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IX.—*On certain sources of loss of Precious Metal in some operations of Assaying.*

BY G. H. MAKINS.

IN the assay of specimens of alloyed gold, the degree of heat used in the first operation, viz., cupellation (when this is carefully performed), is usually somewhat varied, according to presupposed proportions in the alloy,—for example, a much lower temperature being sufficient where the gold is only associated with silver, than where it is also mixed with oxidisable metals, which latter have to be separated entirely by this first operation.

About five years since, I chanced to have before me some 200 assays of gold, wherein the silver also had to be estimated, and in which, for other reasons, an extraordinary degree of heat was required to be employed; and as I made simultaneously with these, several synthetical proofs, I was much struck by the great extent of loss of gold and silver; and satisfied that it could not be entirely due to what is known amongst assayers as cupel absorption, I determined upon examining some of the contents of an iron flue of a cupel furnace, which passed from its hood into a chimney, in order to see if gold had been volatilized along with other metals, and if so, to what extent.

A quantity of apparently carbonaceous matter was therefore taken out of it; and as this flue was at the time recently put up afresh, I had the means of knowing that it had been used for the cupellation of gold assays only.

Upon examination of this material by the microscope under an inch power, it exhibited very distinctly portions of oxide of lead, in yellow masses, little nodules of suboxide of copper, minute grains of silver, together with portions resembling silver reduced from chloride,—the whole mixed with a quantity of carbonized matter containing small grains of unburnt fuel.

From pressure of business at the time, this material was laid aside (after cursory examination sufficient to prove the presence of the metals), until it could be completely examined. This was not done, however, until after the appearance of some collateral matter, communicated to the Society by my late pupil, Mr. Napier.

On further examination, the metallic matters present were found to consist of oxide of lead mixed with small portions of gold, silver, and oxide of copper; and as my object was only to estimate the gold and silver present, I took separate portions, viz., two of 50, and two of 100 grains each. They were each treated with 400 grains of pure lead, that is to say, with eight times the weight of the former two, and four times the latter, each having also its own weight of borax added.

The mixtures were then scorified, and the operation carried to its full extent, so as to diminish as much as possible the quantity of lead for the subsequent cupel process.

The process completed, the specimens were poured in a good fluid condition; the slag (which was quite free from metallic beads) separated; and the resulting metal next subjected to cupellation.

The little buttons so obtained, consisting of pure silver and gold, were then weighed.

From the first two assays (the material operated upon being 100 grains), the resulting buttons weighed (after compensating for silver contained in the lead employed), just .089 grain.

From the second two, upon 200 grains, the buttons weighed .166. If we average these, which are very nearly alike, and calculate the quantity for 1000 grains, we should have a result of .850 grain.

They were next all parted for gold, and the result was .026; equal to .087 in every 1000 grains.

Deducting then the weight of this gold from the weight of the compound metal, we find the quantity of the precious metals in 1000 grains to be,

Gold .. .087

Silver .. .763

Of course I do not attempt to establish any ratio between these quantities and an individual assay; for although the flue whence this material was taken had only been renewed a few months, yet during that time the fumes of many thousand assays had passed through it. But, on the other hand, I would remark, that considering that this flue is removed daily when the furnace is at work, the proportion which the precious metals bear to the whole, is very large indeed.

I will now call attention to a second cause of loss of gold occurring in parting operations, and possibly also in refining upon the large scale, viz., the solution of a portion of gold in the nitric acid used, although the latter is pure and quite free from hydrochloric acid.

Berzelius, in speaking of this fact says, "It must not be forgotten that if nitric acid contains hydrochloric or *nitrous* acid, it will dissolve gold; in truth, the quantity dissolved is considerable in the latter case, but sufficient to lead to an incorrect result." Now, in parting gold by nitric acid, we are generating during the operation quantities of nitrous acid, and consequently have the conditions present for this loss to take place.

Some time since, Mr. Field (the Queen's Assay Master), had in his office a pear-shaped bottle, into which nitric acid was constantly being poured after parting operations: it was thickly coated with gold. He showed this to Sir J. Herschell, who was then Master of the Mint, asserting that it was deposited from an actual solution of the gold. The latter gentleman supposed rather that it was a deposit from mechanically suspended particles; but this could have hardly been the case, as the bottle was a large pear-shaped one, and the gold coated the upper part as thickly as the lower, and very uniformly, which certainly could not have been the case had it been simply a deposit of mechanically suspended particles. It was no doubt, as Mr. Field observed, a good example of deposit from an actual solution.

I tried the following experiment, in order to arrive at some idea of the quantity so taken up in ordinary assaying operations.

Four assay-quantities of pure gold were accurately weighed, then added to the usual proportion of fine silver, and of lead, and cupelled. The buttons then rolled and coiled, were parted with nitric acid. For the boilings, acids were prepared of specific gravity 1.25 and 1.35 respectively.

No. 1 assay was then boiled 20 minutes in the weaker, and afterwards for 13 minutes in the stronger acid, between which operations the cornet was washed with hot distilled water.

No. 2 assay was boiled once in the first, and twice in the second acid.

No. 3. Once in the first, and three times in the second.

And No. 4. Once in the first, and four times in the second; the boilings, as I have said, being continued for 20 minutes in the weak, and for 13 minutes in the second acid.

The several cornets were then washed off with hot distilled water, annealed, and weighed, and the following is the result :—

Calling the weighings before the operations 1000: the first cornet weighed 999.6, the second 992, the third 998.7, and the fourth, 997.9; the loss thus increasing in proportion as we multiply the number of boilings.

Now, the question occurs as to whence the loss arises. I may first say, that it has been suggested that it is due to silver being more completely separated by the repeated boilings.

But in reply to this I can state, that I have examined these cornets over and over again; and that after the first boiling as above described, the amount of silver left in them is very uniformly 1.16 in the 1000 parts. But the difference between 999.6, the weight of the first cornet, and 997.9, that of the fourth, is 1.70; here then, supposing the latter to be entirely free from silver (which is not really the case), we have 0.54 abstracted, a quantity just equal to 3 grains in the troy pound, which loss can only be traced to the removal of gold.

Next: it has been urged, that the appearance of gold in the used parting acid, is due to mechanical causes, dependent upon the friction of an exceedingly soft and spongy body, by its being thrown violently about in a dense acid fluid, and by the rapid evolution of bubbles of acid, or acid vapour, rushing from its surface, all this being of course increased as the density of the acid is increased by evaporation.

I believe that this is not the case, and that in the fluid medium no such abrasion takes place, but that it is a true case of solution,

and by the agency of the nitrous acid evolved. In proof of this I have taken a portion of this acid which had been so used, and after dilution, separated the silver, then evaporated, and obtained small quantities of gold, which were next redissolved in nitro-hydrochloric acid, and proved to be such by the usual tests.

Again, I do not think that the deposit upon Mr. Field's store bottles (to which I have alluded), could have taken place in so regular a manner upon their upper portions without actual solution; for had it been mere mechanical suspension, the metal upon the lower part would of course have been much in excess.

Now, as to the evolution of this nitrous acid. At the first boiling, when the silver is present in such large quantity, nitrous acid is given off most copiously; but probably its solvent action upon the gold is then controlled and checked by electrical action, that is, by the gold becoming the negative, and the silver the positive element in a voltaic circuit; but when the silver is wholly (or nearly) removed, this check no longer exists, and the solution of the gold progresses more rapidly.

Then, with respect to the cause of the evolution of nitrous acid,—of course as I have already said, as long as there is any silver to oxidise, it will be generated; and when the silver is nearly abstracted, the method of boiling adopted by many assayers induces its continuance; for it is scarcely possible to boil an assay in strong acid without some means of disengaging the vapour formed; if some help be not afforded, the acid will "bump" so much as almost, if not quite, to throw it out of the flask. Hence it is the custom with some to introduce a small portion of charcoal, which, from its porosity, tends to the steady evolution of this vapour. Now, if the charcoal be entirely carbonized, it does not materially affect the acid; but if it contain much woody matter not thoroughly carbonized, it is then sure to decompose it, and set nitrous acid free. Indeed, I have for some years ceased to use this body, from its injurious effects upon the acid.

I am aware that the matters mentioned in this paper are somewhat trivial in a scientific point of view; but their commercial importance will be at once admitted, when we remember the enormous values dealt with in this country, and consider, moreover, that they are at times turned over and over again and that

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the question of profit and loss in such commercial operations are much, if not entirely, in the hands of the assayer.

Lastly, this publication may serve to account for some of the discrepancies which are sometimes found between assayers.