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THE MEASUREMENT OF GOLD AND SILVER BUTTONS IN QUANTITATIVE BLOWPIPE ASSAYS.

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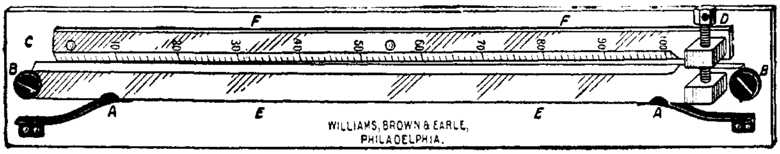
WHEN Harkort, a Freiberg student, invented the quantitative blowpipe assay for gold and silver, in 1824, he was at once confronted with the impossibility of weighing the very small buttons obtained. He surmounted the difficulty by assaying a silver ore repeatedly in the muffle, until he knew with exactness its contents. Then he assayed a standard weight of it by the blowpipe and obtained a button of a certain size whose weight was known from the amount of ore taken. Taking half and a third and a quarter of the weight of ore he obtained smaller buttons of known weight. With these he constructed a scale. He drew two fine slightly diverging lines on white cardboard, placed the buttons between the lines at the points where they fitted, and marked opposite those points the corresponding weights, or, rather, the corresponding silver contents of the ore, assuming a standard weight taken for assay.

Harkort brought the method to the attention of Plattner, the professor of metallurgy at Freiberg, and published his results at his own expense in a small book entitled "Silverprobe vor dem Löthrohr," Freiberg, 1827.

Plattner took up this method in his regular course of instruction, and improved and extended it. One of his principal improvements was the construction of the button scale ruled on ivory, made by the mechanic, August Lingke, at Freiberg. To fix accurately the dimensions of this scale, Plattner assayed a very rich silver ore repeatedly in the muffle until it was known with certainty to contain exactly 3.48 per cent. of silver. He then made repeated blowpipe assays of this ore, obtaining buttons very close together in size and weight. The two lines were then drawn on ivory so that they diverged approximately the diameter of these buttons in 150 millimeters. The buttons were then fitted exactly between the lines, and the point marked 50, the



distance from here to the meeting point of the lines being divided into fifty equal divisions. The exact dimensions of the scale as thus made were 156 mm. from 0 to 50, and the lines 0.9 mm. apart at 50. The weights corresponding to the various numbers were calculated from the number 50 representing 3.48 milligrams of silver (when 100 mg. were taken for analysis), using the assumption that as the buttons were nearly spheres, or, at least, were homologous in shape, their weights would vary as the cubes of their respective horizontal diameters. The weight of the silver button corresponding to any number from 1 to 50 would be therefore $3.48 \times \left(\frac{n}{50}\right)^3$, and thus these weights were all calculated and engraved on the scale opposite the numbers. A similar set of weights was obtained in an exactly similar manner for gold buttons. Thus the Plattner ivory scale was devised and is still used more extensively than any other method of measuring these small buttons.

The defects of the Plattner scale may be enumerated under the heads of :

1. Errors in construction.
2. Errors in using.

The errors in constructing the scale may be as follows:

a. The lines are sometimes not mathematically straight.

b. The lines may be rough or ragged.

c. The lines may not meet exactly at the point marked zero.

d. The lines may not be exactly the right distance apart (0.9 mm.) at the point marked 50.

It is seldom that the best scales made in Freiberg are free from one or more of these defects; I do not believe that more than one out of five is perfect.

The errors in using the scale consist of:

a. Placing the button too high or too low through optical illusion. The button should be tangent to the inside of the lines, and in a strong light the white metallic surface of the button is difficult to see on its outer edge. One investigator has even proposed putting the silver buttons a short time into ammonium sulphide, so as to blacken them and thus facilitate their measurement.

b. Placing the button too high by virtue of parallax, which projects the middle diameter of the button against the scale on which it rests, and makes the button seem to fit higher up than its real diameter. The remedy for this is to sight first down one side of the button, then down the other, each time looking perpendicularly to the scale. This operation is tedious, and takes considerable experience.

c. The button being nearly round, it takes considerable time, patience, and experience to get it to a certain spot on a flat surface. This is not an error of the scale, but an unavoidable inconvenience, which becomes accentuated if the ivory warps, so that the scale does not lie level. A beginner will frequently make a greater mistake in measuring a button than in getting it.

Goldschmidt's Method.—Dr. V. Goldschmidt, of Heidelberg, proposed two improvements:

1. To Remelt the Cupelled Buttons on Charcoal.—This gives to them a more nearly spherical and more uniform shape than is obtained on the cupel. The button is to be removed from the cupel, hammered flat between paper, to clean it, and then touched with the reducing flame, on charcoal, just long enough for it to melt and take the spherical form. Buttons thus remelted will be heavier than cupelled buttons of the same horizontal diameter, and, therefore, heavier than the given weights on the Plattner scale.

2. *Measuring the Horizontal Diameter of Such Remelted Buttons Under the Microscope.*—For this purpose, a divided scale is put into the focus of the eyepiece of a compound microscope magnifying 50 to 100 diameters. A scale of 40 divisions is very suitable, the tenths of each division being estimated when measuring. The buttons are placed on a glass plate, a piece of blue glass gives a nice background, and since they come to rest only on their bases, the horizontal diameter is always in position to be measured. The diameter being known in whole divisions and tenths, reference to a previously constructed table gives the volume and weight of the button, when of gold or silver.

To construct this table, the following ingeniously devised plan was worked out by Goldschmidt : A number of bits of pure gold are melted on charcoal. The buttons obtained are each measured separately, in divisions on the scale. All the buttons are then weighed together, as accurately as possible. The total weight, divided by the specific gravity of gold, gives the sum of the volumes of the buttons. This latter, divided by the sum of the cubes of the separate diameters (expressed in divisions on the scale), gives a function μ. This function is the factor by which to multiply the cube of the diameter of any button to get its individual volume. Expressed algebraically, the above operations are:

$$\frac{\Sigma \text{ weight}}{\text{Sp. gr. gold}} = \Sigma \text{ volumes.}$$

$$\frac{\Sigma \text{ volumes}}{\Sigma \text{ (diam.)}^3} = \text{a function} = \mu.$$

$$\text{Volume of any button} = \mu \times (\text{diam.})^3$$
$$\text{Weight of a gold button} = \mu \times \text{sp. gr. gold} \times (\text{diam.})^3$$
$$\text{Weight of a silver button} = \mu \times \text{sp. gr. silver} \times (\text{diam.})^3$$

From the above data, a table can be constructed showing the weights of gold or silver buttons for every division of the scale up to its full range.

It should be remembered that measurement under the microscope is a very satisfactory laboratory method, but as it requires a compound microscope, it is not suitable for field use or prospector's outfits.

Richards' Scale.—The writer adopts Goldschmidt's idea of remelting the button on charcoal, wherever practicable, but has devised a modification of Harkort's method for measuring the buttons.

The idea is to make two metallic edges perfectly straight, lying on a flat surface, touching each other at one point and held apart at the other extremity by a set-screw, so that the point 100 may indicate a fixed width or separation of almost exactly one millimeter. In reality, the button whose horizontal diameter fits at 100 has a diameter of 1.02 millimeters, but this distance has been so chosen that the volume and consequently the weight of said button are exactly that of a perfect sphere whose diameter is one millimeter. The other numbers on the scale have the same significance; for example, the button whose horizontal diameter fits at 43.5 has the volume and weight of a sphere whose diameter is 43.5 hundredths of a millimeter, and such is the basis on which the table is calculated.

In using the scale, the button is put into the groove, the scale inclined slightly and tapped until the button wedges itself. The tenths of a division are estimated, taking the points where the sides of the button touch the scale as the reading. As the button may sometimes roll with its shorter vertical diameter across the scale, several readings are taken, and the highest reading occurring with regularity is the true horizontal diameter. For instance, among 43.4, 43.4, 41.6, 43.5, 41.8, 43.5, it is evident that 43.5 is the horizontal diameter and 41.6 or 41.8 the vertical. The button can also be observed under the lens, to see how it is lying, at any given reading.

A gentle spring keeps the right-hand strip against the set screw, thus allowing it to be pressed back for cleaning out the slot with a brush or removing a button. The scale is made of hardened aluminum, for lightness, and is set in a velvet-lined leather case. It is made by Williams, Brown, and Earle, of Philadelphia, and sold at the same price as the imported ivory Plattner scales. P. Stoë, of Heidelberg, makes and sells the scales in Germany.

The advantages of this method of construction over the engraved ivory scale are:

1. The edges are perfectly straight, from the method of construction.

2. They meet exactly at the zero point and can be adjusted to the exact distance at 100.

3. The reading is more or less automatic, the errors of placing, parallax, and personal equation being almost entirely eliminated.

The scales are adjusted by the makers, but, if by accident they get out of adjustment, a small rod of wire furnished with each instrument, whose lower end marks a given reading on a correct instrument, provides the means of quick readjustment.

Measuring Gold-Silver Alloy Buttons.—When the button obtained is pure gold or pure silver, any of the above methods give its weight directly. If, however, it is an alloy of the two, and is too small to weigh satisfactorily, but must be measured, the question of determining the silver present as well as the gold is a difficult one. The determination is very much facilitated by using the small case of standard alloys designed by Dr. Goldschmidt, of Heidelberg (made by P. Stoë, Heidelberg, imported by Williams, Brown, and Earle, Philadelphia). This is a small tablet in a brass case, containing small flattened buttons of gold-silver alloys, every 1 per cent. of silver to 20, then every 2 per cent. to 40, and every 4 per cent. to 56, where the alloy becomes silver-white. In using, the alloy button to be tested is hammered flat between paper, put on the plate and examined under the lens by diffused daylight. With a little experience, the button can be placed to one alloy. The observation gives the per cent. of silver in the button. Assayers working by the muffle will also find this a very convenient instrument to save parting where a quick, approximate determination is wanted, or to determine how much silver to add to an alloy to get the right proportions for nitric acid parting.

I have classified the different methods available to the blowpipe assayer as follows:

I. If the button is over 50 per cent. of gold, and therefore colored, melt on charcoal, measure, and note its *volume.* Then proceed by either of the following methods:

(*a*) Flatten out, compare with the standard alloys, and get the per cent. of silver in it. From the table of specific gravities of gold-silver alloys take the specific gravity. Multiply the *volume* of the alloy by its specific gravity; the product is its weight. From the known percentage of silver and gold in it, calculate their respective weights.

(*b*) Melt the button with a button of pure silver having an equal diameter, if the color of the alloy is pale; or of 25 per cent. greater diameter, if the color is brass-yellow; or of 50 per cent. greater diameter, if of nearly pure gold color. Hammer out flat, and part with nitric acid in the usual way. Wrap the gold in a small piece of pure lead foil, cupel, remelt, measure, and thus get its weight and note its volume. Subtract the volume of the gold from the volume of the alloy, and the difference is the volume of the silver. The weight of silver corresponding to this volume is obtained directly from the table.

The writer has verified these two methods of procedure, and found them both reliable. The principle of method (*a*) is due to V. Goldschmidt, but not exactly in the simple form given above. The principle of method (*b*) is based on the fact that gold and silver neither contract nor expand in alloying, which fact the writer has verified by experiment and calculation.

II. If the button is less than 50 per cent. gold, and, therefore, silver colored. Melt on charcoal and note its *volume*. Then proceed by either:

(*a*) Part with nitric acid (remelting with more silver if not attacked). Wrap the gold in lead foil, cupel, remelt, measure, note its weight and volume. Subtract its volume from that of the alloy, getting the volume of the silver, and thence its weight.

(*b*) Measure accurately a pure gold button of approximately the same diameter as the alloy button. Melt together on charcoal, and measure carefully, noting the *volume*. Flatten out the color will be yellow), compare with the standard alloys, and, knowing the volume, compute the weight of gold and silver present. The weight of gold found less the weight of the gold button added, gives the weight of gold in the original assay button. The weight of silver may be obtained by calculation from either the original alloy button or the yellow one after gold had been added.

This method of procedure was suggested by Professor B. W. Frazier, of Lehigh University.

(*c*) Replace on charcoal, and heat intensely in the point of the oxidizing flame. The silver slowly volatilizes, and in one to five minutes the alloy becomes yellowish. It is difficult to drive all the silver off, as the last five or ten per cent. volatilize slowly and probably also take a little gold with them. It is best to stop when the alloy has a pronounced yellow color, measure, note the volume; flatten out, compare with standard alloys, and calculate the weight of gold present. Take the volume of that weight of gold from the table, subtract from the volume of original alloy button, and thus obtain the volume and thence the weight of the silver.

The fact that silver can be volatilized from gold in this way, on charcoal, was described by the writer in the *Journal of the Franklin Institute*, June, 1896.

The writer finds methods I (*a*) and II (*c*) the most suitable for field work; the parting with nitric acid is preferably a laboratory method, and is the most accurate.

Note on the Quantitative Gold or Silver Assay.—The writer makes the fusion on charcoal in preference to a Freiberg carbon crucible, which is often unobtainable. When finished, it is always possible to make the slag quite liquid and then to pour out the lead *in toto*, leaving only clean slag on the charcoal. At first, it will be best to pour out on a cold steel anvil or plate, whence the lead may be picked up and placed at once on the cupel for scorifying. The writer has frequently poured the lead directly from the charcoal on the previously heated cupel, and then commenced immediately to scorify, sometimes without even allowing the lead to set. This will usually succeed for one with a steady hand, and several minutes can thus be saved.

In scorifying, if the blowpipe-tip is advanced almost to the nearer edge of the flame, an oxidizing flame of great power without a well-defined point is obtained, before which the lead oxidizes with great rapidity. 1800 mg. of lead were thus scorified to 300 mg. in two minutes; and, in general,one-half to two-thirds of the time usually consumed in scorification can be saved.

For fine cupellation, it is not absolutely necessary to pre-heat the cupel. The button is placed on the freshly struck cupel, a spot under the button strongly heated, on which the button drops as its melts. Then the cupel is turned slowly, keeping the button half-way up the far side, and the flame always heating the cupel just under it, which is thus dried before the button comes onto it.

By using such devices as the above to save time, the gold or silver assay may often be run through in from ten to fifteen minutes, with an extra five minutes for separately determining gold and silver, if necessary.

Number on the scale.	Weight of gold button.	Weight of silver button.	Volume of the button.	Number on the scale.	Weight of gold button.	Weight of silver button.	Volume of the button.
100ths mm.	mg.	mg.	cu. mm.	100ths mm.	mg.	mg.	cu. mm.
2	0.0001	0.00004	0.000004	42	0.747	0.406	0.0388
3	0.0003	0.00015	0.000014	43	0.802	0.436	0.0416
4	0.0006	0.00035	0.000034	44	0.859	0.467	0.0446
5	0.0013	0.00069	0.000065	45	0.919	0.500	0.0477
6	0.0022	0.0012	0.00011	46	0.982	0.534	0.0510
7	0.0035	0.0019	0.00018	47	1.047	0.569	0.0544
8	0.0052	0.0028	0.00027	48	1.115	0.606	0.0579
9	0.0074	0.0040	0.00038	49	1.186	0.645	0.0616
10	0.0101	0.0055	0.00052	50	1.261	0.686	0.0655
11	0.0134	0.0073	0.00070	51	1.338	0.727	0.0695
12	0.0174	0.0095	0.00091	52	1.418	0.771	0.0736
13	0.0222	0.0121	0.00115	53	1.501	0.816	0.0780
14	0.0277	0.0151	0.00144	54	1.588	0.863	0.0824
15	0.0340	0.0185	0.00177	55	1.678	0.912	0.0871
16	0.0413	0.0225	0.00214	65	1.771	0.963	0.0920
17	0.0495	0.0269	0.00257	57	1.867	1.016	0.0970
18	0.0588	0.0320	0.00305	58	1.967	1.070	0.1022
19	0.0692	0.0376	0.00359	59	2.07	1.126	0.1075
20	0.0807	0.0439	0.00419	60	2.18	1.185	0.1131
21	0.0934	0.0508	0.00485	61	2.29	1.245	0.1189
22	0.107	0.0584	0.00558	62	2.40	1.307	0.1248
23	0.123	0.0667	0.00637	63	2.52	1.371	0.1309
24	0.139	0.0758	0.00724	64	2.64	1.438	0.1373
25	0.158	0.0857	0.00818	65	2.77	1.506	0.1438
26	0.177	0.0963	0.00920	66	2.90	1.577	0.1505
27	0.199	0.108	0.0103	67	3.03	1 649	0.1575
28	0.221	0.120	0.0115	68	3.17	1.724	0.1646
29	0.246	0.134	0.0128	69	3.31	1.802	0.1720
30	0.272	0.148	0.0141	70	3.46	1.881	0.1796
31	0.300	0.163	0.0156	71	3.61	1.963	0.1874
32	0.330	0.180	0.0172	72	3.76	2.047	0.1954
33	0.362	0.197	0.0188	73	3.92	2.133	0.2037
34	0.396	0.216	0.0206	74	4.09	2.222	0.2122
35	0.432	0.235	0.0225	75	4.25	2.313	0.2209
36	0.470	0.256	0.0244	76	4.43	2.407	0.2298
37	0.511	0.278	0.0265	77	4.60	2.504	0.2390
38	0.553	0.301	0.0287	78	4.78	2.602	0.2485
39	0.598	0.325	0.0311	79	4.97	2.704	0.2582
40	0.645	0.351	0.0335	80	5.16	2.81	0.268
41	0.695	0.378	0.0361	81	5.36	2.91	0.278

Number on the scale.	Weight of gold button.	Weight of silver button.	Volume of the button.	Number on the scale.	Weight of gold button.	Weight of silver button.	Volume of the button.
100ths mm.	mg.	mg.	cu. mm.	100ths. mm.	mg.	mg.	cu. mm.
82	5.56	3.02	0.289	92	7.85	4.27	0.408
83	5.77	3.14	0.299	93	8.11	4.41	0.421
84	5.98	3.25	0.310	94	8.38	4.55	0.435
85	6.19	3.37	0.322	95	8.65	4.70	0.449
86	6.41	3.49	0.333	96	8.92	4.85	0.463
87	6.64	3.61	0.345	97	9.20	5.00	0.478
88	6.87	3.74	0.357	98	9.49	5.16	0.493
89	7.11	3.87	0.369	99	9.78	5.32	0.508
90	7.35	4.00	0.382	100	10.08	5.48	0.524
91	7.60	4.13	0.395				

SPECIFIC GRAVITY OF GOLD-SILVER ALLOYS.

Silver. Per cent.	Specific gravity.	Silver. Per cent.	Specific gravity.	Silver. Per cent.	Specific gravity.
0	19.258	34	14.984	68	12.263
1	19.099	35	14.887	69	12.198
2	18.940	36	14.791	70	12.133
3	18.785	37	14.697	71	12.069
4	18.632	38	14.603	72	12.007
5	18.483	39	14.511	73	11.944
6	18.335	40	14.420	74	11.882
7	18.190	41	14.330	75	11.821
8	18.047	42	14.241	76	11.761
9	17.906	43	14.153	77	11.700
10	17.767	44	14.066	78	11.641
11	17.631	45	13.980	79	11.582
12	17.497	46	13.896	80	11.525
13	17.364	47	13.813	81	11.467
14	17.234	48	13.730	82	11.410
15	17.106	49	13.648	83	11.353
16	16.979	50	13.568	84	11.297
17	16.855	51	13.488	85	11.242
18	16.731	52	13.409	86	11.187
19	16.610	53	13.331	87	11.133
20	16.491	54	13.254	88	11.079
21	16.374	55	13.178	89	11.026
22	16.258	56	13.103	90	10.973
23	16.144	57	13.029	91	10.921
24	16.031	58	12.955	92	10.871
25	15.920	59	12.882	93	10.819
26	15.810	60	12.811	94	10.768
27	15.702	61	12.739	95	10.718
28	15.595	62	12.669	96	10.668
29	15.490	63	12.600	97	10.619
30	15.386	64	12.531	98	10.570
31	15.283	65	12.463	99	10.521
32	15.183	66	12.395	100	10.473
33	15.083	67	12.329		

BLOWPIPE LABORATORY, LEHIGH UNIVERSITY,
January 17, 1901.