XLVI.—*Limits of Accuracy attained in Gold-bullion Assay.*

By T. K. ROSE, B.Sc., A.R.S.M., Assistant Assayer, Royal Mint.

SECTION I.

IN a paper read before the Royal Society (*Phil. Trans.*, 1828, 79—96), Mr. James Prinsep, Assay Master of the Mint at Benares, gives an account of experiments on the measurement of high temperatures by differences in the behaviour of a number of silver-gold and gold-platinum alloys when heated. He “made trials in different parts of the same (muffle) furnace. The disparity of heat,” he remarks, “is greater than might be supposed, and where, as in assaying the precious metals, so much depends on the temperature at which the operation is performed, it would be useful to know every difference in this respect obtaining in different countries, and its effect upon the quality or standard of bullion.”

It is not a little remarkable that, notwithstanding the fact that three generations of Assayers have passed away since Mr. Prinsep wrote, no attempt has been made, since 1827, to repeat and extend his experiments, doubtless because it was believed that no trustworthy pyrometer suitable for the purpose had been devised. In the elucidation of other problems of assaying, much work has been done. I

need only refer to the careful experiments conducted by D'Arcet, and by Chaudet, by Pettenkofer (*Bergwerk's freund*, 1849, **12**, 6), Roessler (*Dingl. polyt. J.*, **206**, 85), by Pelouze and Fremy (*Traité de Chimie*), by Kandelhardt, by Bruno Kerl, by C. Tookey (*J. Chem. Soc.*, 1870, **23**, 367), by Robert Barton (*Proc. Roy. Soc. Vict.*, 1875), and by Paul Charpentier (*Compt. rend.*, 1889, **108**, 612), to show that the question of improving the methods used in bullion assaying has engaged the attention of numerous skilful operators. Nevertheless, in 1882, Professor W. C. Roberts-Austen could only write (*Thirteenth Mint Report*, p. 47) that "the errors are certainly comprised within the limits $\pm 1/10,000$ th part, or within a range of $2/10,000$." Even this degree of accuracy (which, I believe, is still considered to be the highest possible) is only attained in the ordinary course of business in assay offices in assaying gold which is nearly pure, or contains, as alloying metals, only copper and silver. The difficulty of obtaining a sample which is representative of a large mass of metal within limits closer than this makes this degree of accuracy sufficient for most ordinary commercial purposes, although in particular instances it is not quite satisfactory.

Regarding the ordinary method of gold assaying, however, as one which may be adopted in conducting scientific research, it is of great interest to ascertain what are the causes of error, and to find out how they may be either avoided or reduced in amount. It was the need of greater accuracy which I felt when conducting some other investigations (including those in the next paper) which led me to this inquiry.

A description of the present practice employed in gold-bullion assaying is unnecessary here, as it would scarcely differ from the detailed account given in Percy's *Metallurgy of Gold and Silver*. It may be mentioned, however, that the "surcharge" is the algebraical sum of the losses of gold sustained during the various operations, and the amount of foreign substances (chiefly silver) existing in the gold cornet at the time when it is weighed. It is generally a positive quantity, and is applied as a correction to the observed weight, being determined by means of synthetic checks or proofs which are subjected to the same conditions as the alloys under examination. In view of this use of checks, it is clear that all constant errors are eliminated from the bullion assay, except that introduced by the use of impure gold. The gold used for checks at the Royal Mint is very carefully prepared, and is equal in purity to the purest gold prepared in other assay offices, as is shown by numerous trials at different times. All other errors are introduced by differences in the conditions to which the respective assay pieces are subjected.

I have found that the chief causes of error are :—

1. Imperfection in even the finest balances which are used.
2. Differences in composition between the controlling check assay pieces and the alloys under examination.
3. Variations in temperature in different parts of the cupellation muffle.

Other causes, such as the use of impure gold (erroneously regarded as pure) for checks, errors of observation in weighing, &c., are easily preventible, and will not again be referred to. There is another set of causes, dependent on the skill of the worker in preparing cupelled buttons for parting, which I have not fully investigated. All these buttons must be flatted, rolled, and annealed in exactly the same manner, otherwise, the physical condition of the fillets being different, the action of the acid on them may not be identical. In particular, rough-edged fillets may suffer loss in the acid by detachment of small fragments. Some of the errors noticed in the experiments described below, and unaccounted for, are probably due to these causes, in spite of the skill possessed by Mr. Joseph Groves, who, at the Royal Mint, performs the operations mentioned above. When, however, efforts are made to reduce the errors resulting from the three known causes, a higher degree of accuracy is attained than has hitherto been believed to be possible, the error being reduced to ± 0.02 per 1000.

Imperfection of the Balances used.

The assay balances in use at the Royal Mint up to the year 1892 would turn under a load of 0.5 gram (denoted by the figure "1000"), on the addition of 0.000025 gram or 0.05 per 1000. The balances at other assay offices are of similar delicacy. The weights of the check-pieces were recorded in terms of "tenths" and "half-tenths" per 1000, whilst the ordinary assays were recorded in terms of "tenths" (that is 0.1 per 1000). The total weighing error in the report of the latter is the algebraical sum of four weighing errors, namely, those on the initial and final weighings of the checks and of the ordinary assays. The Mint Assay Office now contains at least one balance capable of registering a difference of 0.01 per 1000 under a load of 0.5 gram, when the operation of weighing is performed with due precautions. The weighing errors on the old and new balances are as follows.

	Probable errors per 1000.	Maximum errors per 1000.
Old balance—		
1. Checks	± 0.017	± 0.05
2. Ordinary assays	± 0.033	± 0.1
3. Ordinary assays after applying the proof cor- rection	± 0.037	± 0.15
New balance—		
1. Checks	± 0.007	± 0.02
2. Ordinary assays	± 0.007	± 0.02
3. Ordinary assays after applying the proof cor- rection	± 0.01	± 0.04

The probable errors are calculated by the following well-known formula given by Kohlrausch (*Physical Measurements*, p. 9).

If f_1 and f_2 are partial errors, and F is the total error, then

$$F = \sqrt{f_1^2 + f_2^2}.$$

The results were kindly verified for me by Mr. P. T. Wrigley, M.A., of the Royal College of Science, who used a method of integration.

The precautions observed in weighing on the new balance are those given by Kohlrausch. The weighings were performed by substitution, using the method of oscillations, and without allowing for the displaced air. This was permissible, as only the relative weights of bodies which differ very slightly in form and density were required. The same weight was used as a counterpoise throughout; the deviation of the needle for 0.25 milligram was carefully measured, and the subsidiary weights, which were rarely required, were tested before use. Each weighing was performed several times, and the mean of the results, which seldom differed by as much as 0.01, was taken. The maximum error of observation was not greater than ± 0.01 per 1000.

The following is a series of actual weighings taken at random from a large number. The figures in the first column were obtained by weighing in the ordinary manner the cornets resulting from assays made with pure gold; those in the second column, from the same cornets, by using the precautions mentioned above.

ROSE: LIMITS OF ACCURACY

	Surcharge reported as usual, that is, 0.05 per 1000.	Surcharge reported to 0.01 per 1000.
A	+0.45 per 1000	+0.45 per 1000
	0.40 "	0.45 "
	0.50 "	0.47 "
	0.35 "	0.41 "
	<hr/>	<hr/>
Mean	0.425 "	0.445 "
B	+0.15 per 1000	+0.20 per 1000
	0.20 "	0.26 "
	0.20 "	0.22 "
	0.25 "	0.25 "
	<hr/>	<hr/>
Mean	0.20 "	0.23 "
C	+0.35 per 1000	+0.28 per 1000
	0.25 "	0.27 "
	0.20 "	0.22 "
	0.27 "	0.26 "
	<hr/>	<hr/>
Mean	0.27 "	0.26 "
D	+0.90 per 1000	+0.94 per 1000
	1.05 "	0.99 "
	0.90 "	0.96 "
	0.95 "	0.96 "
	<hr/>	<hr/>
Mean	0.95 "	0.96 "

The probable errors on the foregoing results are, on an average, as follows.

	Surcharge reported as usual.	Surcharge reported to 0.01 per 1000.
Mean	± 0.022	± 0.007
On single result. . .	± 0.044	± 0.014

These results show that the probable errors may readily be reduced in practice to one-third the usual amount by the more accurate weighing which very delicate balances render possible.

In the results of all assays recorded below, the weighings were performed with the precautions above referred to.

Differences in Composition of Assay Pieces.

The influence of small differences in composition of the assay pieces has not been recognised as affecting results. The effects of

great differences have been worked out and tabulated by Roessler (*Dingl. polyt. J.*, **206**, 185), Pelouze and Fremy (*Traité de Chimie*), and others.

The variations are usually due to two well known causes.

1. If the proportion of copper is increased, more gold is absorbed by the cupel.

2. If the weight of silver added to the gold is greater or less than $2\frac{1}{2}$ times that of the gold, more silver is left undissolved in the cornet, and appears as surcharge when the cornet is weighed.

Influence of Copper.—This is illustrated by the following results. The weight of silver was, in each case, 1·25 grams, and of lead 4 grams.

Composition { gold.....	916·6	900	800
of alloy { copper... ..	83·3	100	200
Surcharge	+0·25	+0·22	−0·07
	0·26	0·23	0·08
	0·25	0·20	0·07
	0·25	0·18	0·03
Means	+0·25	+0·21	−0·06
The means of another set			
were	+0·14	+0·08	—

Other similar results were obtained.

The difference between the surcharges shows that a variation of the copper present in an assay piece to the extent of a few milliemmes only may give a sensible alteration in the surcharge; consequently, if very accurate work is needed, checks must correspond more exactly with the alloys worked with them than is usually the case. This influence is appreciable, even in the assay of English standard bars and coins, as the alloying metal present in the nearly fine ingots which are melted with copper to form standard bars, although computed as copper, is often in part silver. A standard bar, taken at random from the Mint stock, contained—

Gold	916·7
Silver	11·5
Copper (by diff.)	71·8
	<hr/>
	1000·0

It is clear from the facts already stated that the surcharge on this bar might be sensibly higher than that on a standard bar containing only gold and copper.

Influence of Silver.—The influence of differences of only 3 per cent. in the amount of silver present in the fillets prepared for boiling in the parting acid is shown below. All the assays were made together, each originally containing 1000 parts of pure gold.

The silver in the cornets was determined by difference, after assaying them for gold.

Silver in fillets	2470.0 parts	2400.0 parts
„ cornets	0.59 „	0.56 „
	0.55 „	0.84 „
	0.65 „	0.63 „
	0.57 „	0.78 „
	0.61 „	0.72 „
	0.55 „	—
	0.62 „	—
	0.69 „	—
Means	0.604 „	0.706 „

The difference between these means represents an alteration of the surcharge, as the influence of small additions of silver on the loss of gold is inappreciable. It is evident, therefore, that such variations in the weight of parting silver, as often occur in assay offices, are sources of error. Even if the initial weight of silver be constant, the weight in the fillets may vary from unequal losses in the furnace. This loss was found to be about 1 per cent. when standard gold is being assayed, 1.6 per cent. in the case of gold 800 fine, and 3 per cent. if it is 666 fine.

Influence of other Metals on the Surcharge.—The presence of 5 per cent. of bismuth does not affect the surcharge. The effect of some other metals is given below; all assay pieces contained 1000 parts of gold, 2500 parts of silver, and 91 parts of copper, other metals being added in the proportions indicated.

Metal added..	None.	Antimony, 50 parts.	Zinc, 70 parts.	Tellurium, 33 parts.	Iron, 50 parts.	Nickel, 50 parts.
Surcharge..	+0.42	+0.28	+0.35	+0.02	+0.22	+0.22
	0.44	0.28	0.38	0.12	0.32	0.25
	0.38	—	—	—	—	—

These differences indicate the necessity of employing special checks containing these metals if such be present in the alloys.

Influence of the Temperature of the Muffle on Surcharge.

The results obtained by Mr. Prinsep, in the paper already referred to, are as follows.

					Maximum alloy melted.
Muffle of an assay furnace :	front.....				pure silver
"	"	"	"	: middle (aver-	{ silver, 70 } { gold, 30 }
				age)	
"	"	"	"	: behind (aver-	{ silver, 50 } { gold, 50 }
				age)	

The temperatures at which these alloys melt are

Silver	945° (Violle).
Silver, 70 }	.. 960°.
Gold, 30 }	
Silver, 50 }	.. 990°.
Gold, 50 }	

The melting points given for the silver-gold alloys are based on determinations which I made with the platinum and rhodio-platinum couple.

No other exact experiments on the subject appear to be on record. Differences in temperature between the front and back of the muffle are of course well known to exist, and checks are usually placed in various positions with a view to obtain a mean surcharge value that may be applied to all the assays. Nevertheless, checks cannot conveniently be increased in number sufficiently to detect all the variations of temperature in a large muffle, and the careful mapping out of the usual conditions prevailing in each case is much to be desired.

With this view I conducted the following experiments on the muffle at the Royal Mint. The furnace is specially devised for keeping the temperature of the muffle uniform, being that described in Percy's *Metallurgy of Gold and Silver*, pp. 255—257.

While the experiments were being conducted, the muffle appeared as usual to be at a uniform orange-red heat. It is probable that in the ordinary work of assayers generally differences of temperature exist which are at least as great as those recorded below.

Apparatus employed.—The pyrometer consisted of a thermo-electric couple formed of platinum and rhodio-platinum wires. It was the instrument used by Professor Roberts-Austen in his experiments (*Proc. Roy. Soc.*, 49, 347, and *Proc. Inst. Mech. Eng.*, 1891, 543), and was kindly placed at my disposal by him.

The wires, sheathed in clay pipe-stems, were fixed in a porcelain

tube, the junction being protected by plates of mica. This tube was introduced into the furnace by sliding through another of wider bore fixed in the brick door of the muffle. The inner end of the narrow tube was plugged by clay and coated over with a fusible mixture of sand, pipeclay, and felspar. The galvanometer was shielded from radiation from the furnace, and remained at about a constant temperature, but the zero was frequently determined in order to detect any changes. In calibrating the wire, the effects of heating various lengths of it were noted, and allowance made for the alterations in the deflections of the needle due to this cause. The junction was kept stationary at each point in the muffle until its temperature had become constant, as indicated by the cessation of movement of the spot of light on the scale. The calibration of the wire was kindly effected for me by Mr. H. C. Jenkins, Professor Roberts-Austen's assistant, whose experience and skill in the management of the pyrometer were also of great assistance in carrying out some of the experiments.

The muffle is 15 inches long, and $6\frac{1}{2}$ inches wide, and its full charge consists of 72 assays arranged in 12 rows, the distance between the front and back rows being $10\frac{1}{2}$ inches. The position of the junction was about 1 inch above the cupels in all cases. The error in observation in taking the readings was probably not more than 0.1 mm. on the scale, which was equivalent to 0.32° .

A.

Place.		Time.	Temperature in degrees above m. p. of gold-silver buttons left on the cupel, viz., 952° .
Middle of 1st (front) row of cupels		10.19 A.M.	114.0°
„ „ „ „		10.20 „	113.0
„ 3rd row of cupels		10.21 „	123.0
„ 4th „ „ „		10.22 „	124.0
„ 7th „ „ „		10.23 „	144.0
„ 3rd „ „ „		10.25 „	120.0
„ 11th „ „ „		10.28 „	140.0
Right side, 11th row of cupels . . .		10.29 „	142.5
Left „ „ „ „		10.30 „	140.0
Middle „ „ „ „		10.31 „	139.0
„ 3rd row „ „ „		10.32 „	112.0
„ 7th „ „ „ „		10.36 „	128.0

The assay pieces were charged in between 10.5 and 10.11; cupellation was complete at 10.23, and the charge drawn at 10.47 A.M.

B.

		Time.	Temp. above 952°.
Middle of	3rd row.....	11.3 A.M.	112.5°
„	7th „	11.6 „	131.5
„	11th „	11.8 „	143.0
„	7th „	11.9 „	123.0
„	3rd „	11.12 „	112.5

The assay pieces were charged in between 10.50 A.M. and 10.55; cupellation was complete at 11.8, and the charge was drawn at 11.30. The circuit was accidentally broken at 11.15.

C.

Place.		Time.	Temp. above 952°.
Middle of	3rd row.....	11.56 A.M.	70°
„	7th „	11.59 „	91
„	11th „	12.0 P.M.	102
„	7th „	12.2 „	97
„	3rd „	12.3 „	82
„	11th „	12.8 „	105
„	7th „	12.10 „	98
„	3rd „	12.15 „	88
„	3rd „	12.17 „	91

The assay pieces were charged in between 11.45 and 11.51; cupellation was complete at 12.8, and the charge drawn at 12.25. The muffle appeared to the eye to be decidedly cooler than usual.

These three experiments were conducted on different days. They show that the temperature gradually rises in passing from the front to the back of the muffle, the rate of change falling from 5° per row of cupels at the front to about 2° at the back, whilst along the sides the temperature is 1° or 2° higher than in the middle line. The mean difference in temperature between the 3rd and 7th rows is 15.7°, and between the 7th and 11th rows 10.5°, whilst the mean temperature of the muffle is 107.0°. These differences seem to exercise an effect on the absorption of gold by the cupel. The mean surcharge of the check assays in all the charges, 939 in number, worked off at the Royal Mint between January 1, 1880, and March 11, 1892, is as follows.

Check in middle of		
(a) 3rd row.	(b) 7th row.	(c) 11th row.
+0.1828	+0.1533	+0.1347

Consequently, if, as is probable, the experiments indicate the

ordinary conditions of the muffle, a rise of about 5° would correspond to a diminution in the surcharge of 0.01 per 1000.

In conclusion, the results of some assays on synthetic alloys of gold and copper are appended, in which care was taken to keep the temperature uniform for each set; the amount of silver added was, in each case, $2\frac{1}{2}$ times that of the gold, and the lead 4 grams.

Composition of alloy..	{ gold, 1000 } { copper, 91 }	gold, 800 } copper, 200 }
Gold found.....	999.96	799.74
	.95	.85
	1000.00	.84
	999.93	.71
	.96	.73
	.96	.73
	.97	—
	1000.00	—
Mean	999.966	799.767

In these cases, the surcharge is negative, and if the mean loss of gold is allowed for, the probable errors on single results are respectively ± 0.017 and ± 0.039 .

These results are taken at random from a number of others to show the degree of accuracy I have found practicable. In some cases, perfect agreement to the 1/100,000th part has been obtained in several assays.

The conclusion may be drawn that in the determination of gold in high-grade alloys of gold and copper, or of gold, silver, and copper, whether pure or contaminated by small quantities of lead, bismuth, zinc, antimony, nickel, and some other elements, the error does not exceed ± 0.02 per 1000, if the mean of three concordant results is taken.

SECTION II.

Losses of Gold in Bullion assaying.

The losses of gold can only be incurred in three ways, namely:—

1. Absorption by the cupel.
2. Volatilisation in the muffle.
3. Solution in the acid.

The two latter causes of loss were discussed by the late Mr. G. H.

Makins in a paper "On certain Sources of Loss of Precious Metals in some Operations of assaying," which was read before the Chemical Society and published in their Journal (1860, 13, 77). He found gold and silver in the proportion of about 1 to 9 in the dust taken from a flue used only in gold and silver cupellation, but did not attempt to ascertain the percentage loss of gold by volatilisation. He also showed that large amounts of gold were dissolved by nitric acid in the course of assaying, and attributed the dissolution of gold to the presence of nitrous acid, but supposed that it would not be dissolved in the weaker acid, where nitrous acid was formed in larger quantities, owing to the protective action exercised by undissolved silver, which formed the positive element in the gold-silver couple. The fact that gold is actually dissolved in nitric acid, presumably as oxide, and remains dissolved even after dilution with water, was proved by Mr. A. H. Allen (*Chem. News*, 25, 85). I found, at the Royal Mint, that the spent acid which had been used in the second boiling, during which very little silver is dissolved, after standing for several weeks, contained 1.2 milligram of gold per litre, whilst after dilution with 25 per cent. of water and subsequently standing for several weeks, it was still found to contain 0.45 milligram of gold per litre.

The experiments described below were conducted with a view to ascertain the relative amounts of the losses from the three sources mentioned above. The assays were worked with others in the ordinary course at the Royal Mint, but were boiled in acid in separate vessels.

In estimating the gold and silver in the cupels, the unstained bone-ash was scraped off, and the remainder passed through an 80-mesh sieve by crushing in a clean porcelain mortar. The powdered bone-ash was fused with the usual fluxes in clay pots. The resulting lead buttons, which weighed from 350 to 450 grains, were scorified to a small bulk, cupelled, and parted. The slags, which were very liquid and light coloured, were fused again with litharge and charcoal, and the resulting lead buttons added to the others. My thanks are due to Mr. W. Groves for assisting me in making some of these determinations.

The materials used were all reputed to be pure, and free from gold, but, on assay, there proved to be 6 parts of gold in 1,000,000 parts of the silver, and 9 parts of gold in 13,000,000 parts of the lead. Allowance was made for this, and a blank charge of fluxes and cupel run side by side with the others, and the gold thus found deducted from that found in the real charges.

The gold present in the acids was found by evaporating to dryness with litharge, and fusing, cupelling, and parting the residue.

Table of Losses during Bullion Assay of Gold.

No.	Initial weight.	Silver, &c., present in each cornet.	Surcharge.	Loss of Gold.			Gold recovered.			
				On each assay.	Total.	Mean per assay.	From cupel.	From 1st acid.	From 2nd acid.	Total.
1 a..	Gold, 916·6 Copper, 83·3	0·80 " " "	+0·20	0·60	2·40	0·60	2·05	*	0·05	2·10
			0·20	0·60						
			0·20	0·60						
			0·20	0·60						
b..	Gold, 800 Copper, 200	0·70 " " "	-0·05	0·75	3·15	0·79	2·65	*	0·05	2·70
			0·10	0·80						
			0·10	0·80						
			0·10	0·80						
2 a..	Gold, 916·6 Copper, 83·3	0·73 " " "	(i) +0·34	0·39	1·75	0·44	1·43	0·05	0·08	1·56
			(ii) 0·30	0·43						
			(iii) 0·30	0·43						
			(iv) 0·23	0·50						
b..	Gold, 800 Copper, 200	0·60 " " "	-0·02	0·62	—	0·607	1·81	0·05	0·08	1·94
			-0·05	0·65						
			+0·05	0·55						
			—	—						
3 a..	Gold, 1000 Copper, 91	0·60 " " "	(i) -0·06	0·66	2·72	0·68	2·03	0·12	0·18	2·33
			(ii) -0·17	0·77						
			(iii) -0·07	0·67						
			(iv) -0·02	0·62						
b†.	Gold, 1000 Copper, 91	" " " "	(i) -0·23	0·83	3·05	0·76	2·65	0·12	0·18	2·95
			(ii) -0·17	0·77						
			(iii) -0·20	0·80						
			(iv) -0·05	0·65						

* Not estimated.

† The assays in b were 4 rows further back in the furnace than a: the greater loss is probably caused by a higher temperature.

Samples of the acids, before being used for parting, were treated in the same way, and the gold thus found was deducted from the results.

The results are given in the table on p. 712.

All the weights recorded in the table are in milliemes (half milligrams) and decimals thereof. The silver and other impurities in the cornets was estimated by difference, the mean of four results being taken. The greater loss of gold observed when the surcharge is low is caused by a high temperature of cupellation.

The strengths of the acids used were

No. 1.	Sp. gr. 1.25,
No. 2.	„ 1.32.

The large quantity of gold dissolved in Exp. No. 3 may possibly be due to the fact that the fillets were annealed at a higher temperature than usual, and were very soft and "blistered."

The sets marked *a* and *b* were, in each experiment, cupelled at the same time (other assays being also present) and boiled together; it was assumed that equal amounts of gold were dissolved from each set of four assays.

The amount recovered from the cupels includes the microscopic beads of metal, easily seen under a 2-inch objective, which may be frequently detected forming a broken ring close to the cupelled button.

It will be noticed that in each experiment detailed in the table the amount of gold recovered is less than that originally lost, but the difference between these cannot be said, with certainty, to represent the amount volatilised in the muffle, as the errors of five separate determinations are all accumulated here. These errors may, to a certain extent, counterbalance each other, and it is unlikely that they are all in one direction, as in each case the estimations were corrected by the results of check assays made at the same time. The degree of reliance to be placed on the results may be gathered from an inspection of the table. It seems fair to draw the conclusion that the usual loss by volatilisation in an ordinary bullion assay (which approximates in composition to the 916 standard) is probably less than 0.1, but not less than 0.05, per 1000.