THE ASSAY OF MERCURY ORES.

BY GEORGE T. HOLLOWAY.

(Read at the Meeting, February 7, 1906.)

ALL the mercury of commerce is obtained by the roasting of cinnabar (HgS) in a current of air. The sulphur burns to the dioxide, and the liberated mercury, together with such native mercury as is frequently associated with the cinnabar, distils over and is collected in condensers and flues. Despite the enormous difficulty which is experienced in condensing the mercury and minimizing loss by leakage and flouting, the cheapness of the process and its comparative simplicity render it possible to treat

ores of extremely low value, and the bulk of the mercury now produced has been obtained from ores containing an average of between $\frac{1}{2}$ per cent. and 1 per cent. of the metal. It is true that ore as rich as 7 to 8 per cent. is worked at Almaden, in Spain, the oldest and richest mine in the world; but at Idria (Austro-Hungary), Nikitowka (South Russia), and Napa Consolidated Mines (California) respectively standing second, third, and fourth in order of production, the ore averages well under 1 per cent., as it does also in all other mines whose outputs are sufficiently large to count as factors in the world's production, which is stated to have amounted in 1904 to 3,581 tons of 2,240 pounds.

Cinnabar and native mercury usually occur impregnating or disseminated throughout limestones, dolomites, sandstones, etc. Copper and other ores frequently contain mercury, but not in quantity sufficient for extraction on the large scale. Bituminous matter commonly occurs in association with it, and in a few districts, as in Kweichow (China), antimony sulphide is met with, and seriously interferes with the extraction on account of the flouring of the mercury. The cinnabar and native metal, although frequently found in masses and occasionally in crystals, is practically all so mixed with the gangue and is so friable, and, notwithstanding its great density, so easily lost when "dressed," that no dressing plant has been found capable of treating it profitably, and although hand-picking is occasionally practised, almost the whole of the ore is roasted exactly as it leaves the mine.

The old method of assay consisted in heating a mixture of the ore with iron filings or litharge or lime to redness in a glass tube closed at one end and bent down at the other, which latter dipped into water. A length of magnesite or sodium bicarbonate at the closed end of the tube permitted the generation of a stream of carbonic acid gas to drive the remaining mercury vapour out of the tube after the ore had been decomposed. The mercury was collected, dried, and weighed as metal.

This method is excellent for picked or rich material assaying, say, 20 per cent. or more, and, as stated later, is still probably the most accurate for such material, on account of the large amount of ore which can be taken for assay, but is absolutely useless for the ordinary ore, which probably accounts for 99 per cent. of the world's output. Wet processes are inapplicable to such ore. The well-known Eschka process (*Zeit. für Anal. Chem.*, vol. ii., p. 334), in which a small quantity of the ore was heated with iron filings in a small crucible, and the evaporated mercury was collected on a weighed disc of gold, was therefore introduced. The gold disc was cup-shaped, and was formed with a flange fitting on the crucible top. It contained cold water, which was occasionally renewed during the progress of the test. The mercury became condensed on the gold, which, after being weighed, only required to be heated gently to drive off the mercury ready for the next test.

As regards accuracy, Eschka's process leaves little to be desired, and the use of a strip of gold foil placed at the open end of a small ignition tube of about $\frac{1}{8}$ -inch bore, in which a mixture of iron filings and a mineral or salt containing mercury is heated, forms a most delicate test for mercury.

The presence of mercury to the extent of only $\frac{1}{100}$ of 1 per cent. may thus be proved, and accurate estimations may be made when the total mercury only amounts to $\frac{1}{10}$ th per cent.

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In 1898, R. E. Chism (*Engineering and Mining Journal*, October 22, 1898, p. 486) introduced a modification in which the gold cup was replaced by a piece of silver foil pressed into shape into the top of the crucible, and his results appear to have been perfectly satisfactory.

The modification about to be described differs from that of Eschka or Chism only in the construction and arrangement of the apparatus, and is shown in the accompanying drawing.

Some difficulty is experienced in fitting the gold cup or silver foil "mercury-tight" to the crucible top, and the cooling water requires frequent renewal, as the collecting power of gold or silver is much reduced when warm. The author therefore employs a flat sheet of "fine" silver, which may be purchased of any thickness at about 3s. 6d. per ounce troy, and which, after annealing by warming to dull redness for a few seconds in a flame, may be rubbed perfectly flat between two surfaces of glass or wood. The silver may conveniently be somewhat thinner than a visiting-card, and is cut into a circular disc, F, about 2 inches in diameter, weighing from 2 to 6 grams according to its thickness. If of the former weight, it can be conveniently weighed on an assay balance, but it must be held up to the light and examined to insure absence of pin-holes, which often occur in thin foil, and which spoil the assay through escape of mercury. The crucible A may conveniently be of the deep form shown, and about $1\frac{3}{4}$ inches wide by $1\frac{3}{4}$ inches deep, and is ground down perfectly flat at the mouth on emery-paper. An ordinary Berlin porcelain crucible is used. A square plate, E, of silver foil about $\frac{1}{2}$ inch wider than the plate F is used as a cover. The plates E and F are kept cool by a round copper vessel, B, about 2 inches in diameter, with pipes, C, soldered in as shown for entrance and exit of the cooling water. The vessel B consists of a spun cap of copper soldered upon a flat copper disc with a turned up rim, D, which collects such water as occasionally condenses on the cooler. The copper may be about $\frac{1}{16}$ inch thick. The top of a round tin box would serve equally well for the body, but it is advisable to have the bottom of copper on account of its high conductivity. A piece of tin, G, cut out to receive the crucible, localizes the heat around the crucible bottom and rests on an ordinary tripod stand.

The ore to be assayed is heated with iron filings free from grease. The filings are best prepared by heating a quantity of several pounds in a covered crucible to a fair red heat for about an hour. All grease, etc., having thus been driven off or

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carbonized, the cooled crucible is opened; the top layer of the filings, if at all oxidized, is removed, and the filings are sifted. Those which pass through a 60-mesh sieve and those which pass a 30-mesh sieve are kept in separate stoppered bottles.

The ore is prepared by grinding it very finely, and may be dried before assay if containing no free mercury; but if, as commonly happens, any native mercury is present in a finely-divided state, practically the whole of it may be lost in drying. In that case it must be assayed as received and calculated out on the dry weight. The loss of mercury in drying may be ignored in the determination of *moisture* in any ordinary ore, as it would scarcely affect the result even in the second decimal place.

The amount of ore to be taken for assay depends on its richness, as the silver foil has only a limited power of retaining mercury.

It is advisable to weight out: 2 grams if the ore contains under 1 per cent. of mercury; 1 gram if the ore contains between 1 and 2 per cent. of mercury; 0.5 gram if the ore contains between 2 and 5 per cent. of mercury; 0.25 gram if the ore contains between 5 and 10 per cent. of mercury.

If the ore contains over 10 per cent., correspondingly less should be taken.

The ore is carefully mixed in the crucible with about 10 grams (roughly weighed) of the 60-mesh iron filings, and the mixture is covered with about 5 grams of the 30-mesh filings, even when only so small an amount as 0.25 gram of ore is used. The crucible is placed in the holder G on a tripod stand, the cleaned, flattened, weighed silver disc F is placed on the crucible with the disc E above to keep it clean, the cooler B is placed over all, and a weight is placed on the cooler to prevent displacement. Water supplied through a rubber tube traverses the cooler. A small Bunsen or spirit flame is brought beneath the crucible, the flame being of such a size as to just make the crucible bottom red, but so that the crucible is not red more than $\frac{1}{8}$ inch up the side. The heat is continued for twenty minutes, draughts being carefully excluded, as a draught may easily deflect so small a flame and practically stop the distillation. The iron removes the sulphur and also conducts the heat so that the mercury distils off and is collected by the disc F. After twenty minutes, the flame is removed, and after fifteen minutes' cooling the disc F is removed, dried by placing it in a water-oven for a few minutes, or by holding in tweezers and waving above a flame for a few seconds, cooled, and weighed. The assayer must decide for himself which method to use, and how long to allow for the drying. He should experiment on the disc from one of his assays by damping it, drying, and reweighing until he ascertains the conditions which insure drying without loss of mercury. When the ore contains bituminous matter, as sometimes happens, and as is shown by the smell or by a black or brownish stain on the foil, it is necessary to wash the foil with alcohol and dry as above before weighing.

Until the operator is experienced, it is advisable to reheat the crucible with another weighed piece of foil to insure that all the mercury has been driven off, but this is not usually found to be necessary. If the assay has been satisfactory, the mercury will all be seen as a dull or bright perfectly circular film on the foil, exactly the size of the crucible rim. If it extends beyond, which may occur either from too much

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ore having been taken, so that the silver cannot properly retain the resultant mercury, or from careless flattening or adjustment of the foil, the assay must be repeated.

When first using the apparatus, the operator should experiment by repeatedly assaying the same sample, varying the temperature and time until he finds the conditions which yield the highest result. Half a dozen such tests, occupying in all not over three or four hours, will suffice for gaining perfect control over the method. By coupling together a number of coolers with rubber tubes and arranging a row of the assays on a bench, one may easily carry on a dozen assays at a time in a confined space. An inverted $\frac{1}{2}$ -gallon Winchester, fitted up like an inverted wash-bottle, and having a regulating clip on its indiarubber discharge tube, will suffice for cooling a battery of a dozen assays. The water leaving the last cooler should not feel more than lukewarm.

When the assayer is experienced, he can allow the distillation of one set to continue without watching, while weighing the discs from the previous set.

The special precautions to be observed are : (1) Avoidance of excessive heating of the crucible. The edge of the covering foil E should never feel warm to the fingers. (2) Cleanliness and perfect flattening of the silver foil F. (3) Careful adjustment of the foil and coolers and of the weights on the coolers to insure contact all round the crucible top. (4) Careful drying of the foil. (5) Avoidance of draughts. (6) Allowance of the full time mentioned (fifteen minutes) for cooling before removing the foil, lest uncondensed mercury vapour be lost.

Although gold has a greater affinity for mercury than silver possesses, and is therefore theoretically better, silver has a greater collecting power weight for weight, and a greater conductivity, and has been proved by comparative tests to give at least equally correct results. No comparative figures are given, because the results are identical within the limits of experimental error. Indeed, if anything, the new method gives slightly higher results.

The silver can be used an indefinite number of times, and appears, on account of its greater porosity after prolonged use, to improve.

When elaborate care is used, the method, as tested by diluting down a weighed small quantity of pure cinnabar or pure mercury sulphide or oxide, has been found extremely accurate, but under ordinary conditions a slight loss from leakage may be expected, and the difficulty of sampling such an ore as cinnabar renders the danger of error greater. The cinnabar is extremely heavy and the gangue is usually decidedly light, and the fact that cinnabar commonly occurs as little rich patches in the gangue even in the case of very low-grade ore, and is therefore practically freed during crushing, renders it extremely liable to settle, despite the most careful mixing, and to further accentuate the danger of inaccuracy through sampling. This danger is not great when the ore contains under 10 per cent. of mercury, and may be overcome with care ; but when the ore contains 20 per cent. or upwards, it is advisable to distil, say, 10 or 20 grams of the ore in a glass tube with iron filings by the old method already mentioned.

The error due to sampling is, of course, then only one-twentieth or one-fortieth of the probable error on a 0.5 gram sample, and the loss from leakage is practically nil. Such ores, however, seldom require to be assayed, and, as already stated, the

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old method is practically impossible on average ores. With such low-grade ores it yields the mercury in beads so small that they can scarcely be collected and dried without heavy loss, and it is extremely cumbrous and slow.

On rich ores, the results by the author's method are sometimes too high and sometimes too low, either result being attributable to difficulty in sampling. As, however, the results are usually slightly low on ores containing over 20 per cent. of mercury when done without excessive precautions, the loss is probably due to leakage.

In the case of average ores, the total loss is so small as to be negligible, and duplicate results on a 1 per cent. ore should agree to within 0.05 per cent., a result which cannot be equalled by any wet method.

Experiments have been made in which the iron filings are replaced by reduced iron, or by copper, or by litharge, lime, etc. ; but, apart from the extreme convenience of iron filings, the other materials have shown no advantage whatever, and litharge and lime are distinctly less effective.

The author is informed that the method works well with salts of mercury, and there is no apparent reason why it should not do so, although the iron filings would in some cases have to be replaced by one of the agents mentioned above, or by some other decomposing agent. He has, however, had practically no experience on this point.

The process has been employed in his laboratory for five or six years, and the apparatus has been sent to mercury mines in Russia, China, Italy, and British Columbia, where it has been in constant use. At two mines, the gold cup process which was then in use has been abandoned in its favour on account of its greater convenience and speed, and at all these mines it has been constantly employed for valuing, selling, or buying the crude ore, for assaying tailings, and for controlling the working of the furnaces, etc. The above description may therefore be taken as that of a proved rather than a suggested method of assay.

DISCUSSION.

The PRESIDENT (Mr. Bevan) asked if the process could be used on a larger scale than Mr. Holloway had indicated, using a larger quantity of the ore.

Mr. HOLLOWAY said that the use of a larger quantity of ore did not increase the accuracy of the method if one had a good balance ; in fact, the process worked better with the small quantities recommended in the paper.

Mr. KITTO said that for many years he had used a gold cup having a fairly large cavity, and had found no difficulty in getting very accurate results without the addition of the ingenious apparatus which Mr. Holloway had described. He had been much interested in the device for automatically cooling the silver foil. Probably where, as in a mine, a large number of determinations had to be made, it would be very useful, but under ordinary circumstances he really did not think it necessary to complicate the very simple original apparatus. He had had no difficulty in getting the flange of the gold cup firmly fixed and accurately adjusted to the edge of the crucible.