

ORIGINAL PAPERS

A STUDY OF THE QUALITY OF PLATINUM WARE WITH SPECIAL REFERENCE TO LOSSES ON HEATING¹

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There was presented at the 49th Meeting of the American Chemical Society an account² of the examination of the purity of a number of platinum crucibles by a thermoelectric method in which the crucible forms one element of a thermocouple. This method has been found useful by ourselves and others for the ready classification of platinum utensils of various kinds and especially for the determination, in the case of purchases of platinum ware, whether or not such articles conform to specifications as to platinum purity. This thermoelectric test, which in no way mars the crucible or other article examined, is now a part of the routine of the Bureau of Standards and many samples of platinum have been so tested the past year; these were secured for the most part through Dr. W. F. Hillebrand, Chairman of the Committee of the American Chemical Society on "Quality of Platinum Utensils."

In Table I is shown the quality of platinum utensils of various sorts expressed in terms of equivalent iridium content as measured thermoelectrically at this Bureau. Of the 164 pieces examined it is seen

TABLE I.—CLASSIFICATION OF PLATINUM WARE SUBMITTED TO BUREAU OF STANDARDS FOR THERMOELECTRIC PURITY TEST

CLASS OF WARE INVESTIGATED	Crucibles	Crucible covers	Dishes	Misc.	TOTAL No.
No. pieces of each class.....	84	47	11	22	164
Equivalent Ir-content—per cent					
0.0 to 0.5.....	36	26	9	0	26
0.5 to 1.0.....	17	23	36	18	20
1.0 to 2.0.....	34	38	19	9	31
2.0 to 4.0.....	13	13	36	27	17
4.0 to 25.0.....	0	0	0	45	6

that nearly 75 per cent have impurities equivalent to over 0.5 per cent of iridium, and of the crucibles, 65 per cent have over 0.5 equivalent iridium content. Dishes and miscellaneous ware, in which stiffness is usually required and which are often not subject to heating and weighing, are heavily charged with impurities, usually iridium, the miscellaneous ware showing, for example, nearly half of the samples with over 4 per cent iridium.

In addition to data on the purity of platinum ware now in use, more exact information was desired by the committee concerning the losses on heating. The experiments here outlined, it is believed, furnish information concerning losses sustained by platinum crucibles of several grades of purity when subjected to continued heating. By suitable acid treatment after heating, it has been possible to give an estimate of the relative amount of iron present, and the crucibles have also been examined microscopically, and through the kindness of Dr. Burrows, magnetically.

As will be shown, a combination of these several methods, or some of them, usually gives sufficient data

¹ Paper read at the 50th Meeting of the American Chemical Society, New Orleans, March 31 to April 3, 1915. It will be published in full as a Scientific Paper of the Bureau of Standards.

² "A Thermoelectric Method for the Determination of the Purity of Platinum Ware," by George K. Burgess and P. D. Sale, *THIS JOURNAL*, 6 (1914), 452.

for the ready classification of various grades of platinum ware.

METHOD OF DETERMINING LOSSES ON HEATING—For an exact determination of the loss in weight of a crucible on heating, ignition over the blast lamp is not satisfactory. A preliminary series of experiments, using electric resistance furnaces with platinum and other metals as heating coils, carried out by members of the chemical staff of this Bureau, showed that one could not expect to obtain consistently reliable results in a furnace containing metal. A considerable number of measurements of losses on heating at sev-

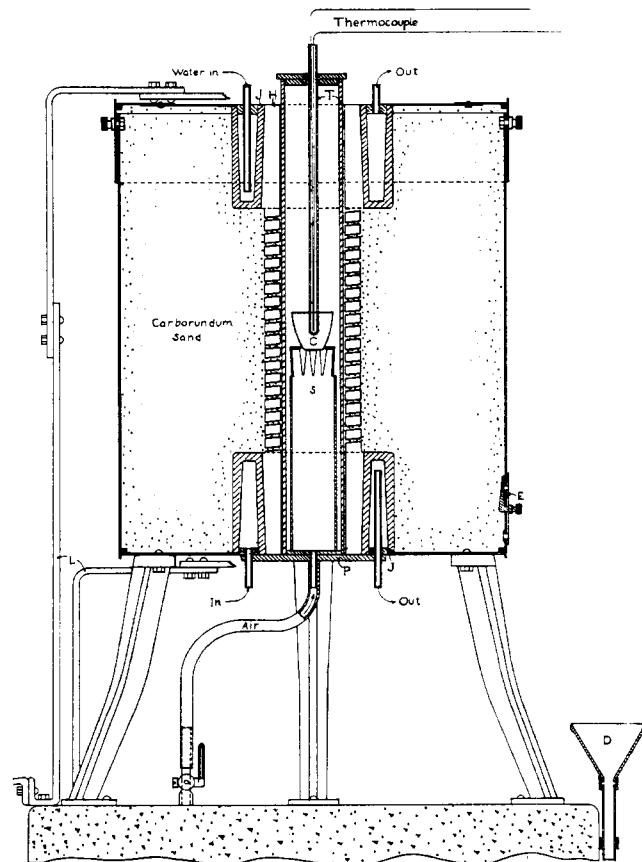


FIG. 1—HEATING FURNACE

C—Platinum Crucible H—Graphite Heater P—Bottom Cover Plate
D—Water Drain J—Water Jackets S—Crucible Support
E—Sand Emptying Door L—Current Leads T—Marquardt Protecting Tube

eral temperatures were so taken, but no very definite conclusions can be drawn from these preliminary observations, which were obtained before the thermoelectric method of classification was put into practice.

The method finally adopted for determining heat losses in crucibles is based on the use of a metal-free electrically heated furnace, similar to one which had been in use for other purposes at the Geophysical Laboratory, accompanied by exact weighings of the crucible before and after each heating of 2 hours duration at 1200° C., together with a weighing to determine the iron loss after washing in acid.

The essentials of the furnace are shown in Fig. I. The heating spiral *H* is of graphite set into brass water-cooled terminals. The crucible *C* is supported on a Marquardt porcelain stand, *S*, as shown and enclosed within a tube, *T*, of the same material. Temperatures were measured by a platinum platinum-rhodium thermocouple enclosed in Marquardt. The furnace takes about 3.5 kw. A. C. at 1200° C.

For a region of about three crucible heights at the

ACID TREATMENT—Iron and other soluble materials were removed, and determined by weighing, after each heating. For several of the crucibles examined, the characteristic reddish coating due to iron oxide appeared after each heating. The acid treatment consisted in boiling the crucible for 5 min. in 25 per cent hydrochloric acid contained in a large covered porcelain crucible.* The iron was determined by precipitation with ammonia upon ashless filter paper,

TABLE II—HEATING AND ACID TREATMENT ON PLATINUM CRUCIBLES (MILLIGRAMS PER CM²).—(SEE TABLE III FOR KEY TO CRUCIBLES)

E. M. F. measurements: Millivolts at 1100° C., crucible vs. pure Pt (I, I')													
Heat treatment loss: Milligrams per 100 cm ² , for 2 hrs. heating at 1200° C. (II, III, IV)													
Acid treatment loss: Milligrams per 100 cm ² , for 5 min. boiling in 25 per cent HCl (II', III', IV')													
Recovered Fe ₂ O ₃ : Milligrams per 100 cm ² , per treatment with NH ₄ OH and ignition on ashless paper (IX, X, XI, XII)													
Crucible reference letter	a	b	c	d	e	f	g	h	i	j	k	l	m
I E. M. F. at beginning	0.10	0.50	0.65	0.70	0.70	1.90	2.80	3.00	6.40	6.70	7.00	7.30	9.30
I' E. M. F. at end	0.07	0.50	0.62	0.70	0.70	1.85	2.80	2.95	5.95	6.10	6.00	6.50	9.30
II E. M. F. mean I and I'	0.09	0.50	0.64	0.70	0.70	1.88	2.80	2.98	6.18	6.40	6.50	6.90	9.30
II 1st heat, 2 hr. at 1200° C.	2.18	1.98	2.16	1.27	2.46	2.00	1.08	1.38	7.47	1.94	6.24	2.16	1.74
II' 1st acid, 25 per cent HCl	0.05	0.24	0.06	0.19	0.83	0.16	1.76	3.82	0.81	9.50	1.14	5.33	0.46
II + II'	2.23	2.22	2.22	1.46	3.29	2.16	2.84	5.20	8.28	11.44	7.38	7.49	2.20
III 2nd heat, 2 hr. at 1200° C.	0.84	0.96	1.93	1.36	0.26	2.20	2.18	0.43	4.42	4.93	5.45	2.32	1.08
III' 2nd acid, 25 per cent HCl	0.30	0.35	0.18	0.17	0.56	0.09	0.99	1.24	0.16	1.84	0.39	2.47	0.13
III + III'	1.14	1.31	2.11	1.53	0.82	2.29	3.17	1.67	4.58	6.77	5.84	4.79	1.121
IV 3rd heat, 2 hr. at 1200° C.	1.85	2.04	1.61	1.63	2.02	2.16	2.36	0.75	4.38	3.23	2.94	5.08	1.00
IV' 3rd acid, 25 per cent HCl	0.06	0.15	0.11	0.09	0.26	0.07	0.40	0.34	0.08	0.66	1.01	2.79	0.10
IV + IV'	1.91	2.19	1.72	1.74	2.28	2.23	2.76	1.09	4.46	3.89	3.95	7.87	1.10
V Σ II, III, IV, heat loss	4.87	4.98	5.70	4.28	4.74	6.36	5.62	2.56	16.17	10.10	14.33	9.86	3.82
VI Σ II', III', IV', acid loss	0.41	0.74	0.35	0.45	1.65	0.32	3.15	5.40	1.05	12.00	2.54	10.59	0.69
VII Σ V, VI, total loss	5.28	5.72	6.05	4.73	6.39	6.68	8.77	7.96	17.22	22.10	17.17	20.13	4.51
VIII Total change E. M. F.	0.03	0.00	0.03	0.00	0.00	0.05	0.00	0.05	0.45	0.60	1.00	0.80	0.00
IX Iron as Fe ₂ O ₃ after II'	0.147	0.125	..	0.099	0.544	0.005	1.080	0.794	0.052	0.520	0.090
X Iron as Fe ₂ O ₃ after III'	0.216	0.202	..	-0.022	0.357	0.113	0.272	0.714	0.026	0.603	0.168
XI Iron as Fe ₂ O ₃ after IV'	0.103	0.102	..	0.123	0.628	0.270	0.072	0.454	0.057	0.295	0.004
XII Total iron as Fe ₂ O ₃	0.466	0.429	..	0.200	1.529	0.388	1.424	1.962	0.135	3.418	0.262
XIII Total iron compared to T. L. in %	8.82	7.50	..	5.16	23.95	5.81	16.25	24.65	0.78	15.46	7.59
XIV Total iron compared to acid L. in %	100.00	58.00	..	53.30	100.00	45.40	36.35	12.87	28.45	100.00
XV Total acid compared to T. L. in %	7.76	12.93	..	9.50	25.80	4.78	35.95	67.80	6.10	54.30	5.51

center of the furnace, there was maintained a practically uniform temperature, 1200° C., and this inner portion of the furnace never became blackened. A slight current of air was maintained about the crucible, as shown, but great care was taken, by means of a sand and paraffine seal, at *P*, to prevent vapors passing from the heating spiral into the inner chamber. The crucible was not placed in the furnace until this had reached 1000° C.; a temperature of 1200° C. was

ignited in platinum for 1 min. at about 1200° C., and weighed as ferric oxide.

EXPERIMENTAL RESULTS—Fourteen crucibles were carried through a series of identical operations consisting of a determination of their equivalent iridium or rhodium content by the thermoelectric method¹ (see lines I, I' of Table II); the determination of losses of weight after each of three heatings of two hours each at 1200° C. (see lines II, III, IV, each followed

TABLE III—CLASSIFICATION OF WARE BY E. M. F., VOLATILIZATION, CHEMICAL, MAGNETIC AND PHOTOGRAPHIC DATA

Crucible reference letter	Mean E. M. F. millivolts	Equivalent content Per cent	Equivalent Fe (magnetic) Per cent	Wt. of Fe remaining magnetic test	Maker's chemical statement Per cent	RELATIVE Fe by VI Table II	Fe by susceptibility	Fig. II	CLASSIFICATION with reference to
a	0.09	0.05	0.05	0.0001	0.018	1.0	1.0	Pt	Pt
b	0.50	0.10	0.19	0.0022	0.576	1.8	26.0	Rh or Pt	Pt-Rh
c	0.64	0.20	0.29	0.9	..	Pt-Ir	Pt-Ir
d	0.70	0.21	0.30	0.0012	0.194	1.1	14.0	Pt-Ir or Rh	Pt-Ir-Fe
e	0.70	0.21	0.30	0.0007	0.112	4.0	8.0	Pt-Ir	Pt-Ir-Fe
f	1.88	0.55	0.85	0.8	..	Pt-Ir	Pt-Ir
g	2.80	0.90	1.29	..	0.70 Ir	7.7	..	Pt-Ir-Fe	Pt-Ir-Fe
h	2.98	1.00	1.40	0.0010	0.106	8.5	11.0	Pt-Rh	?-Fe
i	6.18	2.30	3.53	..	2.37 Ir	2.6	..	Pt-Ir	Pt-Ir
j	6.40	2.40	3.70	0.0110	1.859	0.5 to 1.5 Ir	29.0	Pt-Ir-Fe	Pt-Ir-Fe
k	6.50	2.42	3.75	6.3	..	Pt-Ir-Fe	Pt-Ir
l	6.90	2.65	4.15	0.0050	0.198	26.0	6.0	Pt-Ir-Fe	Pt-Ir-Fe
m	9.30	3.75	7.30	1.7	..	Pt-Rh	Pt-Rh
n	9.70	3.95	7.95	0.5	..	Pt-Rh	Pt-Rh

KEY TO CRUCIBLES		Previously heated		Previously heated	
a	Heraeus normal thermoelement platinum	Bought	1911	h	Baker & Company
b	Johnson, Matthey & Co., best crucible ware	1911	17 hr.	i	Baker & Company, special analyzed make
c	Johnson, Matthey & Co., best crucible ware	1913	67 hr.	j	American Platinum Works, commercial ware
d	American Platinum Works, "Tiegel Platin" (Heraeus)	1911	24 hr.	k	Baker & Company, commercial ware
e	J. Bishop & Co., specially refined ware	1911	31 hr.	l	Baker & Company, commercial ware
f	Baker & Company, special analyzed make	1912	12 hr.	m	Baker & Company, special Rhodium ware
g	Quenessen De Belmont, Legendre & Cie	1911	10 hr.	n	Baker & Company, special Rhodium ware

then attained in about 10 min. and held constant for exactly 2 hrs. and cut off, the crucible being removed 10 min. later or at about 900° C.

Crucible weighings were made on an enclosed precision balance, at first to 0.001 mg. and later to 0.01 mg. as this latter was found sufficient. All weights are reduced to a common basis of loss per 100 cm² of total crucible surface.

by determination of loss by acid treatment, lines II', III', IV', and of iron content, lines IX, X, XI). As seen from Table III, these fourteen crucibles range in equivalent iridium content from 0.05 (*a*) to 2.65 (*l*) per cent; crucibles *m* and *n* were supposed to be 90 platinum-10 rhodium; but as measured thermoelectrically, they contain 7.30 and 7.95 per cent

¹ Loc. cit.

rhodium, respectively, the former having been used considerably and the latter an unused crucible; some of the others are of unknown composition and the non-platinum content of each is expressed both in terms of iridium and rhodium (see lines 2 and 3 of Table III). In Table IV the heating and acid losses are given for four crucibles which underwent additional heating.

The microscopic observations were helpful in finally classifying the crucibles in terms of their main impurity—iridium or rhodium (see last line of Table III), as it was found that the crystalline structures

TABLE IV—LOSSES IN WEIGHT DUE TO HEATING AND ACID TREATMENT ON FOUR CRUCIBLES IN MILLIGRAMS, PER 100 CM², AFTER SUCCESSIVE 2-HOUR HEATINGS AT 1200° C

Treat- ment	CRUCIBLE <i>n</i>			CRUCIBLE <i>l</i>			CRUCIBLE <i>h</i>			CRUCIBLE <i>c</i>		
	Heat	Acid	Total	Heat	Acid	Total	Heat	Acid	Total	Heat	Acid	Total
1st	0.98	0.00	0.98	4.30	0.77	5.07	6.24	1.14	7.38	2.16	0.06	2.22
2nd	2.30	0.18	2.48	2.32	2.47	4.79	5.45	0.39	5.84	1.93	0.18	2.11
3rd	0.61	0.02	0.63	5.08	2.19	7.27	2.94	1.01	3.95	1.61	0.11	1.72
4th	1.44	0.13	1.57	7.40	2.60	10.00	3.78	0.60	4.38	2.34	0.09	2.43
5th	1.21	0.04	1.25	4.04	2.37	6.41
6th	0.81	0.06	0.87
Total	7.35	0.43	7.78	23.14	10.40	33.54	18.41	3.14	21.55	8.04	0.44	8.48
Av.	1.23	0.07	1.30	4.63	2.08	6.71	4.60	0.79	5.39	2.01	0.11	2.12

characteristic of these alloying metals imparted their appearance to the unetched crucible even when present in small percentages. On fresh platinum ware containing considerable rhodium a characteristic bluish color will usually appear after heating to a dull red.

The presence of iron appears to manifest itself in the microphotographs by pitting after heating. The relative amounts of iron in several crucibles were also determined, after the last heating and washing, by measurement of the magnetic susceptibility by a solenoid and balance method in a field of 60 gauss, the crucibles being arranged only approximately in the same order by chemical analysis following heating and by the magnetic measurements (see Table III). It is also of interest to note that iron-free platinum appears to have a susceptibility of zero, and that the susceptibility of "platinum" ranges from 1 to 125. A value of about 20, in the same units, has usually been found for the susceptibility of pure platinum, due undoubtedly to the presence of iron. The total amount of iron in a crucible cannot be determined readily from the magnetic measurements, as is seen by comparison of the magnetic and chemical data of Table III; and the iron, which is supposedly in solution in the platinum, on heating diffuses to the surface as fast as removed by oxidation, thus tending to establish an equilibrium between the iron oxide, oxygen and the iron-platinum solution at the temperature of the experiment. The iron was found non-uniformly distributed in some of the crucibles. The iron washed out in three acid treatments is seen to be greater than the total iron content calculated as iron from the magnetic data, showing that the Fe-Pt alloy containing only a few hundredths per cent iron is paramagnetic and also, from the data, that the susceptibility is not proportional to the iron content.

Considering further the inferences to be drawn from the results recorded in Tables II, III and IV, it is seen that, taking the E. M. F. as a criterion of purity, there is a purification of all crucibles containing over 0.5 per cent iridium after heating. The

platinum-rhodium crucibles (*m* and *n*) do not change composition on heating; that is, the iridium passes out of the crucible and the rhodium does not appreciably.

The losses on heating and after acid treatment are seen to be fairly uniform for each crucible. For some of the less pure crucibles the loss in washing is greater than the heating loss (notably for crucibles *h*, *j*, and *l*). The total heating losses per 100 cm². range from 4.28 to 16.17 mg. for 6 hrs. at 1200°, and the total acid losses (due mainly to iron) from 0.32 to 12.00 mg., for the crucibles containing iridium. For the platinum-rhodium crucibles, *m* and *n*, containing 7 to 8 per cent rhodium, the total losses on heating and washing together are one-fourth less than for the heating loss alone for purest platinum (crucible *a*). In general, there is no relation between the acid loss and loss on heating of crucibles containing both iridium and iron, showing the independence of the determination of loss of soluble and insoluble materials by these

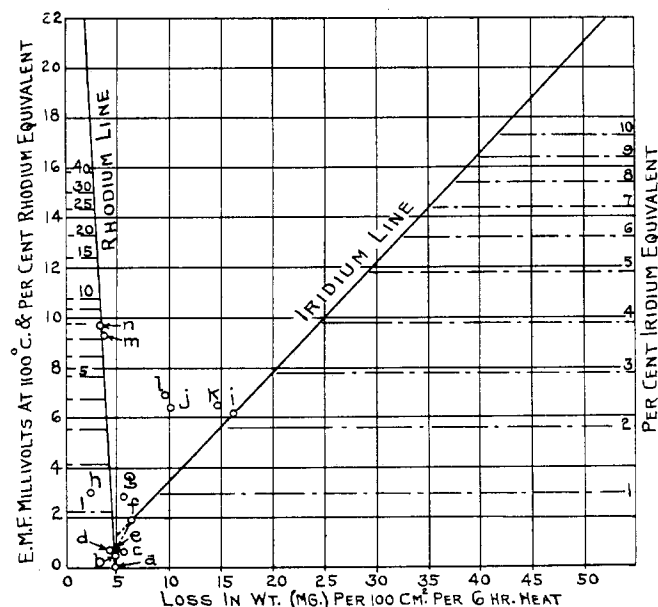


FIG. 2—VOLATILIZATION VS. THERMOELECTRIC FORCE

methods, although relatively large amounts of iron appear to lower somewhat the losses on heating that would otherwise be observed (see crucibles *h*, *j*, *l*). The acid losses are seen to vary from all iron to only 13 per cent iron.

THE PREDICTION OF HEATING LOSSES—The question arises, can the probable loss on heating of a given crucible of unknown composition be predicted from these data? Although a definite answer cannot be given, nevertheless the observations point to a reasonable probability of affirmative reply.

Consider Fig. 2, in which the heating losses are plotted against E. M. F. at 1100° C. against pure platinum for each of the 14 crucibles. The purest crucibles *a*, *b*, *c*, *d* and *e* all lie close together at 5 mg. loss and less than 1 millivolt. The platinum-rhodium crucibles *m* and *n* lie on a line inclined to the left of 5 mg., and which would reach to the heat loss for pure rhodium as a limit. The platinum-

iridium crucibles *f* and *i*, containing negligible iron, lie on a line inclined to the right of 5 mg. The platinum-iridium crucibles containing considerable iron, *h*, *l*, *j* and *k*, lie to the left of the iridium line; *h* may also contain rhodium.

It would follow, therefore, that one would expect a crucible nearly free from iron (which fact is readily tested by heating over the blast lamp) with a measured E. M. F. of say 8 millivolts against pure platinum, to lose 4 mg. per 100 cm². of surface in 6 hours at 1200° C. if made of a rhodium alloy of platinum, and would expect it to lose about 20 mg. if of an iridium alloy. The distinction between these iridium and rhodium alloys may usually be made microscopically, the former having definite smooth crystals with heavy boundaries and the latter a less pronounced and more irregular type of crystals. When iron is present these heat losses will be reduced somewhat and may be halved, since the effective disintegration area is reduced by the layer of iron oxide. Fig. 2 may therefore be used, at least approximately, as a basis for estimating losses on heating of platinum crucibles for the usual products found on the market and Fig. 2 is probably reliable for practically iron-free crucibles containing up to 40 per cent rhodium or to perhaps 10 per cent iridium.

In view of the fact that a satisfactory determination of the loss on heating for any type of crucible can be made only by elaborate experimentation, it is evidently of interest to be able to substitute the simple thermo-electric test and microscopic examination.

SUGGESTIONS AS TO SPECIFICATIONS—What is desired in a crucible for exact analytical work is a material which will strictly maintain its weight on heating and on treating with strong acid after heating; which will not exude any oxidizable or soluble matter on heating; which will not crack or develop other mechanical defects; and which is stiff enough to handle conveniently with tongs. Some of these requirements appear to be simultaneously difficult of realization in the present state of our science and of the art of working platinum and its alloys.

Iridium, which adds stiffness to platinum, renders the crucible subject to proportionally greater losses of weight on heating. The presence of iron appears to lower materially the heat losses but is very objectionable on account of the formation of a soluble oxide coating. The purest platinum is usually not stiff enough, although two or three of the apparently purest crucibles here examined were unaccountably stiff, perhaps because of the presence of a small amount of osmium or silica. Rhodium both stiffens the crucible and lowers the heat and acid losses and is much to be preferred to iridium as an alloying element, and crucibles containing small amounts of rhodium, say from 3 to 5 per cent, are to be preferred to crucibles of pure platinum. As the rhodium content is increased the crucible may develop cracks in service.

A requirement which might reasonably be met, at not too great expense for highest grade crucibles, would be: platinum containing 3 to 5 per cent rhodium,

practically free from iron and iridium, and containing no other detectable impurities. For most purposes, these requirements could be checked by assuring one's self that the E. M. F. at 1100° C. against pure platinum was less than 8 and greater than 5 millivolts; that the characteristic crystal structure was that of rhodium and not iridium; and that no iron hydroxide precipitate was obtained after ignition for two hours over strong blast and applying the acid treatment as above described. If pure platinum were preferred, the E. M. F. at 1100° C. should be less than 1 millivolt. If other stiffening ingredients than rhodium be allowed, the 1 millivolt E. M. F. requirement should be maintained.

SUMMARY AND CONCLUSIONS

I—There were examined by the thermoelectric method 164 pieces of platinum ware of which 26 per cent contained less than 0.5 per cent iridium and 67 per cent less than 2 per cent of iridium. Of 84 crucibles 36 per cent contained less than 0.5 per cent iridium and 87 per cent less than 2 per cent iridium.

II—A method has been developed for determination of the exact loss on heating of platinum crucibles, by means of a suitable electric furnace containing no heated metal parts.

III—Fourteen crucibles of various makes and grades were examined for loss in weight on heating and after acid treatment following each heating. Their magnetic susceptibilities were also determined. The susceptibility of pure platinum is zero and the range of susceptibility for seven crucibles is 1 to 125.

IV—The heating losses per 100 cm². of practically iron-free crucible surface at 1200° C. ranged from 0.71 mg. to 2.69 mg. per hour, the lesser losses being for crucibles containing rhodium and the greater losses being associated with iridium.

V—Iron appears to lessen somewhat the loss of weight on heating but its presence is objectionable on account of the soluble oxide formed on the crucible surface. The chemical analyses and magnetic measurements place the crucibles in only approximately the same order as to iron content; the magnetic susceptibility is not, however, proportional to the iron content.

VI—It appears to be possible, from a thermoelectric and microscopic examination of a crucible, to predict its probable loss of weight on heating within limits close enough for analytical purposes.

VII—Suggestions are offered concerning the specifications of highest grade platinum crucibles, including the substitution of rhodium to 5 per cent for iridium, and the practical elimination of iron.

VIII—Whether crucibles have been long in use or not, after the first two or three heatings and acid washings, appears to have little or no effect in their behavior as to losses on heating and washing.

We wish to express our obligation to Dr. W. F. Hillebrand who has furnished many valuable suggestions which have aided the progress of this investigation.

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