

SOME EXPERIMENTS ON THE QUANTITATIVE EFFICIENCY
OF THE MARSH-BERZELIUS METHOD FOR THE
DETECTION OF ARSENIC.*

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We were led to make this investigation by the following observations: 1st. That when a solution containing a small quantity of arsenic is brought into the evolution flask of a Marsh apparatus the evolution of arseniuretted hydrogen is copious and regular for a short time, but it then diminishes very rapidly, and will often give no mirror after the lapse of twenty minutes. 2d. That when the evolution is slow and regular, and the decomposition chambers are together not less than three inches long, and that portion of the tube in which the deposition of the arsenic is to take place is sufficiently narrow and long, no arsenic escapes, either by being carried forward and out of the tube mechanically, or in the form of arseniuretted hydrogen.

It is stated that in the detection of arsenic by means of Berzelius' modification of Marsh's method, enough arseniuretted hydrogen always escapes to give arsenic spots on porcelain. We find this to be true whenever the evolution of hydrogen is rapid, or the quantity of arseniuretted hydrogen is relatively very large, and the temperature of the decomposition chamber is not proportionately increased. If the evolution of hydrogen is too rapid, arseniuretted hydrogen, though present in relatively small quantities, may escape decomposition in chambers of the length given, even though they are kept at a dull red heat. We found it necessary in our experiments so to regulate the evolution of the hydrogen that it burnt with a flame not exceeding 5-6 mm. when issuing from an opening of about 1 mm. diameter.

Two grams of resublimed arsenious acid were dissolved in a sodic carbonate solution, and the solution diluted to 1 litre. The following determinations were made with this solution:

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	Quantity of Sol. used.	Duration of the feeding.	Per cent of As found.	Duration of Experiment.
1.	50 cc.	45 min.	98.80	2 hrs. 00 min.
2.	"	"	98.99	2 hrs. 30 min.
3.	"	"	98.56	4 hrs. 30 min.
4.	"	"	98.94	2 hrs. 30 min.
5.	"	55 min.	99.26	2 hrs. 30 min.

In experiment 3, the evolution of gas was so rapid and irregular at the beginning that a portion of the arseniuretted hydrogen escaped decomposition and was lost. The solution was fed through a burette, and the gas was dried by being passed over calcium chloride. In some experiments made previous to those recorded we used soda-lime as a dryer, with results varying from 91.60 per cent. to 94.30 per cent. of the arsenic present. The soda-lime was examined and found to contain arsenic. We attributed the low results to the action of the caustic alkali on the arseniuretted hydrogen, and substituted pure calcium chloride for the soda-lime. In each of the five experiments given above we used a fresh portion of the calcium chloride; because we noticed that when the same calcium chloride was used in more than one or two experiments, or until it had become coated with its aqueous solution, arseniuretted hydrogen seemed to be retained, and the results correspondingly lowered. In one series of experiments in which the same calcium chloride was used four times we obtained the following results: 1st. 98.94 per cent.; 2d. 97.75 per cent.; 3d. 96.36 per cent.; 4th. 94.51 per cent. In two others in each of which the calcium chloride was used three times we obtained: 1st. 99.26 per cent.; 2d. 98.70 per cent.; 3d. 98.20 per cent. in one series, and, 1st. 98.94 per cent.; 2d. 95.00 per cent.; 3d. 94.70 per cent. in the other.

A very small drying tube was found to be sufficient. The one used was about 5 cm. long and rather more than 1 cm. in diameter.

In testing the applicability of this method to the determination of arsenic in minerals we selected an arseno-pyrite which had been analysed and found to contain 43.44 per cent. arsenic.

Two grams of this mineral were brought into solution by

aqua regia, and the solution evaporated down with addition of sulphuric acid, and heated to expel the last traces of nitric acid. After this had been effected the solution was diluted to one litre, and two determinations of arsenic were made, with the following results: 32.15 per cent., 32.60 per cent. We attributed the low result—only 74.08 per cent. of the arsenic present—to the fact that the arsenic was present in the form of arsenic acid. One-half litre of the solution was taken and the arsenic acid reduced to arsenious by boiling with a solution of sulphurous acid. Four determinations were made with this solution, giving us 36.90 per cent., 37.55 per cent., 37.25 per cent. and 37.00 per cent. A subsequent determination, made from another sample treated in the same manner, gave 36.80 per cent. arsenic. The last solution differed from the solution of arsenious acid in that it contained a salt of iron. A measured portion of the solution precipitated with sulphuretted hydrogen, and a solution of arsenious acid prepared by dissolving the arsenic trisulphide in acid sodium sulphite, with subsequent addition of sulphuric acid, and boiling to expel all sulphur dioxide from the solution. Some of the sulphur and arsenic trisulphide which separated out did not redissolve in this solution; it was filtered off and brought into solution in another portion of acid sodium sulphite. The solutions were united and boiled with a slight excess of sulphuric acid. The solution remaining clear, it was supposed that all the polythionates had been destroyed, but the solution gave a precipitate of sulphur and arsenic trisulphide when brought into the evolution flask, and arsenic trisulphide was deposited in the tubes. The rest of the solution (200 cc.) was evaporated down with the addition of sulphuric acid. It remained clear until it had been reduced to less than 50 cc., when a further separation of sulphur and arsenic trisulphide took place. The temperature of the solution was not determined. This precipitate was brought into solution and added to the main portion. Two determinations of the arsenic in this solution gave 41.67 per cent. and 41.53 per cent. arsenic. The arsenic was precipitated from the solution of another sample as the trisulphide, which was brought into solution in fuming nitric acid, evaporated down with sulphuric, and heated to expel the last traces of nitric acid, the

arsenic acid reduced by solution of sulphurous acid, and the solution diluted up to 1 litre. Two determinations of the arsenic in this solution gave 41.55 per cent. and 41.52 per cent. of arsenic. We found no difficulty in reducing the arsenic acid in a sulphuric acid solution by means of a strong sulphurous acid solution, the reduction being completely effected within $1\frac{1}{2}$ hours.

The next mineral experimented with was a tetrahedrite. The sample was brought into solution, the arsenic acid reduced and thrown down with the antimony and copper, the antimony and arsenic sulphides were dissolved out and separated by means of acid potassium sulphite. The arsenic was thrown down from this solution by sulphuretted hydrogen, and finally obtained in solution as arsenious acid. Two determinations of arsenic were made by this solution; one gave 4.20 per cent., the other 4.16 per cent. of arsenic.

A second sample was treated in the same manner, and two determinations made with this solution gave 3.81 per cent. The arsenic in a third portion of this solution was determined as magnesian-pyro-arsenate, and gave 3.801 per cent. of arsenic.

The zinc used was "C. P." bar zinc, but while it was free from arsenic, the amount of carbon contained in the different samples varied greatly, and only a few of them dissolved without any residue. The facts (1) that the presence of about 33 per cent. of iron in the arseno-pyrite reduced the amount of arsenic obtained by more than 10 per cent., (2) that our highest results were obtained with the purest zinc which we succeeded in procuring, (3) that, when two experiments were made with the same bar of zinc, one-half of it being used in each, they agreed better than when they were made with different zincs, suggesting that the constant deficit in our determinations, even after we had eliminated other sources of error so far as we could, might be due to the influence, probably galvanic, of the carbon in zinc. We endeavored to establish this by using some bar zinc which was very rich in carbon. The other conditions of the experiments were the same as in the first series given. The results obtained were 95.8 per cent., 95.2 per cent., 95.05 per cent. of the arsenic introduced into the flask. Another determination

was made with the addition of copper sulphate solution, and we obtained 69.30 per cent. of the arsenic. In the early part of our investigation we brought, in some experiments, platinic chloride, in others a spiral of platinum wire, into the evolution flask, and obtained such low results that we rejected them.

In all of these experiments the arsenic was deposited in two tubes; 97 per cent. on an average being deposited in the first tube, and all of the rest in the second. A third tube was used in a number of the experiments, but in no instance was any arsenic obtained in it.

The most convenient tube was found to be a hard glass tube with a total length of 18 cm. The decomposition chamber was 6 cm. long and 1 cm wide. That portion in which the deposition took place was about 10 cm. long and 6 mm. wide. The second tube was of the same form, but the decomposition chamber need not be more than one-half as long.

Our conclusion is that the method will give satisfactory results under the following conditions:

- 1st. The zinc must be free from carbon and pure in other respects.
- 2d. The arsenic should not be present in the form of arsenic acid.
- 3d. Iron, copper, platinum or their salts, and probably the other heavy metals and their salts, must be absent.
- 4th. The calcium chloride should be neutral and should not be used more than once.
- 5th. The feed and evolution of the gas should be both slow and regular, and the decomposition chamber kept at a dull red heat.