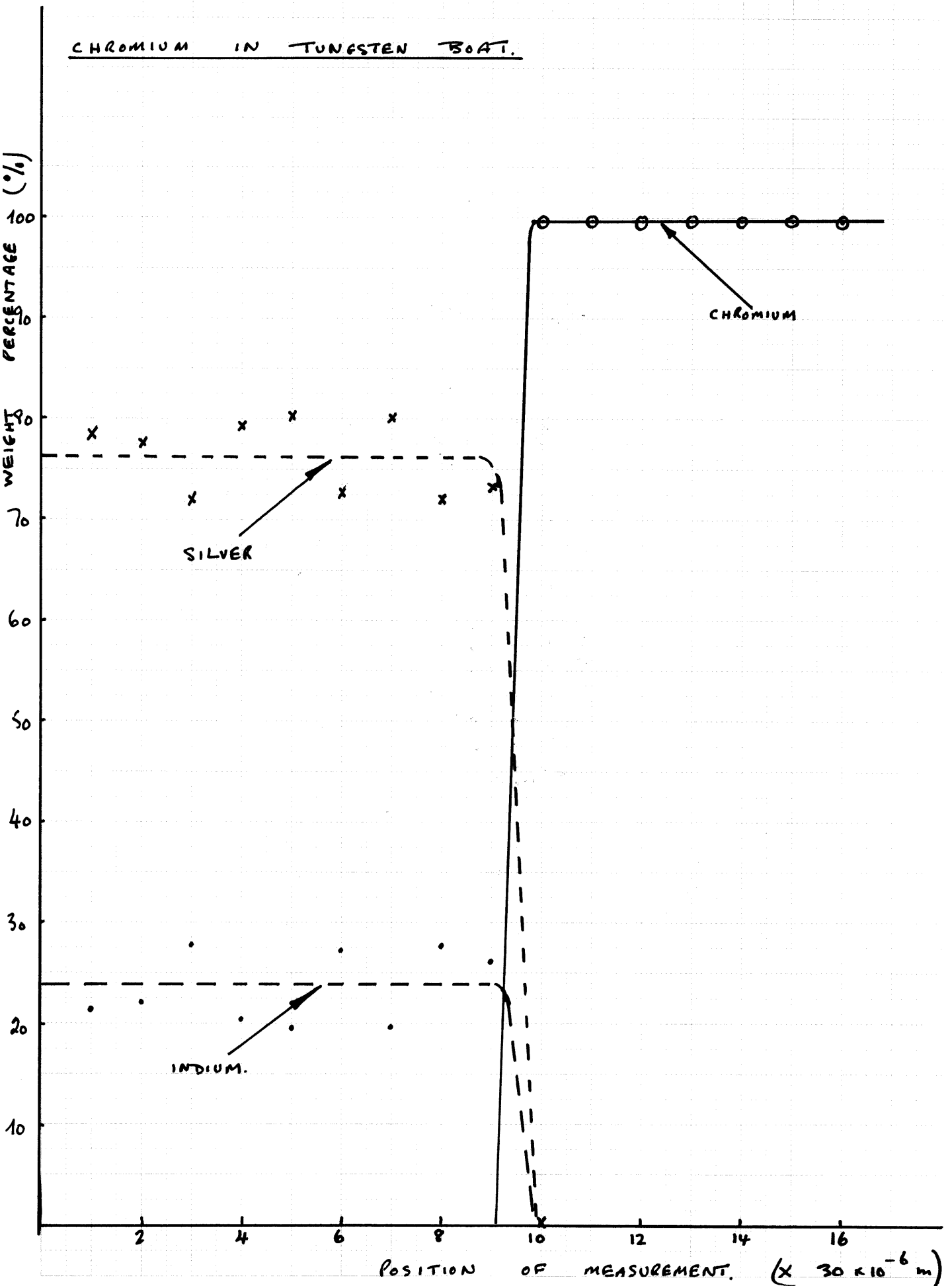


FIGURE 12. DISTRIBUTION OF CHROMIUM, SILVER & INDIUM

FROM S.E.M. STUDY OF SILVER-INDIUM ALLOY PLACED ON

CHROMIUM IN TUNGSTEN BOAT.



CHEMICAL FAMILY OF MATERIAL.	ENCLOSURE MATERIAL	MIGRATION OF ENCLOSURE MATERIAL INTO Au-Ge EUTECTIC ALLOY (%WHT)	MIGRATION OF Au-Ge EUTECTIC ALLOY INTO ENCLOSURE MATERIAL (%WHT)	COMMENTS.
<u>I</u> VI A	TUNGSTEN	0	0	EXCELLENT
<u>I</u> VI A	MOLYBDENUM	0	7 ± 1 (5 ± 1)	GOOD.
<u>I</u> VI A	CHROMIUM	$4.4 \pm 0,2$	$1,9 \pm 0,1$ (0)	FRAGMENTATION OF CHROMIUM AT SURFACE. OTHERWISE FAIR.
<u>I</u> V A	TANTALUM	0	$2,2 \pm 0,1$ (0)	VERY GOOD
<u>I</u> V A	NIObIUM	53 ± 5	0	VERY POOR RAPID ALLOY DETERIORATION.
<u>I</u> V A	ZIRCONIUM	18 ± 1	$1,5 \pm 0,1$ (0)	POOR. LOCALIZED GERMANIUM CONCENTRATION.
<u>I</u> V A	TITANIUM	23 ± 2	0	POOR. RAPID ALLOY DETERIORATION
<u>III</u> A	YTTRIUM	14 ± 1	23 ± 1 (21 ± 1)	POOR

(CORRECTED VALUES IN BRACKETS)

TABLE 1 SUMMARY OF MIGRATION EFFECTS IN Au-Ge ALLOYS.