THE RETENTION OF ARSENIC BY IRON IN THE MARSH-BERZELIUS METHOD.[1]

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AN extended discussion of the determination of arsenic in small quantities has recently been published in the English chemical journals and several chemists have called attention to the fact that different samples of zinc produce mirrors of varying intensity from like amounts of arsenic.

The Joint Committee of the Society of Chemical Industry and the Society of Public Analysts in reporting the details to be followed in carrying out the Marsh-Berzelius method state that "It is important to note that some pure zinc is, from a cause at present unknown, not sufficiently sensitive; that is to say, the addition of minute quantities of arsenic produces no mirror."[2] O. Hehner[3] states that he found some zinc which, while retaining the arsenic in the form of rods, did not do so when granulated, and further claims that the addition of platinic chloride renders the reaction less delicate. Again[4] the same author finds that minute quantities of arsine are not evolved when aluminum and sodium hydroxide are used as a source of the hydrogen, and that even so much as 0.2 mg. in 25 cc. of solution gives no mirror. Wöhler as far back as 1839 stated that when arsenical pig iron is dissolved in dilute sulphuric acid the arsenic does not pass off with the hydrogen but remains as a salt of arsenic acid.[5] Headden and Sadler[6] found that very low results for arsenic were obtained by the Marsh-Berzelius method on arsenopyrite, FeAsS. The amounts were increased by removing the iron, and they suggest that, as much better results were obtained on duplicates from the same bar of zinc, one-half being used in each, the difficulty might be due to the carbon present. They later state[7] that the addition of copper sulphate or platinic chloride also made the results much lower.

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[1] Read at the Pittsburg meeting of the American Chemical Society.

[2] *J. Soc. Chem. Ind.*, **21**, 95 (1902).

[3] *Ibid.*, **20**, 194.

[4] *Ibid.*, **20**, 200.

[5] *Ann. der Pharm.*, **31**, 95 (1839).

[6] *Am. Chem. J.*, **7**, 341.

[7] *Ibid.*, p. 342.

Sautermeyer[1] found that even when 0.1 gram of arsenic trioxide was purposely added he could get no reaction for arsenic when 1 gram of iron was dissolved in dilute hydrochloric acid in a Marsh apparatus and the flame allowed to play on porcelain. The test works, however, when 2.5 grams of zinc are added to the iron. Under these conditions 1 mg. of arsenic may be detected although it comes off slowly. No quantitative determinations were made.

Although the results obtained by the before-mentioned authors would seem to indicate that the presence of iron was highly deleterious the fact seems to have been entirely lost sight of by chemists and in most instances the investigators themselves attribute their low results to other causes or, at least, do not state the necessity for the absence of iron. In fact the contrary is frequently true and recommendations to add ferric chloride to insure regularity of flow of gas will often be found in the literature, even so well known an authority as Mr. A. H. Allen[2] recommending that the zinc always contain, at least, a trace of iron to insure the regular evolution of hydrogen and the formation of uniformly deposited brown mirrors. This condition will probably almost always exist, as our experience has been that it is almost impossible to purchase zinc free from iron.

Our attention was called to the fact that the Marsh-Berzelius method often fails to give up, as arsine, all the arsenic present, by repeated failures to obtain in the form of mirrors the weight of arsenic which had been added to the generator, while a careful examination of the gas that had passed through the heated tube proved it to be arsenic-free. The remaining arsenic, therefore, could be in the generator only. To overcome the difficulty we used the zinc in rod form and then the same zinc granulated, zinc containing carbon and zinc carbon free, but found they all retained arsenic. We also tried many samples of zinc, but while different percentages of the arsenic present were recovered we were not able to obtain any sample of zinc that yielded all the arsenic that had been added.

In order to investigate the question, relatively large amounts of zinc were used and varying amounts of arsenic added. We soon found that if a too large amount of arsenic, relative to the escaping

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[1] *Chem. Ztg.*, **15**, 1021.

[2] *J. Soc. Chem. Ind.*, **21**, 94 (1902).

hydrogen was present, as arsenious acid, it was reduced first to the metallic and not to the gaseous state. This is probably so well known that the fact is seldom mentioned, but it was at the time new to us. By never using more than a few centigrams of arsenic trioxide this difficulty was avoided and the residues left in the generator, which with some samples of zinc were voluminous, were arsenic-free or so nearly so as to yield but a faint brown coloration in place of a mirror. These residues consisted generally of lead and carbon but as we could trace no relation between their presence and the retentive action of the zinc there will be no need to mention them further. The retained arsenic was, therefore, in the solution.

The solution left in the generator was filtered, acidified with strong nitric acid to prevent volatilization of arsenious chloride, if present, and was evaporated to hard dryness over a free flame. As the last of the water passed off a brick-red precipitate, intermixed with the zinc chloride, was formed, which was insoluble in water and strong nitric acid. The zinc chloride, together with any lead chloride, was dissolved out with hot water and was now found to be iron-free and to still yield no further mirror of arsenic. In fact, subsequent trials showed this to be a most excellent method of preparing pure zinc chloride free from iron, as the iron was quite perfectly separated even when considerable quantities had been added. The brick-red precipitate, on being dissolved in concentrated hydrochloric acid and again treated in the Marsh apparatus, yielded a large part of the arsenic which had been retained, as arsine, but again a portion was held back. By twice repeating the process of evaporation of the solution with nitric acid and re-treating the red precipitate formed, almost all of the arsenic added was recovered.

To determine the character of the red precipitate, a quantity was prepared, carefully washed and dried in a steam-bath. Washing was difficult, unless quickly done, as the precipitate had a decided tendency to become colloidal and it was found by no means as simple to free it from zinc as it had been to free the zinc chloride from iron. Samples were finally secured which were zinc-free. Several samples prepared in this manner were found to contain only iron, water and arsenic. No nitrogen was present. The material was therefore a hydrated iron oxide carrying arsenic.

Several attempts to determine in what form the arsenic was held have met with failure. The arsenic appears to be not an essential constituent of the red precipitate for it is present in very varying amounts and we have prepared an exactly similar compound arsenic free.

An analysis of two separate samples showed them to contain:

	Fe_2O_3.	As.
Sample 1	86.4	0.75
Sample 2	87.1	1.53

In both instances the arsenic was deposited as a mirror and weighed, as the quantity was so small compared to the iron that the ordinary gravimetric separation proved inadmissible. Accordingly the amounts are lower than the reality. A few of the actual experiments performed in this preliminary work will prove of interest.

(1) With no iron present but that contained in ordinary reagent "arsenic-free" zinc:

Arsenic-free, granulated zinc, containing iron, lead and carbon as impurities used and 0.05 gram of arsenic trioxide, in solution in hydrochloric acid were added. A considerable residue of lead and carbon remained, which, after being washed, dissolved in nitric acid, and re-treated in a Marsh apparatus, yielded a mere trace of arsenic. The solution evaporated to dryness with nitric acid, over free flame, gave a brick-red precipitate which, after being carefully washed, dried, dissolved in hydrochloric acid and re-treated in a Marsh generator yielded a mirror weighing 0.0025 gram. The zinc chloride and washings from the red precipitate were arsenic-free.

(2) With an excess of iron salt added:

Arsenic-free stick zinc was used. Several cubic centimeters of a concentrated solution of ferric chloride and 0.3 gram of arsenic trioxide was added in hydrochloric acid solution. Results as in (1) except that a large amount of the red precipitate was formed and a determination of a portion of it gave a mirror equivalent to 0.032 gram of arsenic in the whole.

(3) To find the proportion of arsenic recovered when the red precipitate is re-treated in a Marsh apparatus:

Arsenic-free zinc containing iron, hydrochloric acid, and 0.00506 gram of arsenic were used.

First mirror deposited 0.00425 gram; held back by iron 0.00081 gram.

The generator solution was evaporated with nitric acid, the red precipitate washed, dissolved in hydrochloric acid, and re-treated in the Marsh apparatus.

Second mirror deposited 0.00055 gram; held back by iron 0.00026 gram.

The generator solution was evaporated with nitric acid, the red precipitate washed, dissolved in hydrochloric acid, and re-treated in the Marsh apparatus.

Third mirror deposited 0.0001+ gram.

(4) To find if the same action took place when sulphuric acid was used instead of hydrochloric acid:

87 grams zinc, 25 grams ferrous sulphate in crystals, 0.5 gram arsenic trioxide, and dilute sulphuric acid were used. After the action ceased the sulphates were all precipitated by barium chloride, filtered, the solution treated with nitric acid and evaporated as before. The red precipitate formed easily and, being treated once in the Marsh generator, gave a mirror weighing 0.0054 gram.

In all of the experiments to follow, the method of Marsh-Berzelius, as outlined by the Joint Committee of the Society of Chemical Industry and the Society of Public Analysts[1] was used, care being taken to remove by lead acetate any hydrogen sulphide or selenide that might be present, as Rosenheim[2] and others have shown that selenium has a marked inhibitive action on the formation of mirrors. The mirrors were, however, weighed instead of being compared to standard mirrors as the nature of the investigation necessarily precluded their use, we being unable to procure any zinc that did not retain some arsenic. Many attempts were made to procure, on the market, iron-free zinc, but without success. The purest obtainable contained but 0.0011 per cent., which would ordinarily be considered as a mere trace. When looked at from the standpoint of the small amounts of arsenic determinable by the Marsh method it is, however, considerable. It may be well also to state here that our experience shows us that zinc in the so-called powdered form in which the grains are much the same size and approximately 1 mm. in

[1] *J. Soc. Chem. Ind.*, **21**, 94 (1902).

[2] *Chem. News*, **83**, 280.

diameter, is much the best form to use, as it gives a large surface for action and a corresponding uniformity in the flow of gas, which can be obtained from no other form.

Using the purest zinc obtainable, containing 0.0011 per cent. iron, no arsenic, and leaving no residue or but a mere trace, in the generator, when slight excess of acid was added, we next proceeded to determine the effect of adding known amounts of iron and of ferric chloride. Some 30 to 40 grams of zinc were used for each experiment. In order to obtain an alloy of iron and zinc we used the zinc in the rod form, added iron reduced by hydrogen, fused the whole and granulated. The alloying was fairly successful when small amounts of iron were used but was seldom complete with the larger quantities. Each sample made was proved to give no mirror itself before the addition of any arsenic.

A preliminary experiment on the purest (Fe 0.0011 per cent.) zinc gave results as follows: Arsenic taken, 0.0050 gram; arsenic found, first mirror, 0.0048 gram.

On evaporating with nitric acid and re-treating the small amount of red precipitate formed, a light brown mirror, too small to be weighed, but representing a small fraction of a milligram was obtained. This is especially noteworthy as showing that even with this small amount of iron some arsenic is retained.

EXPERIMENTS WITH ZINC ALLOYED WITH IRON.

The alloying was not always perfect, especially with the larger amount.

1. Alloy, 100 grams zinc; 0.2 gram iron: Arsenic taken, 0.0025 gram: first mirror, 0.0008 gram, 32 per cent.

2. Alloy, 100 grams zinc: 1 gram iron: Arsenic taken, 0.0050 gram; first mirror, 0.0017 gram, 34 per cent.

3. Alloy, 100 grams zinc: 5 grams iron: Arsenic taken, 0.0050 gram; first mirror, 0.0017 gram, 34 per cent.

4. Alloy, 100 grams zinc; 20 grams iron: Arsenic taken, 0.0050 gram: first mirror, 0.0025 gram, 50 per cent.

EXPERIMENTS TO SHOW THE EFFECT OF FERRIC CHLORIDE IN THE GENERATOR SOLUTION.

1. 30 grams purest zinc, with 0.2 per cent. iron as $FeCl_3$ added to generator: Arsenic taken, 0.0050 gram; first mirror, 0.00345 gram, 69 per cent.

2. 30 grams purest zinc, with 1 per cent. iron as $FeCl_3$ added to generator: Arsenic taken, 0.0050 gram; first mirror, 0.0027 gram, 54 per cent.

3. 30 grams purest zinc with 5 per cent. iron as $FeCl_3$ added to generator: Arsenic taken, 0.0050 gram; first mirror, 0.00295 gram, 59 per cent.

4. 30 grams purest zinc with 20 per cent. iron as $FeCl_3$ added to generator: Arsenic taken, 0.0050 gram; first mirror, 0.0016 gram, 32 per cent.

5. 30 grams purest zinc with 15 per cent. iron as $FeCl_3$ added to generator: Arsenic taken, 0.0001 gram; first mirror, less than 0.000001 gram.

From the results of our work we are forced to the conclusion that iron, whether as an alloy with the zinc or in the generator as a soluble salt, must be avoided, if exact quantitative results are desired. Whenever iron was present, even in small amounts, we have never failed to find arsenic in the red precipitate of hydrated iron oxide, formed by evaporating the liquid contents of the generator with nitric acid. This fact must give rise to serious error in the determination of very small amounts of arsenic by the use of standard mirrors, unless special precautions are taken, and it is for the determination of these small fractions of a milligram that the Marsh-Berzelius method finds its special application. Although our results do not show any definite amounts of arsenic retained by a given percentage of iron present as impurity we are inclined to believe that the amount retained would be fairly definite where the amount of iron present was very small. If this is true, the method of using standard mirrors, so universally adopted, will give results of essential accuracy, if the precaution be taken to always prepare the standards from the same zinc to be afterwards used in the analysis. It is also necessary that the zinc be as nearly free from iron as can possibly be obtained and that soluble salts of iron be kept out of the generator. It, accordingly, will be necessary in preparing solutions containing iron for analysis to reduce them and distil off the arsenic, as arsenious chloride, before adding to the generator. As a qualitative test we have never failed to get a mirror, even with iron present, when as much as 0.01 mg. of arsenic was added.

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