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Effects of copper on the cupellation of silver

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EFFECTS OF COPPER ON THE CUPELLATION OF SILVER.

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The object of this work is to find the effect of copper in the cupellation of silver.

Our method of attack was:

1st. To find the effect of varying the amount of copper with constant lead and constant temperature.

2nd. Effect in cupellation of varying the temperature and the lead in the presence of a constant amount of copper.

3rd. To determine the rate at which the copper is removed during cupellation.

R.W.Lodge in his book on Assaying states,"If a lead button contains much copper,CuO will be formed with the PbO and this,when absorbed by the cupel,seems to take silver with it into the cupel."

Throughout the work temperatures were determined with a LeChetelier pyrometer, the junction being kept in contact with the muffle floor close to the cupel.

The silver absorbed by the cupel in each case as well as that which volatilized was determined.

The cupels were crushed through 80 mesh and the following charge used:

Litharge	90 grams.
Borax	30 "
Soda	15 "
Argols	2.5 "
Silica	2.0 "

From each cupel a four gram sample was saved for the determination of the copper absorbed. All copper determinations were made by the Iodide method.

Table I.

Cupellation Losses.

Temperature Constant (980°) — Lead Constant (20 grams) — Copper Varying.

Silver grams.	Copper		Weight of Silver Bead	% of Silver Loss	Weight of Silver in Cupel.	% Loss in Cupel.	% Volatilized.	% Copper absorbed by cupel.
	% of Lead	grams						
0.10000	0.25	0.05	0.09645	3.55	0.00288	2.88	0.67	95
0.10003	0.50	0.10	0.09641	3.61	0.00291	2.91	0.70	93
0.10003	0.75	0.15	0.09649	3.64	0.00289	2.89	0.75	89
0.10008	1.00	0.20	0.09632	3.75	0.00283	2.83	0.92	89
0.10000	1.50	0.30	0.09605	3.95	0.00291	2.91	1.04	81
0.10000	2.00	0.40	0.09613	3.87	0.00281	2.81	1.06	85
0.10009	2.50	0.50	0.09609	4.00	0.00281	2.81	1.19	87
0.10008	3.00	0.60	0.09603	4.05	0.00329	3.29	0.76	91
0.10006	3.50	0.70	0.09571	4.34	0.00312	3.12	1.22	85
0.10007	4.00	0.80	0.09538	4.68	0.00338	3.38	1.30	95
0.10012	4.50	0.90	0.09376	6.35	0.00338	3.38	1.51	82
0.10000	5.00	1.00	0.09470	5.30	0.00358	3.58	1.72	84
0.10005	0.00	0.00	0.09696	3.08	0.00243	2.43	0.65	

Several cupellations were tried with 1.6 grams of copper (and above) to 20 grams of lead. All these froze at 980 degrees C. Above 0.7 grams of copper the silver beads were flat but gave no test for copper.

Note especially that there is a decided increase in the loss of silver up to 2% copper and then the loss drops and increases again. These irregulatities were first thought to be erratic results but a second trial showed the same irregularities. There appears to be no considerable increase in the volatilization due to increased copper, therefore increased loss is due to increased cupel absorbtion.

Table II.

Cupellation Losses - Temperature Constant (880°) - Lead Constant (20 grams) - Copper Varying.

Silver Grams	Copper		Weight of Silver Bead.	% of Silver Loss	Weight of Silver in Cupel	% Loss in Cupel	% Volatilized	% Copper absorbed by Cupel.
	% of Lead	grams						
0.10012	0.25	0.05	0.09811	2.01	0.00187	1.87	0.14	91
0.10006	0.50	0.10	0.09785	2.20	0.00204	2.04	0.16	89
0.100085	0.75	0.15	0.09763	2.45	0.00225	2.25	0.20	69
0.10005	1.00	0.20	0.09785	2.20	0.00200	2.00	0.20	88
0.100055	1.50	0.30	0.09764	241	0.00210	2.10	0.31	89
0.10001	2.00	0.40	0.09746	2.55	0.00220	2.20	0.35	88
0.10005	2.50	0.50	0.09723	2.82	0.00236	2.36	0.46	92
0.10000	3.00	0.60	0.09716	2.84	0.00224	2.24	0.60	86
0.10000	3.50	0.70	0.09694	3.06	0.00242	2.42	0.64	94
0.10006	4.00	0.80	0.09685	3.20	0.00240	2.40	0.80	92
0.10004	4.50	0.90	0.09657	3.47	0.00258	2.58	0.89	91
0.10005	5.00	1.00	0.09548	4.56	0.00352	3.52	1.04	87
0.10009	0.00	0.00	0.09808	2.01	0.00188	1.88	0.13	

Note at this temperature there is a decided increase in the loss of silver up to 0.15% copper and then the loss drops and increases again.

Silver beads from the above cupellations were flat when more than 0.7 grams of copper was present but we found no trace of copper in the beads.

Table III

Cupellation Losses.

Temperature Constant (740°) – Lead Constant (20 grams) – Copper Varying.

Silver grams.	Copper		Weight of Silver Bead.	% of Silver Loss	Weight of Silver in Cupel.	% Loss in Cupel.	% Volatilized	% Copper absorbed by cupel.
	% of Lead	grams						
0.10008	0.25	0.05	0.09887	1.21	0.00113	1.13	0.08	96
0.10003	0.50	0.10	0.09878	1.25	0.00115	1.15	0.10	91
0.10000	0.75	0.15	0.09870	1.30	0.00138	1.38	0.09	89
0.10000	1.0	0.20	0.09855	1.45	0.00130	1.30	0.15	88
0.10007	1.5	0.30	0.09826	1.81	0.00167	1.67	0.14	91
0.10000	2.0	0.40	0.09850	1.50	0.00130	1.30	0.20	81
0.10011	2.5	0.50	0.09831	1.80	0.00164	1.64	0.16	84
0.10008	3.0	0.60	0.08826	1.72	0.00158	1.58	0.14	89
0.10010	3.5	0.70	0.09810	2.00	0.00183	1.83	0.18	87
0.10005	4.0	0.80	0.09790	2.15	0.00195	1.95	0.20	88
0.100045	4.5	0.90	0.09790	2.15	0.00190	1.90	0.25	89
0.10010	5.0	1.0	0.09778	2.32	0.00204	2.04	0.28	91
0.10009	0.0	0.0	0.09889	1.20	0.00111	1.11	0.09	

All cupels in the above table showed feathers of litharge crystals. Same tendency for beads to flatten when using over 0.7 grams copper. No copper was found in the beads.

Notice that an increase in copper at this temperature (740 degrees C.) does not cause as great an increase in the silver loss as was the case at the preceeding higher temperature (980 and 880 degrees C).

Also that loss drops with 2% copper and then increases again.

Table IV.

Cupellation Losses.

Temperature Constant (980°) – Copper Constant (0.1 grams) – Lead Varying.

Silver grams.	Lead grams	Copper grams	Weight of Silver Bead.	% of Silver Loss	Weight of Silver in Cupel.	% Loss in Cupel.	% Volatilized	% Copper absorbed by cupel.
0.10008	10.0	0.1	0.09647	3.60	0.00263	2.62	0.98	64
0.10002	15.0	0.1	0.09672	3.29	0.00197	1.97	1.32	53
0.10000	20.0	0.1	0.09634	3.65	0.00141	1.48	2.24	88
0.10006	25.0	0.1	0.09597	4.04	0.00180	1.79	2.25	92

Table V.

Lead and Copper Same as in Table IV. – Temperature (880°)

0.10000	10.0	0.1	0.09783	2.17	0.00187	1.87	0.30	82
0.10004	15.0	0.1	0.09770	2.34	0.00193	1.93	0.41	55
0.10006	20.0	0.1	0.09747	2.60	0.00158	1.57	1.03	51
0.10015	25.0	0.1	0.09750	2.64	0.00135	1.34	1.30	70

Table VI.

Cupellation Losses.

Temperature Constant (740°) — Copper Constant (0.1 grams) — Lead Varying.

Silver grams.	Lead grams	Copper grams	Weight of Silver Bead	% of Silver Loss	Weight of Silver in Cupel.	% Loss in Cupel.	% Volatilized	% Copper absorbed by cupel.
0.10000	10.0	0.1	0.09884	1.16	0.00111	1.11	0.05	49
0.10000	15.0	0.1	0.09882	1.18	0.00111	1.11	0.07	73
0.10004	20.0	0.1	0.09876	1.28	0.00115	1.15	0.13	69
0.10000	25.0	0.1	0.09876	1.29	0.00116	1.16	0.13	59

The above results show that the increase in lead increases the loss as time of driving is lengthened, also the higher the temperature the more loss resulting.

The following table shows temperature at which lead with given amounts of copper will freeze in cupellation.

Table VII.

The Following Shows the Results Which Were Obtained on Cupelling 20 Grams of Lead With Varying Amounts of Copper and the Time Which the Buttons "Drove" Before Freezing.

Copper grams	0.05	0.10	0.15	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.0
Temp. C.	670°	670°	680°	700°	705°	700°	710°	710°	720°	725°	735°	735°
Time.	17	18	16	16	15	17	14	14	14	20	12	12

The cupels were opened at 750° and then slowly brought to the front part of the muffle. The temperature of muffle floor at point where each froze was observed.

Behavior of Copper in the Lead Button.

It is not generally known just at what period of cupellation the copper is eliminated most rapidly. Can there be a concentration of copper in the lead?

To follow out the above results we tried five cupellations each,consisting of 20 grams of lead and one gram of copper. The first cupel was drawn fro m the muffle after two minutes of "driving" and was cooled rapidly. The second was removed after the end of four minutes and the third after six minutes,etc. The temperature of cupellation was 850 degrees C.

Table VIII.

Per Cent Copper and Lead Eliminated.

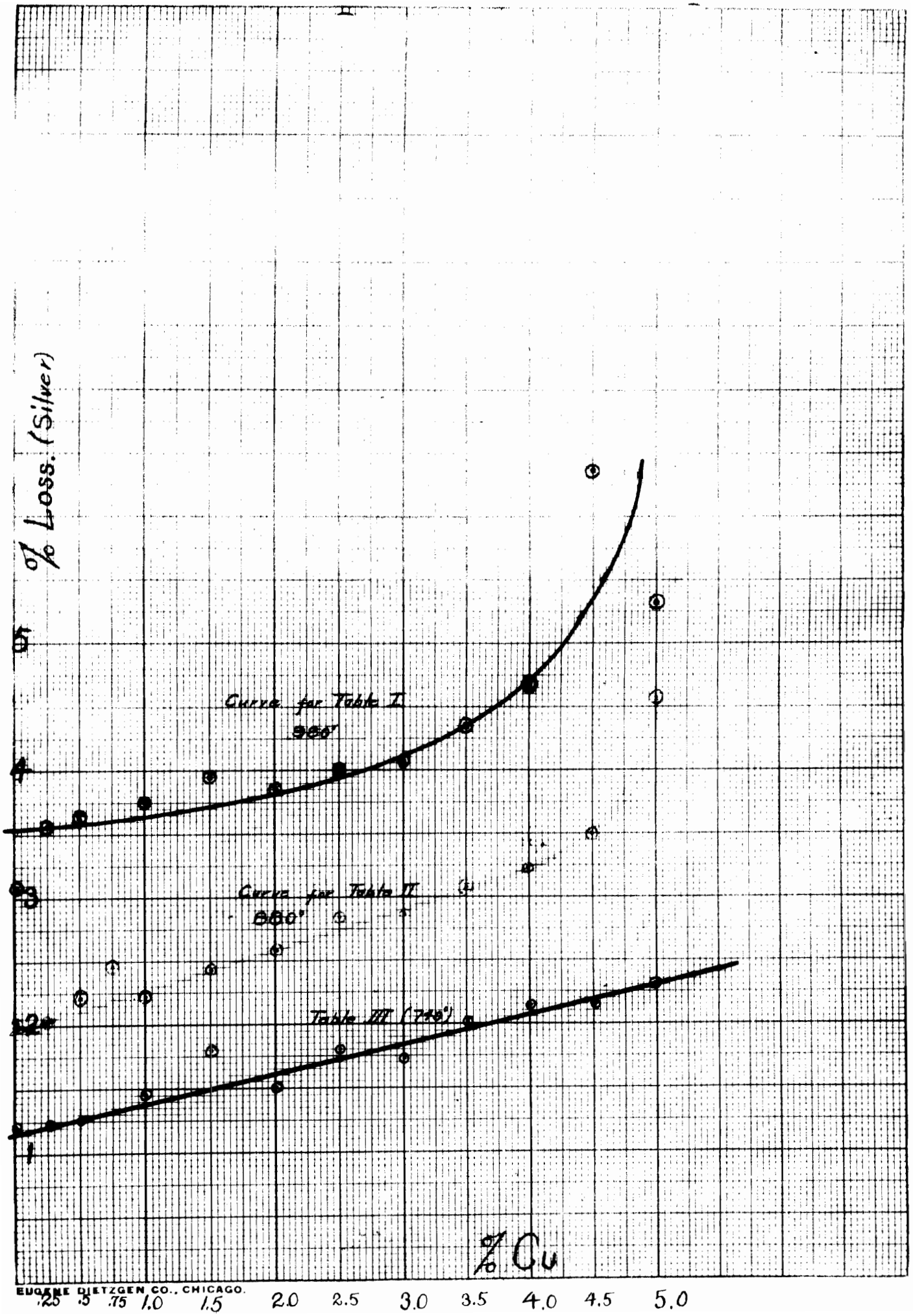
Temperature Constant (850°) — Lead Constant (20 grams) — Copper Constant (1.0 grams)

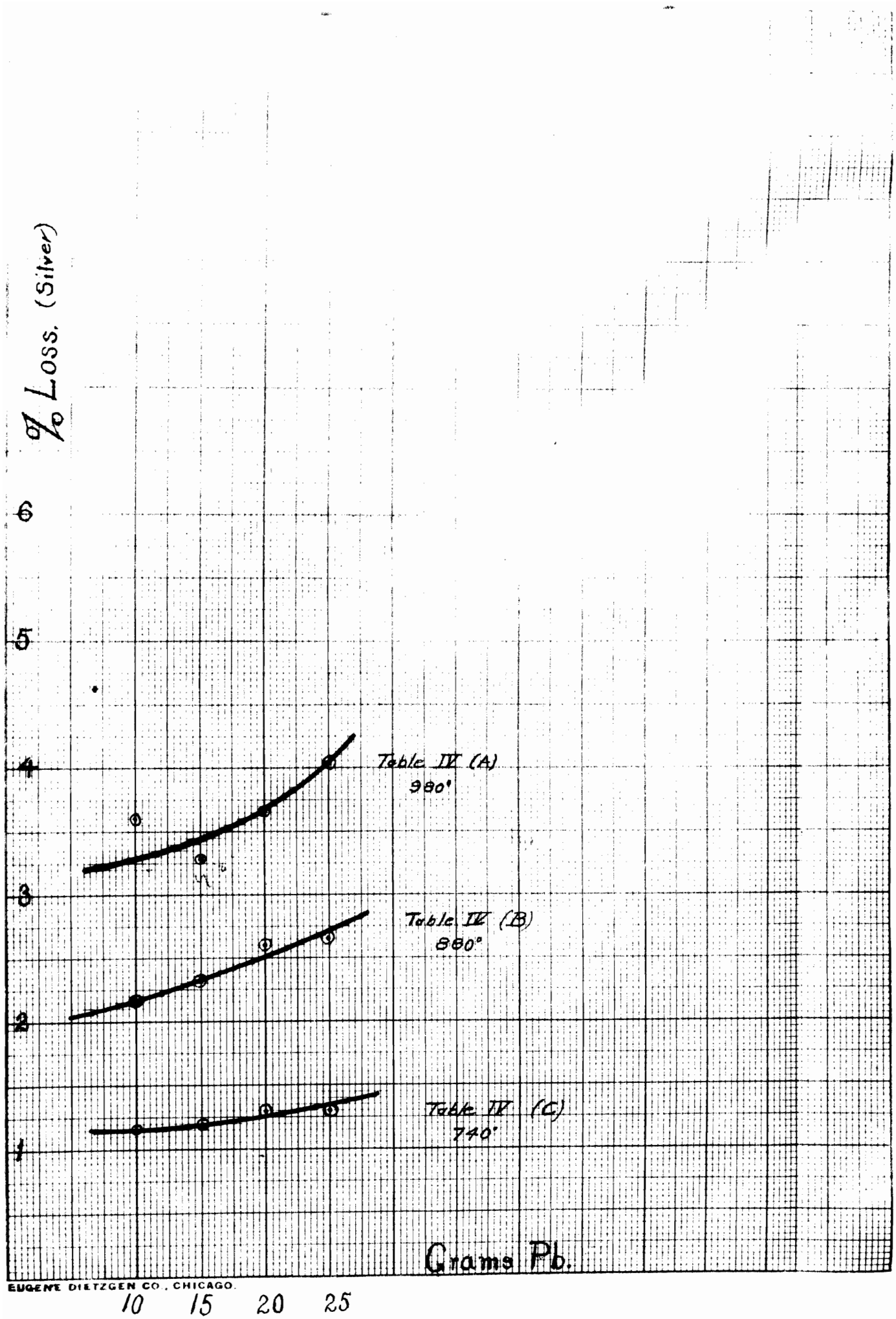
Number.	1	2	3	4	5
Weight of Lead.	15.55	12.0	9.2	7.55	6.25
% Lead Eliminated.	22.25	39.85	54.0	62.25	68.75
Weight of Copper	0.5424	0.4634	0.4140	0.2381	0.1887
% Copper Eliminated.	45.76	53.66	58.60	76.19	81.13

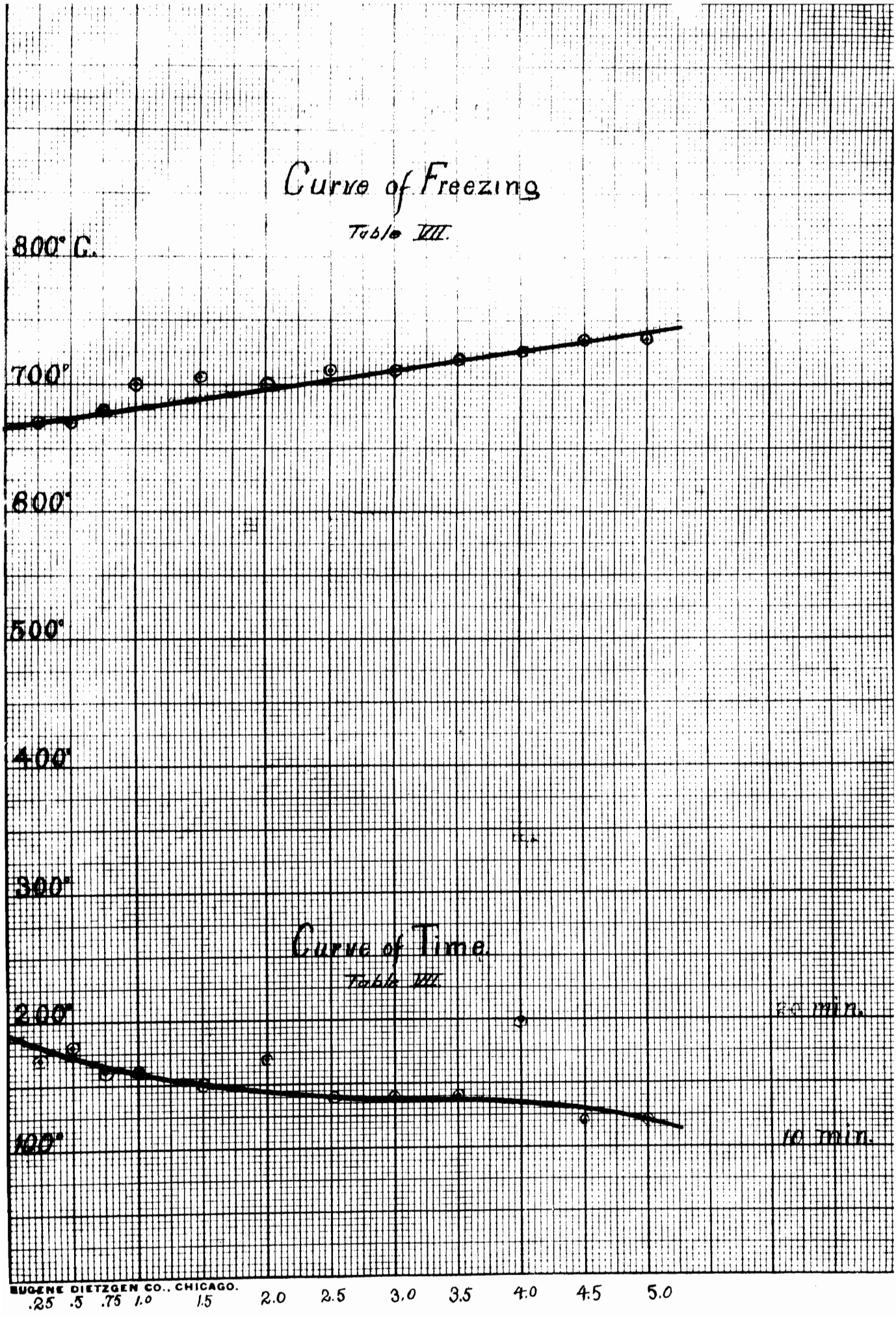
From the above it appears that the copper is eliminated at least as fast as the lead and that there is no concentration in the lead button.

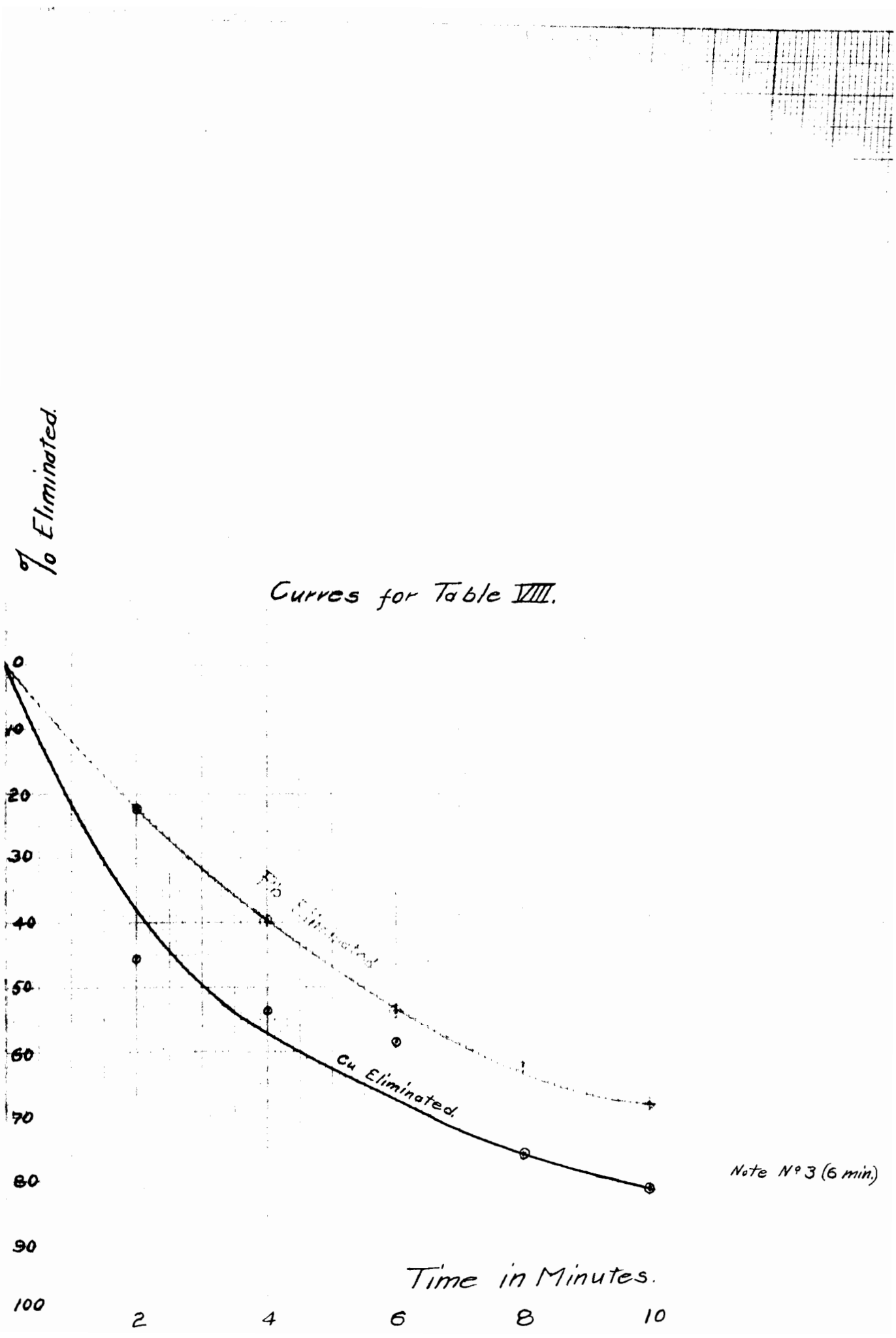
At the end of ten minutes driving there was elimihated 68% of the lead and 81% of the copper. For some reason the copper and lead are not absorbed in regularly increasing amounts.

Note in first two minutes that while 22% of the lead is being oxidized 45% of the copper is removed from the lead. During the next two minutes 17% of the total original lead is oxidized but only 8% of the copper.


% Loss. (Silver)
Curve for Table I
960°
Curve for Table II
860°
Table III (748°)
% Cu
.25 .5 .75 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0
EUGENE DIETZGEN CO., CHICAGO.




Curve of Freezing
Table VII.
800° C.
700°
600°
500°
400°
300°
Curve of Time.
Table VII.
2.00'
100°
10 min.
EUGENE DIETZGEN CO., CHICAGO.
.25 .5 .75 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0


% Eliminated.
Curves for Table VIII.
0
10
20
30
40
50
60
70
80
90
100
Cu Eliminated
Cu Eliminated
Note N° 3 (6 min.)
Time in Minutes.
2
4
6
8
10

All our work shows(note expecially the tables) the extreme inportance of having the correct temperature during cupellation.

With a high temperature the loss is higher. With increasing percent of copper the losses increase in a greater proportion than the copper increased. At 740 degrees C. the loss is low and up to one gram of copper the loss is about as low as if no copper were present. In the curves we find a point where the loss drops and then increases again.

In all cupellations it was noticed that the button containing copper up to 0.4 grams opened before those containing no copper. The reason for this may be that the heat evolved by the formation of CuO aids in fusing the lead button (PbO formed makes some heat also).If the lead button contains a small amount of copper (0.4%) the extra heat needed to fuse CuO may be small because the PbO can easily dissolve small amounts of CuO. If,however,the copper gets large,then due to the great amount of CuO formed the PbO cannot dissolve it and the button opens at a higher temperature.

The temperature of the muffle floor was approzimately 100 degrees C.higher than the temperature about 1/8 inch above the lead button. This appears to be contrary to the statements that the heat generated by the oxidation of the lead raises the temperature just above the cupel 100 degrees C. It may be that on the surface of the lead itself where the PbO is formed the temperature may be higher.

At high temperatures as in Table I (980 degrees C) there was a greater tendency for the beads to sprout than at 740 degrees. It is evident,therefore that high temperatures favor sprouting.

and sprouting is due to the button suddenly giving off the oxygen which it absorbed during cupellation and the higher the temperature the more liquid is the silver, therefore absorbs more oxygen during cupellation. Also the purer the silver button the more nearly it is apt to sprout at low temperature of cupellation. There may be a little copper left in the button which would tend to prevent sprouting.

Our work shows no trace of copper in the silver buttons.

The above does not include the raising of the temperature at time of blicking.

The increased loss in silver due to the presence of Copper at the ordinary cupelling temperature (740 degrees C) is slight if the copper percent be below 2%. 2% of copper causes an additional loss of silver of only 0.2 of 1%. This is evident by the results of Table III in which the cupellation having 2% copper has a loss of 1.3% silver while the cupellation under the same conditions and same time, excepting that copper is absent, shows a loss of 1.11% silver.

The copper absorbed by the cupels in all tables was on the average of 90% of the copper put into the lead button.

Ore.

A massive ore consisting of bornite and chalcocite running 62.6% copper. This ore was assayed,using three different crucible charges and one scorification.. The ore was crushed through 100 mesh,rolled and sampled.

Scorification Charge.

.1 A.T.	Ore	
70 grams	Pb.	
1.5 "	Borax	
1.0 "	Si02	

Ore Assayed 8.4 oz to ton
8.6 oz. to ton

Th lead button was not hard,therefore no rescorification was necessary.

Reducing Power of Ore.

Charge	Ore	3 grams
	PbO	80 "
	Soda	3 "
	Borax	5 "
	Borax Cover.	
Weight of Lead button		16.5 grams
Reducing Power		5.5

Crucible Charge No.I

High Litharge and low Soda.

Ore	0.5 A.T.
Soda	20 grams.
Borax	10 "
Litharge	150 "
KNO3	13 "
Silica	6 "

Borax Cover.

Ore Assayed	8.2 oz/ton
	7.9 "

A "G" crucible was used for this charge,the fusion done in a pot furnace. A 40 minute fusion gave a 22 gram button. Slag was fluid. Buttons were not hard so that scorification was not required. In cupellation the silver beads blicked after 28 minutes driving.

A four gram sample of the slag was saved for the determination of copper. This determination gave 12 % of total copper in ore removed by the slag

Crucible Charge No.II

Low litharge and high soda.

Ore	0.5 A.T.
Soda	30 grams.
Borax	10 "
Litharge	90 "
KnO3	13 "
Silica	6 "

Borax Cover.

Fusion took 40 minutes and slag poured well. The lead button was so hard and brittle that when it was hammered small particles broke off and were lost. The weight of button recovered was 24 grams. Although the button was cupelled at 850 degrees C. it froze after 25 minutes driving.

As in the previous case the amount of copper removed by the slag was determined. This showed a removal of 8.5% Copper.

Nails method.

Ore	0.5 A.T.
Soda	30 grams.
Borax	8 "
Litharge	30 "
Silica	2 "
Nails	3

A forty minutes fusion gave a 29 gram button. On top of the button was a layer of matte. It was hard,brittle and black. Did not scorify the button.

The slag was fairly fluid and black.

This button froze after 30 minutes of driving at a temperature of 850 degrees C.

The slag removed 5% of the copper in the ore.

From the preceeding results on the different charges we conclude that with high litharge and low soda more copper is removed by the slag. This is due to the oxidizing of the copper by the litharge so the slag can take it up/

Summing up our work,keeping in mind the problem which we set out to do at the beginning,what is the effect of copper on the cupellation of silver.

1st. When the copper varies,the lead,silver and temperature were constant.Noting tables I,II and III Copper does not effect the loss of silver as much as increased temperature.

2nd. When the copper is constant and the temperature and lead varies. Tables IV,V,VI,and VII show that the increase in lead increases the loss as time of driving is longer,also the higher the temperature the more loss resulting. Also that 0.1 of a gram of copper in the presence of as small amount of lead as 10 grams shows no appreciable extra loss of silver.

3rd. To determine at what rate the copper is absorbed by the cupel and if there is a concentration of copper in the lead as the cupellation proceeds.

Noting table VIII we see that the copper is eliminated faster in the first two minutes of driving,also there seems to be no concentration of copper in the lead.

We found no copper in any of the blicked silver beads. This is contrary to the usually accepted statement that there is copper in the silver buttons,resulting from the cupellation in the presence of copper.