PURIFICATION OF MERCURY.

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The constant use of the mercury cathode in this laboratory necessitates the frequent purification of very impure mercury. According to the methods described in the text-books a great deal of time is required if anything like complete purification is desired. Furthermore, little is known of the relative efficiency of the methods so that the worker simply chooses the one that strikes his fancy. It therefore becomes desirable to know how to obtain the purest mercury in the least time and with simple apparatus.

The usual methods are, first, to draw air through the metal contained in a wide inclined tube bent up at the end; second, to shake with mercurous nitrate, ferric chloride or potassium dichromate, in a separatory funnel; third, the method of L. Meyer,[1] to let fall in a fine stream through a long column of mercurous nitrate; fourth, to purify electrolytically by making the mercury the anode in a nitric acid solution;[2] and fifth, to distil. No one who has tried the first of these will think very highly of its speed or efficiency. The shaking in a separatory funnel requires no construction of apparatus and is probably the favorite method. The surface of contact between the metal and the solution is, however, relatively small and long shaking is obviously required to dissolve the impurities present in the mercury. Washing through a column of mercurous nitrate containing free nitric acid is excessively tedious, provided the opening of the funnel from which the mercury falls is sufficiently fine to give a thin enough stream. Moreover, this opening frequently becomes choked and the funnel must be removed and cleaned. Various automatic arrangements have been used to return the mercury to the funnel,[3] but they are more or less complicated and have no advantage in point of time. The electric purification is also time-consuming, requires efficient stirring and is not particularly effective.

For the removal of silver and gold, of course, distillation is necessary. This is usually done under reduced pressure in one of the various forms of still which have been proposed. Hulett and Minchin[4] have shown that unless the mercury is distilled in a current of air and with no bumping, the more volatile metals such as zinc or cadmium are not removed. The distillation apparatus they describe yields mercury of a high degree of purity, as shown by their careful testing.

[1] *Z. analyt. Chem.*, **2**, 241 (1863).

[2] Wolff and Waters, *Bull. Bureau of Standards*, **3**, 623; **4**, 1 (1907).

[3] *E. g.*, Desha, *Am. Chem. J.*, **41**, 152 (1909).

[4] *Phys. Rev.*, **21**, 388 (1905). The oxidation of the zinc or cadmium by the air is an important factor in the purification.

The writer has been using a modification of the L. Meyer method, which is very rapid and, as recent measurements show, very efficient. Instead of the mercury being delivered from a funnel drawn out to a fine point, a separatory funnel is used, the delivery tube of which is slightly narrowed 0.5 cm. from the lower end. Over this end is bound with twine a piece of rather closely woven muslin. The mercurous nitrate solution is contained in a piece of glass tubing 1.5 m. long and 2 cm. in diameter. The narrow delivery tube at the bottom is bent up 25 cm. This is more than usual, as it is necessary to have the height of the mercury in the wide tube about 5 cm. so that the tiny globules which fall will have time to coalesce before they reach the small tube, otherwise the mercury will not be delivered dry, or it may even be swept out of the tube followed by the entire solution of mercurous nitrate.

The end of the tube of the separatory funnel over which the cloth is bound should dip below the surface of the mercurous nitrate solution. This diminishes the surface tension of the mercury so that the fine streams running through the cloth break up into very minute globules. Unless the surface of the mercury is clean the funnel cock should be closed just before all the mercury has entered the stem of the funnel, as the dirt thus carried into the stem would clog the cloth.

By this arrangement, instead of one stream of mercury, as in the ordinary form of the apparatus, we have several hundred streams, finer than is practicable with the usual drawn-out funnel, and a number of them may be choked by particles of solid amalgam or dirt, before the flow of mercury is sensibly diminished. The rate of flow need only be limited by the rapidity with which the globules coalesce on reaching the bottom. The rapidity of the washing and the large surface of mercury exposed are obvious.

In order to test the efficiency of the purification, the method of Hulett and Minchin (*loc. cit.*) was used. In this method the electromotive force of the mercury to be tested is determined against pure mercury obtained by distillation in a current of air. The globules of mercury are placed on little mounds of paraffin in a crystallizing dish, through which contact is made by means of platinum wires. The electrolyte is normal potassium chloride saturated with mercurous chloride. To introduce the globules the writer used a fountain-pen filler instead of the ladles recommended by Hulett and Minchin. For measuring the small differences of potential there was used a Lippman electrometer capable of detecting 0.0001 volt.

To compare the relative efficiency of the washing described above, some zinc was added to mercury till it showed an e. m. f. against pure mercury (distilled as above) of 1.10 volts. Of this 800 g. were taken and washed four times through the modified L. Meyer apparatus, which

took five minutes. It then showed an e. m. f. of 0.0013 volt against pure mercury. Another portion of 300 g. was shaken five minutes in a separatory funnel with some of the same solution. At the end of this time it showed an e. m. f. of 0.23 volt. On shaking five minutes longer the e. m. f. dropped to 0.0104 volt. It is thus evident that the modified L. Meyer method is far more rapid and efficient.

A large quantity, 3 kg. of mercury, was then purified. It had been used for mercury cathode work and was very impure. It was first allowed to stand over night in a large shallow dish containing dilute sulphuric acid. A piece of platinized platinum foil was put into the acid in electrical contact with the mercury. The large overvoltage of hydrogen on mercury prevents the solution of metals from the mercury unless this precaution is taken. This mercury was then run through the apparatus five times, which required twenty-five minutes. It was then tested and showed an e. m. f. of 0.0002 volt against distilled mercury. One more washing, making six times in thirty minutes for 3 kg., yielded mercury which differed from the distilled by less than 0.0001 volt, the limit of sensibility of the electrometer. This corresponds, according to Hulett and Minchin, to less than one part of zinc in ten billion of mercury.

The advantage of the use of cloth instead of the usual drawn out fun nel is so obvious that it seems unlikely that the writer is the first to use it.[1] Since, however, it is not recommended by the standard text-books on laboratory methods, it will doubtless be of interest to those handling mercury to know how it may be purified in a very short time and with very simple apparatus, a degree of purity being obtained comparable with that of distilled mercury.

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NOTE.

Quantitative Determination of a Dissolved Substance in Presence of Suspended Material. — It frequently becomes desirable to determine the total amount of some substance in a solution which also contains an unknown amount of a precipitate or other foreign substance. If an aliquot part of the whole volume is taken and the whole amount of substance calculated from the amount found in the part taken, an error is introduced, the amount of which depends on the relation be-

[1] Gooch (*Am. J. Sci.* [3], **44**, 239 (1892)) has recommended a scheme whereby a stream of mercury is "atomized" by a blast of air and then allowed to fall into a funnel provided with a gooseneck and containing mercurous nitrate. The apparatus, however, requires some time to construct and adjust, and the globules of mercury fall through only a few centimeters of solution instead of 1.5 m. as in the apparatus here described.