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THE ACCURACY OF THE COMMERCIAL ASSAY FOR SILVER.¹

BY FREDERIC P. DEWEY.

It is generally considered that the fire assay for silver is remarkably accurate when properly carried out. Ricketts says, page 79, "The assay for gold and silver, if conducted carefully, is one of great accuracy. Duplicates of silver should agree to within one-half ounce Troy per ton" (xxx).

In general, and particularly when only small amounts of silver are present, the prevalent idea is correct, but, as shown by the above extract from Ricketts, in considering the accuracy of silver assays, too much stress is laid upon the agreement between duplicates, and I hope to show that, while the actual accuracy of the ordinary fire assay is, in many cases, very great, yet for commercial purposes still greater accuracy is required.

The main conditions which lead to accuracy are the possibility of using large quantities of material and the accuracy attainable in weighing the button, and these apply more particularly when only small amounts of silver are present. When, however, large quantities of silver are present we cannot carry on the process so successfully with so large a quantity of material, and, if we could, we might get a button too large to weigh on a button balance, and thus sacrifice some delicacy of weighing.

It has long been known that there are three sources of loss in assaying; first, from silver going into the slag; second, by silver absorbed by the cupel; third, from volatilization of silver. In dealing with rich materials corrections have been applied, and in the case of bullion it has been sought to correct for all losses by

¹ Read before the Washington Section, April 12, 1894.

running a check assay as near as possible like the test. When, however, we come to consider large quantities of ore, even though they carry only a moderate number of ounces of silver per ton, it is found that greater accuracy of assay for silver is necessary even for this class of material.

This is most clearly shown by a "clean-up" run by the Russell process for lixiviating silver ores. Fifty tons of ore, carrying by the ordinary assay 2,178 ounces of silver, or 43.43 ounces per ton, were treated by the Russell process, and 2,149 ounces of silver recovered, or 99.6 per cent. of the silver shown by the ore. In addition to this the tailings showed 272.25 ounces, or 12.5 per cent. Making a total of 111.5 per cent.

After a thorough investigation of this anomalous result the samples were re-assayed, but the slags and cupels were saved and also assayed, and the results added to the main assay. By this proceeding the ore showed 3.53 ounces more per ton, and the per cent. of silver saved was reduced to 91.5 per cent. Adding to this the 12.5 per cent. remaining in the tailings we have 104 per cent. The increase of silver found in the slag and cupel amounted to 8.1 per cent. of the silver in the ore, and the excess of 4 per cent. on the total may perhaps be assumed as about the volatilization loss in this case.

Attention having been called to the importance of this well-known, but hitherto unappreciated inaccuracy in silver assaying, the Russell Process Company has collected many statistics upon the subject, and I am indebted to a forthcoming pamphlet upon the subject of "plus clean-ups" for much information. I am also indebted to Mr. H. E. Wood, assayer, of Denver, Col., and to the Dewey-Walter Refining Company for many figures used in this paper.

In general, the percentage of the inaccuracy of the ordinary commercial assay varies inversely with the value of the material assayed when figured upon that value.

In order to see this most clearly it is necessary to compare results on the same class of material, and, preferably, made by the same assayer under practically constant conditions. Sometimes when a series of individual results differs irregularly, if the results are grouped considerable regularity may appear. For

instance, on looking at a series of miscellaneous results on ores running from fifteen to forty ounces per ton no regularity may appear, but if the results are grouped in periods differing by five ounces per ton they may become very regular in the variation. While different assayers working on the same material may show some regularity, they may also vary greatly.

For instance, a group of results on tailings arranged according to the increase in value by commercial assay shows as follows:

Material.	Grade. Ounces per ton.	Value commercial assay. Ounces per ton.	Value in slag and cupel. Ounces per ton.	Corrected value. Ounces per ton.	Percentage in slag and cupel.
Tailings.....	1- 3	1.8	0.5	2.3	21.8
"	"	2.8	0.4	3.2	12.5
"	3- 5	3.0	0.6	3.6	16.7
"	"	3.9	1.0	4.9	20.0
"	"	4.0	0.5	4.5	11.4
"	5- 7	5.5	0.6	6.1	10.0
"	"	6.0	1.3	7.3	17.8
"	"	6.2	1.2	7.4	16.1
"	7- 9	7.5	1.4	8.9	15.7
"	"	8.3	0.9	9.2	10.1
"	9-11	9.6	1.6	11.2	14.3
"	"	9.7	1.6	11.3	14.2
"	"	9.8	1.3	11.1	10.0
"	11-13	12.2	1.8	14.0	13.0
"	15-20	17.5	1.6	19.0	16.9
"	"	18.5	1.8	20.3	8.9

When, however, we take out of this table the results by a single assayer, we have:

Material.	Grade. Ounces per ton.	Value commercial assay. Ounces per ton.	Value in slag and cupel. Ounces per ton.	Corrected value. Ounces per ton.	Percentage in slag and cupel.
Tailings.....	1- 3	1.8	0.5	2.3	21.8
"	3- 5	3.9	1.0	4.9	20.
"	5- 7	6.0	1.3	7.3	17.8
"	7- 9	7.5	1.4	8.9	15.7
"	9-11	9.6	1.6	11.2	14.3
"	11-13	12.2	1.8	14.0	13.
"	13-20	18.5	1.8	20.3	8.9

When we group results by five ounce periods we have:

Material.	Grade. Ounces per ton.	Value commercial assay. Ounces per ton.	Value in slag and cupel. Ounces per ton.	Corrected value. Ounces per ton.	Percentage in slag and cupel.
Tailings.....	1-5	2.8	0.7	3.5	18.
"	5-10	7.8	1.1	9.2	15.2
"	10-15	12.2	1.8	14.0	13.
"	15-20	18.0	1.7	19.7	8.6

It has been found that the character of the ore influences the results. In three kinds of ores, base, containing seventy-five per cent. sulphurets, partially oxidized, and completely oxidized, carrying from 16.5 to 34.6 ounces of silver per ton, the percentages of silver found in the slag and cupel were as follows:

Base.	Intermediate.	Oxidized.
5.7	8.2	9.8
6.8	7.8	11.3

the results on the top line being obtained by scorification and those on the bottom line by crucible assay, of the same ore in each case.

It follows then, that when ores consisting of mixtures of altered and unaltered material are considered, the proportion between these two should be known and allowed for when comparing results on similar grades of ore, if one would discover the regularity in the variation of the results.

Again, whether the ore is raw or roasted, or has been washed, influences the result, roasted ore being generally more inaccurate than raw.

A heterogeneous table of results on ores running from ten to fifty ounces per ton is as follows:

Material.	Grade. Ounces per ton.	Value commercial assay. Ounces per ton.	Value in slag and cupel. Ounces per ton.	Corrected value. Ounces per ton.	Percentage in slag and cupel.
Ore	10-15	12.5	1.3	13.8	6.4
"	15-20	17.6	1.8	19.4	9.0
"	20-25	22.4	1.9	24.3	7.8
"	"	23.1	2.0	25.1	8.0
"	"	23.8	4.8	28.6	13.0
"	"	23.9	4.5	28.4	15.8
"	"	24.1	5.9	29.7	18.8
"	"	24.3	3.3	27.6	12.0
"	25-30	26.6	2.5	29.1	8.6
"	"	27.	4.0	31.0	13.0

Material	Grade. Ounces per ton.	Value commercial assay. Ounces per ton.	Value in slag and cupel. Ounces per ton.	Corrected value. Ounces per ton.	Percentage in slag and cupel.
Ore	25-30	27.2	2.9	30.1	9.7
"	"	28.	4.6	32.6	14.1
"	"	28.4	3.	31.4	9.0
"	"	28.9	1.6	30.5	5.0
"	"	29.7	2.8	32.5	8.6
"	30-35	30.4	3.6	34.0	10.6
"	"	30.6	2.0	32.6	6.1
"	"	30.7	3.9	34.6	11.3
"	"	31.6	3.4	35.0	10.0
"	"	31.8	2.3	34.1	7.0
"	"	31.9	3.9	35.8	10.9
"	"	32.3	3.7	36.0	10.0
"	"	33.	4.1	37.1	10.8
"	"	33.1	2.8	35.9	7.8
"	"	33.6	3.2	36.8	8.7
"	35-40	36.7	3.1	39.8	7.8
"	"	36.9	3.3	40.2	8.2
"	"	37.4	4.3	41.7	10.0
"	"	37.65	2.25	39.9	5.6
"	"	38.2	2.8	41.0	6.8
"	40-45	42.1	3.	45.1	6.7
"	"	42.3	2.3	44.6	5.2
"	"	42.4	2.4	44.8	5.4
"	"	44.7	4.3	49.	8.8
"	45-50	45.5	2.4	47.9	5.0

The variation shown by the above table is very diverse, but the following grouping by five ounce periods, and according to the character of the ore, shows the inverse variation beautifully :

Material.	Grade. Ounces per ton.	Value commercial assay. Ounces per ton.	Value in slag and cupel. Ounces per ton.	Corrected value. Ounces per ton.	Percentage in slag and cupel.
Roasted ore ..	20-25	23.5	3.2	26.7	12.
" ..	25-30	27.3	3.5	30.8	11.4
" ..	30-35	31.6	2.8	34.4	8.1
" ..	35-40	36.8	3.2	40.0	8.
" ..	40-45	42.3	2.7	45.0	6.
Raw ore.....	20-25	24.2	4.6	28.8	16.
" ..	25-30	27.7	3.5	31.2	11.2
" ..	30-35	31.8	3.8	35.6	10.7
" ..	35-40	37.5	3.3	40.8	8.1
" ..	40-45	43.5	3.3	46.8	7.1
" ..	45-50	45.5	2.4	47.9	5.

While the amount of silver recovered from the slag and cupel in the case of ordinary ores is small, when stated per ton of ore, yet when a year's operations, involving ten, twenty, thirty, or more thousands of tons, are considered the difference between an ordinary and a corrected assay amounts to quite a respectable sum, and becomes well worthy of consideration in these times of low prices for silver.

When we consider rich materials, such as high-grade ore and the products of the Russell process, for instance, the slag and cupel loss on a single ton becomes considerable, and with very rich products, such as lixiviation sulphides, particularly when they carry a large percentage of copper, as in the regular Russell sulphides, this loss may amount to several hundred ounces per ton. It has been customary to use the slag and cupel assay on rich products and it was employed on the "clean-up" referred to.

I am indebted to Mr. H. E. Wood, assayer, No. 1,744 Arapahoe St., Denver, Col., for a series of results on sulphides, varying from poor to rich.

The following details give the results on assaying sulphides—scorification method. 1-20 A. T. of sulphides used, and scorification slag and cupel from original assay then rescorified and cupelled with result shown. Classified according to the grade the losses were as follows:

Under 500	Average of 1 Lot.....	4.170 per cent.		
500 to 1,000	" " 6 Lots.....	2.910	" "	" "
1,000 " 1,500	" " 14 "	2.996	" "	" "
1,500 " 2,000	" " 9 "	2.540	" "	" "
2,000 " 2,500	" " 12 "	2.109	" "	" "
2,500 " 3,000	" " 21 "	1.867	" "	" "
3,000 " 3,500	" " 19 "	1.860	" "	" "
3,500 " 4,000	" " 19 "	1.821	" "	" "
4,000 " 4,500	" " 10 "	1.695	" "	" "
4,500 " 5,000	" " 7 "	1.700	" "	" "
5,000 " 5,500	" " 4 "	1.845	" "	" "
5,500 " 6,000	" " 4 "	1.895	" "	" "
6,000 " 6,500	" " 1 Lot.....	1.630	" "	" "
6,500 " 7,000	" " 4 Lots.....	1.777	" "	" "
7,000 " 7,500	" " 2 "	1.640	" "	" "
7,500 " 8,000	" " 1 Lot.....	1.420	" "	" "
8,000 " 8,500	" " 3 Lots.....	1.537	" "	" "
9,000 " 9,500	" " 3 "	1.460	" "	" "

10,500 to 11,000	Average of 1 Lot	1.570 per cent.
11,500 " 12,000	" " 1	1.340 " "
12,000 " 12,500	" " 1	1.270 " "
17,000 " 17,500	" " 1	1.260 " "

The average slag and cupel absorption on the 144 lots was 2.03 per cent. of the total contents.

The following table shows the results obtained on eleven lots of regular Russell sulphides when assayed by the following method:

"Weigh out one-twentieth ($\frac{1}{20}$) of an assay ton of sulphides, fifty-five grams of granulated test-lead, and two (2) to three (3) grams of fused borax. One-half of the lead is put in the bottom of the scorifier and hollowed out; the sulphides are put into the hollow and the rest of the lead poured over them; the borax is then placed on top. The assay is then conducted in the usual way. The slag and cupel shall be ground up and assayed, and the result added to the main assay."

This method is the result of a great deal of work and has been adopted as most suitable for this class of material.

In the table are given, first, the results of plain scorification assay; second, the ounces per ton found in the slag and cupel; third, the percentage in slag and cupel; fourth, the total silver found by adding the slag and cupel silver to the scorification silver by one assayer; fifth, the total silver as found by another assayer upon the same samples, and finally, the difference between the two assayers.

Ounces per ton by commercial assay.	Ounces per ton in slag and cupel.	Per cent. in slag and cupel.	Total ounces per ton.		Differences.	
1st assayer.	1st assayer.	1st assayer.	1st assayer.	2nd assayer.	Plus.	Minus.
8,675.20	144.11	1.622	8,819.31	8,782	37.31
10,074.25	189.35	1.844	10,263.60	10,119	144.60
10,783.35	189.	1.720	10,972.35	10,938	34.35
10,902.30	194.38	1.752	11,096.68	11,220	123.32
11,015.73	191.69	1.710	11,207.42	11,090	117.42
11,238.40	175.22	1.535	11,413.62	11,548	134.38
11,828.75	176.72	1.471	12,005.47	12,046	40.53
12,566.55	199.21	1.560	12,765.76	12,821	55.24
12,665.85	199.87	1.553	12,865.72	12,841	24.72
13,001.65	229.84	1.737	13,231.49	13,187	44.49
13,625.50	226.52	1.635	13,852.02	13,919	66.98

On comparing results on individual lots considerable variation will be found between the two assayers, but on considering the total amount of silver involved the difference becomes quite small. By the first assayer these eleven lots contain 236,418.99 ounces of silver, while by the second they contain 236,483.88 ounces, the difference between the two being only 54.89 ounces. This amount is 0.0232 per cent. of the smallest total of ounces found, and 0.0095 per cent. of the weight of sulphides involved. This shows that when carefully and properly executed the method gives concordant results on averaging a sufficient number of assays.

As showing the difference which may occur by this method of assaying, besides noting the individual difference above, between the two assayers, it may be added that one of these found the following difference on assaying the same sample at different times :

No. 1.....	144 ounces per ton.
" 2.....	90 " " "
" 3.....	112 " " "

Making a difference of 527.36 in the total silver involved.

Also on a lot of sulphides containing 218,324 ounces¹ by one assayer, a second assayer obtained 0.587 per cent. less on the same samples, and in a second comparison between the first assayer and the same smelting works, representing 156,091, the difference was 1.355 per cent.

The following results were obtained in my laboratory by Mr. Charles Earl:

Total silver. Ounces per ton.	Silver in slag and cupel. Ounces per ton.	Percentage in slag and cupel.
9,156.3	244.	2.664
9,590.	257.5	2.685
9,828.2	250.	2.543
10,077.95	198.25	1.967
10,456.	266.	2.544
10,759.	244.5	2.272
10,861.5	282.5	2.6
11,700.2	198.66	1.697
12,087.8	233.3	1.93
13,804.5	250.33	1.813

¹ *Trans. A. I. M. E.*, Pamphlet Edition. Product and Economical Results of the Marsac Refinery for the year 1892, by C. A. Stetefeldt, p. 9.

In using this method Mr. Earl usually starts four assays of each sample. As he has found the charge rather destructive to scorifiers it is not unusual to lose an assay. In two sets of four results the differences between the highest and lowest individual results were 49.6 and 95 ounces per ton. In five sets of three results the differences were 36, 54, 94, 98, and 152.2 ounces per ton. As each one of a set of assays was carried through under practically the same conditions as the others these differences may seem rather high, but the total ounces represented by these seven assays by Mr. Earl was 121,346.53 ounces, while another very expert assayer by this method, working upon the same samples, found 121,446.56 ounces, showing a difference of only 99.93 ounces on the total number of ounces involved. The following table shows the individual variations:

Total ounces per ton.		Differences.	
		Plus.	Minus.
6,769	6,847	78
9,400.3	9,430	29.7
9,590	9,524	66	...
9,928	9,880	48	...
10,078	10,119	41
10,456	10,446	10	...
10,759	10,833	74

The following tables summarize a large quantity of determinations and are taken from the pamphlet by the Russell Process Company referred to:

Material.	Grade. Ounces per ton.	Value commercial assay. Ounces per ton.	Value in slag and cupel. Ounces per ton.	Corrected value. Ounces per ton.	Percentage slag and cupel.
Lead carbonate...	I- 50	5.2	0.8	6.0	15.4
" " ...	50- 100	64.8	3.2	68	5.1
" " ...	100- 500	447.6	12.4	460	2.6
Base sulphides...	100- 500	394	37	431	8.6
" " ...	500- 1,000	766	41	807	5.1
" " ...	1,000- 1,500	1,227	36	1,263	2.9
" " ...	2,000- 3,000	2,527	88	2,615	3.2
" " ...	3,000- 4,000	3,289	113	3,402	3.2
" " ...	4,000- 5,000	4,962	116	5,078	2.2
Regular sulphides	100- 1,000	493	45	5,538	8.4
" " ...	1,000- 2,000	1,624	83	1,707	4.9
" " ...	2,000- 4,000	2,807	60	2,867	2.1
" " ...	4,000- 6,000	5,291	98	5,389	1.8

Material.	Grade. Ounces per ton.	Value commercial assay. Ounces per ton.	Value in slag and cupel. Ounces per ton.	Corrected value. Ounces per ton.	Percentage slag and cupel.
Regular sulphides	6,000- 8,000	7,362	110	7,472	1.5
" "	8,000-10,000	8,604	128	8,732	1.5
" "	10,000-12,000	10,538	150	10,698	1.5
" "	12,000-14,000	12,842	218	13,060	1.7
" "	14,000-16,000	14,866	180	15,046	1.2
Refinery residues,	14,000-16,000	15,952	159	16,111	1.
	Fine.	Fine.	Fine.	Fine.	
Base bullion	300- 500	400	8	408	2.
Fine "	998- 1,000	987	11.5	998.5	1.2

Material assayed.	Grade of value.	Range of inaccuracy.	Average inaccuracy.
Tailings	1- 20	18 - 8.6	13.7
Washed ore	15- 35	13 - 10.0	10.4
Raw ore	20- 50	16 - 5.0	9.7
Roasted ore	20- 45	12 - 6.0	9.1
Lead carbonate	50- 100	5.1- 2.6	3.8
Base sulphides	1,000- 5,500	5.0- 1.8	3.0
Regular sulphides	2,000-16,000	2.8- 1.2	1.7
Copper-silver bullion, 300 "fine"		2.0	2.0
Fine bullion, 999.3 "fine"		1.1	1.1

In a number of cases the slag and cupel have been assayed separately, but there does not seem to be any uniformity of results, except that the cupel silver is generally much greater than the slag silver, although in one case they were both the same, 0.8 ounce. In a set of twenty-nine assays, running from tailings at 6.2 ounces per ton to ore at 44.7, the cupel silver varied from 0.8 to 5.4 ounces per ton, and the slag silver from 0.1 to 1.8 ounces per ton; the lowest cupel silver was on 18 ounce ore and the highest on 24.1 ounce ore; the lowest slag silver was on 26 ounce ore, and the highest on 32.4 ounce ore, and both these assays were made by the crucible method. In only two cases was the cupel silver less than 1 ounce per ton, and one of these was on the 6.2 ounce per ton tailings, and in only two cases was the slag silver over 1 ounce per ton.

In the case of the nearly proof silver produced at the Marsac refinery, by the writers process, the straight assay shows 987 fine, corrected for slag and cupel absorption it becomes 998.5 fine, as given in the table, while with a check assay to correct the volatilization loss it becomes 999.3 fine.

When we come to consider the percentage of inaccuracy when figured upon the total material assayed we find that it is somewhat irregular but generally it follows the silver contents of the material, and in the case of rich products, becomes very large. Thus, in 2.3 ounce tailings the silver equals 0.0079 per cent. of the total and a 21.8 per cent. loss on this equals only 0.0017 per cent. of the total. On the other hand, in a 17,500 ounce sulphide the silver equals 60 per cent. of the total, but the comparatively small loss of 1.26 on this equals 0.756 per cent. of the total.

The following table gives a few results upon this point:

Material.	Grade. Ounces.	Silver per cent. of total.	Inaccuracy per cent. of silver.	of total.
Tailings.....	2.3	0.0079	21.8	0.0017
Ore	20.3	0.0696	8.9	0.0062
"	30.5	0.1011	5.	0.0051
"	31	0.1063	13.	0.0138
"	49	0.1680	8.8	0.0148
Base sulphides ...	431	1.477	8.6	0.12602
" " ...	5,078	17.41	2.2	0.38302
Regular sulphides	5,538	18.98	8.4	1.59432
" "	10,698	36.33	1.5	0.54495
" "	15,046	51.58	1.2	0.61896
" "	17,500	60.00	1.26	0.756

The question is sometimes asked if some wet method would not be better than fire assaying, but at present no such method is available.

While the correction for slag and cupel loss is easily made, and ought always to be made when accurate statistics are kept, there is yet the volatilization loss to correct, and some means of doing this is very desirable. While a check assay answers very well for bullion it would hardly be possible to construct check material for the varying characters of ores and products ordinarily met with.

As chemists we should all be interested in attaining the highest accuracy possible in our analytical work, but in this case, aside from the question of accuracy, and also the money value of the silver involved, when many thousand tons of ore are considered, this point has a very important practical application in indicating and bringing out unsuspected losses in mill opera-

tions. For instance, in one case, by ordinary assays of the ore, the mill showed to be extracting 87 per cent. of the silver in the ore, which was considered good work. Corrected assays of the ore showed, however, that the extraction was only 79.3 per cent. This led to an investigation, which showed that there was a volatilization loss of 10.9 per cent. in roasting the ore. This has been cut down to 5 per cent., with the expectation of reducing it still more.

In another case the extraction plus the tailings silver was 102.7 per cent., but corrected assays showed it to be only 87.1 per cent. This was brought up to 97 per cent.

These figures show that the commercial assays of ores are too unreliable if accurate mill statistics are desired.

THE ACHIEVEMENTS AND AIMS OF PHYSICAL CHEMISTRY.¹

By J. E. TREVOR.

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CHEMICAL changes, in common with all other natural processes, are in their ultimate nature transformations of energy. The study of chemical processes is therefore a study of the energy phenomena which they involve. Chemical reactions may absorb or take up heat, changes of density may occur whereby work is done, electrical energy and radiant energy may be produced. But the mutual relations of heat, work, electricity, and the like, involving the characteristic factors, temperature, pressure, tension, force, potential, etc., form the subject-matter of the science of Physics, and hence it is that the study of chemical processes as such has come to be known as the *Physical Chemistry*. The object of this branch of science is to discover the simple relations connecting the various types of chemical phenomena, and to make of these relations a coherent whole.

The Physical Chemistry is a new science. Up to eight years ago nothing serious had been attempted in the way of generalization. Very important discoveries had been made before that time it is true, yet they were of a wholly disconnected character and their bearing upon a general theory of chemical processes

¹ Read before the Midwinter Fair Congress of Chemists at San Francisco, June 7, 1894.