

**On an alleged fallacy in Marsh's process for the detection of arsenic / by
Arthur Gamgee, M.D.**

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Prof. J. B. Russell
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ON
AN ALLEGED FALLACY
IN
MARSH'S PROCESS FOR THE DETECTION
OF ARSENIC.

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BY ARTHUR GAMGEE, M.D.,

ASSISTANT TO THE PROFESSOR OF MEDICAL JURISPRUDENCE IN THE UNIVERSITY
OF EDINBURGH.

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IN the *Journal de Pharmacie et de Chimie* for December 1863, M. Blondlot published a highly interesting little memoir, entitled 'Recherches toxicologiques sur la transformation de l'Arsenic en hydrure solide, par l'hydrogène naissant, sous l'influence des composés nitreux ou de la pression.' The statements made in this paper are of the greatest importance to toxicologists, as, if proved to be true, the gravest doubts would be cast upon a large number of the analyses for arsenic which have been performed in medico-legal cases during the last few years. It is needless to insist upon the propriety of being accurately acquainted with the fallacies to which any scientific process is liable, more especially of a process furnishing evidence which may lead to the death of a fellow creature; on the other hand, it is equally important that we should not be deterred by alleged fallacies, which have no existence except in the imagination of their originators, from using with confidence valuable and really reliable methods of investigation.

It has long been known that under certain circumstances either the conversion of arsenical compounds into the gaseous hydride of arsenic (AsH_3), through the agency of nascent hydrogen, is altogether prevented, or the gas having been formed, is subsequently decomposed. Copper, mercury, and chlorate of potash have been shown to act in this way.¹ M. Blondlot has, in the memoir to which allusion has already been made, endeavoured to show that under two other circumstances the conversion into gaseous hydride of arsenic is prevented, the solid hydride of arsenic being instead produced.

¹ See Dr Taylor on Facts and Fallacies connected with the Research for Arsenic and Antimony, etc., in Guy's Hospital Reports, Third Series, vol. vi., 1860.

These circumstances are—

1st, When the acid used for the evolution of the hydrogen contains a nitrous compound.

2d, Under the influence of pressure.

The first of these circumstances is the one which is of greatest interest to us in a toxicological point of view, and the accuracy of which I hope to disprove.

According to M. Blondlot, if the sulphuric acid made use of in Marsh's process¹ happens to contain a trace of a nitrous compound, as well as a trace of arsenic, the hydrogen evolved by its action upon zinc will, when tested, be found to be perfectly pure. On heating a tube through which the gas is passed, no deposit of metallic arsenic will take place, the arsenic present in the sulphuric acid having, under the influence of the trace of nitric acid, been converted into the solid hydride. The operator will therefore assume the purity of his reagents. When he now proceeds to add the fluid which he wishes to test, if the latter contain any organic matter, it will neutralize the action which the nitric acid alone would exert, and any arsenic present in the sulphuric acid would then be evolved in the form of the gaseous hydride; the operator will consequently obtain a deposit in the tube through which the heated gas is passed, due (he will suppose) to arsenic present in the substance examined, but in reality originally present in the sulphuric acid which he had erroneously considered to be pure.

The formation of solid hydride of arsenic is, according to Blondlot, most easily seen. If zinc be treated with dilute sulphuric acid containing a trace of a nitrous compound, and then an arsenical compound be added, brown flocculi will soon be seen to float about the fluid; these flocculi consisting of solid hydride of arsenic. Solutions of cane sugar, or almost any organic matter, will check this reaction.

The statements of M. Blondlot are of so important a nature, and have been made in so positive a manner, that I undertook, at the request of Professor MacLagan, a series of experiments, to endeavour to determine their accuracy; and the results to which I have arrived are so entirely at variance with those of the French chemist, that I have thought fit to publish them. They show conclusively, I believe, that in actual practice nitrous compounds do not interfere with Marsh's process, and they almost disprove the formation of a solid hydride of arsenic under the influence of these compounds. Before proceeding to an account of my own experiments, I may call attention to the fact that Blondlot has not given the least *proof* that the solid hydride of arsenic is formed under the circumstances which he alleges. He merely noticed, I suppose, that under certain circumstances, when adding an arsenical compound to a mixture of zinc and dilute

¹ M. Blondlot seems to assume in his paper that sulphuric acid is invariably used for evolving the hydrogen.

sulphuric acid containing a little nitric acid, no *arsenical mirrors* were obtained on passing the gas evolved through a heated tube, and that in these cases brown flocculi were always seen floating about the fluid. M. Blondlot has not sufficiently considered that the fact of not obtaining an arsenical mirror is no proof of the non-evolution of gaseous hydride of arsenic, and that no inference whatsoever can be drawn from brown flocculi floating about the fluid of Marsh's apparatus, as such are nearly always formed on dissolving even the present zinc used in toxicological investigations.¹

The first experiments which I undertook in order to test M. Blondlot's statements were directed to the investigation of the following points:—

1st, Does a trace of a nitrous compound so interfere with Marsh's process as to prevent the formation of mirrors of metallic arsenic?

2d, If nitric acid, or any other nitrous compound, does so interfere, to what extent does it do so?

3d, Does the addition of organic matter to the fluid containing dilute sulphuric acid, nitric acid, and arsenic, promote the evolution of arseniuretted hydrogen?

The plan of my experiments was the following:—I made certain standard solutions which contained a known amount of arsenic in a certain volume. I determined how large a deposit of metallic arsenic I could obtain from different quantities of these solutions when subjected to Marsh's process; the bulk of the dilute acid being always the same, as also its composition (56 cubic centimetres, or about 2 fluid ounces, of a mixture of one part of chemically pure sulphuric acid of specific gravity 1.838.76, and five parts of distilled water, being used). I then added the same quantity of the standard solutions to the same quantity of dilute sulphuric acid and zinc, the acid containing a known percentage of nitric acid, and I observed whether I obtained mirrors of metallic arsenic, and if their size was equal to that of the deposits obtained when the pure acid was used.

The number of standard solutions which I employed was three, which were labelled A, B, and C.

Solution A contained 1 gramme (15.434 grains) of pure arsenious acid in 1000 cubic centimetres of distilled water. One cubic centimetre of this solution was therefore equal to .001 gramme, or between the one and two hundredths of a grain of arsenic (.0154 gr.).

Solution B was made by diluting 100 cubic centimetres of solution A to 1000 cubic centimetres. One cubic centimetre of this solution was therefore equal to the 10th of a milligramme, or

¹ I have been quite unable ever to obtain a piece of pure zinc which was entirely soluble in dilute sulphuric or hydrochloric acids, certain traces of flocculi being always left undissolved. My experience on this point is, I am certain, that of every one. I am at present engaged in an examination of their nature.

between the one and two thousandths of a grain of arsenic ($\cdot 00154391$).

Solution C was prepared by diluting 100 cubic centimetres of solution B to the bulk of 1000 cubic centimetres. One cubic centimetre was therefore equal to the 100th part of a milligramme (or to between one and two thousandths of a grain) of pure arsenious acid.

These solutions enabled me to add with the greatest accuracy excessively small and known weights of arsenious acid. The apparatus I made use of for the performance of Marsh's process was fitted up exactly as Dr Alfred Taylor recommends; the evolved gas being made to pass through a sufficiently large chloride-of-calcium tube, which contained, besides chloride of calcium, a considerable quantity of cotton wool which had been dipped in solution of acetate of lead and then dried. To the chloride-of-calcium tube was fitted a tube of hard German glass, free from lead, which was drawn out in two or three different places, so that its diameter did not exceed the tenth of an inch. The free extremity of the tube was either drawn out to a jet, or bent at a right angle, for the convenience of dipping it into liquids. As stated above, the bulk of the dilute sulphuric acid employed, whether pure or containing a percentage of nitric acid, was always the same, so that the experiments admit perfectly of comparison. Before adding the portion of fluid containing arsenic I nearly always lighted the jet of hydrogen, so as to have a knowledge of the rate of the evolution of the gas, and heated the horizontal tube behind one of the constrictions to dull redness. Operating in this manner I found that I could obtain from one cubic centimetre of solution B (containing 1-10th of a milligramme or $\cdot 001543$ grain of arsenious acid) a large mirror of metallic arsenic, which could be abundantly identified. On the other hand, one cubic centimetre of solution C (corresponding to the 1-100th of a milligramme, or between the one and two ten-thousandths of a grain of pure arsenious acid, yielded, after heating the tube through which the gas was passed for nearly an hour, a faint, but very pretty and distinct mirror of metallic arsenic.

The first experiment which I tried to ascertain whether nitric acid checks the development of gaseous hydride of arsenic, or prevents the formation of mirrors in the tube through which the gas is passed, was a comparatively rough one.

Experiment 1.—A Marsh apparatus had placed in it pure zinc and two ounces of a mixture of one part of sulphuric acid of specific gravity 1838.71, and five parts of water. When hydrogen was freely evolved, the gas delivery tube was heated to redness behind the constriction, and 30 grain measures of nitric acid were added; then one cubic centimetre of arsenical solution A (containing one milligramme = $\cdot 015434$ of pure arsenious acid). A very distinct mirror of metallic arsenic was obtained in the constricted portion of the tube.

Exp. 2.—A Marsh apparatus had placed in it pure zinc, and the acids exactly as in last experiment. Two cubic centimetres of solution B (containing 2-10ths of a milligramme, or $\cdot 00154 \times 2$ of pure AsO_3) were added. No mirror was obtained. A large quantity of a saturated solution of cane sugar was added. No deposit, however, was obtained.

Exp. 3.—Two oz. of mixture of dil. HO, SO_3 and 1 cubic centimetre of solution B ($= 1\text{-}10\text{th}$ of a milligramme, or $\cdot 0015434$ of pure AsO_3) added. Two very good deposits obtained.

These experiments were repeated, and identical results obtained. They show, 1st, that when sulphuric acid contains an enormous percentage of nitric acid, the production of mirrors from *very* small quantities of arsenic is checked, although this property seems to be possessed only to a slight extent, as sulphuric acid, containing about 13 per cent. of anhydrous NO_3 , prevented the formation of mirrors from the 500th of a grain of arsenic, though not from the 100th. In experiment 2, when no deposit was obtained, sugared water was largely added, but no effect followed; in all my experiments when I found that nitric acid prevented the formation of mirrors, I added to the apparatus a saturated solution of sugar, invariably with the result that no deposit resulted; results altogether at variance with the statements of M. Blondlot. My subsequent experiments were conducted with sulphuric acid containing always the same quantity of nitric acid. Five cubic centimetres of nitric acid of specific gravity 1400.27 (containing about 57 per cent. of nitric anhydride), were diluted to 100 cubic centimetres with sulphuric acid of density 1838.76 (containing about 96 per cent. of the monohydrated acid). The mixture of nitric and sulphuric acids contained, therefore, nearly 3 per cent. (2.99 parts) of NO_3 in 100 of the mixed acids. The mixture was diluted to 600 cubic centimetres.

Exp. 4.—A Marsh apparatus worked with two fluid ounces of the above-mentioned mixture of dilute nitric and sulphuric acids. One cubic centimetre of solution B ($= \cdot 0001$ gramme of AsO_3) added. A very good mirror of arsenic was obtained. This mirror was mixed with a little white deposit inside the tube, which was taken to be sulphur. (See *Exp. 5.*)

Exp. 3. was repeated, and exactly the same sized deposit was obtained. It was compared with a deposit obtained by adding 1-10th of a milligramme to a Marsh apparatus worked with dilute sulphuric acid, containing no nitric acid. In the latter case the mirror appeared to be rather larger than the one obtained in *Exp. 3.*, and there was no white deposit inside the tube.

The above experiments, which are merely some of a numerous series, and which were thoroughly confirmed by repetition, appear to show, 1st, That when, in Marsh's process, the gas is evolved by the action of dilute sulphuric acid upon zinc, if the sulphuric acid contains an enormous quantity of nitric acid, the formation of

mirrors from an extremely minute quantity of an arsenical compound is checked; the extent to which this occurs, depending both upon the amount of the arsenical compound added to the acid mixture, and to the amount of nitric acid present in the latter. Thus, whilst sulphuric acid, containing 13 per cent. of anhydrous NO_3 , did prevent the formation of mirrors from about 1-500th of a grain of arsenic, it did not do so when the quantity of arsenic amounted to the 1-100th of a grain. On the other hand, with an acid containing about 3 per cent. of nitric acid, good mirrors were obtained from the 1000th of a grain, although their development was to a certain extent checked.

2dly, That when nitric acid prevents the formation of mirrors of arsenic, the addition of an organic fluid, such as sugared water, exerts no influence in causing their appearance.

The practical objections to Marsh's process, conducted even with dilute sulphuric acid containing a trace of nitric acid, fall to the ground completely, as no sulphuric acid will be, I presume, ever found in commerce containing as much as 3 per cent. of anhydrous NO_3 , the point at which the acid appears at all perceptibly to influence the formation of a mirror.

Having disposed of the practical bearings of M. Blondlot's memoir, there remains only for solution the following question:—

When nitric acid, mixed with the dilute sulphuric acid used in a Marsh apparatus, checks the promotion of mirrors of arsenic, does it do so by preventing the evolution of arseniuretted hydrogen? and if so, does it give rise to a solid hydride of arsenic? The following experiments give a decisive answer, I think, to this question:—

Exp. 5.—A Marsh apparatus was worked with two ounces of dilute sulphuric acid (1—6); when the evolution of gas had taken place freely, I added 30 grain measures of nitric acid. The gas delivery tube was then heated, and 1.5 cubic centimetre of solution B of AsO_3 added ($= .00231$ grain). No mirror of arsenic was observed, but a white film formed inside the constricted portion of the tube exactly where the mirror of arsenic ought to have made its appearance. When the tube had cooled, the deposit inside the constricted portion of the tube was examined microscopically; *it was found to consist of a magnificent ring of crystals of AsO_3 .*

Exp. 6.—A Marsh apparatus was fitted with a gas delivery tube bent at right angles. Two ounces of dil. sulphuric acid, mixed with half a drachm of nitric acid, were placed in it, and then 1 cubic centimetre of solution B (1-10th of a milligramme of AsO_3) added. The end of the tube was made to dip into a small quantity of a strong solution of nitrate of silver. Before the arsenical solution was added, no blackening of the nitrate of silver solution occurred; but immediately after, the solution became quite dark. As means had been taken for arresting any sulphuretted

hydrogen which might have been generated in the apparatus, the blackening was evidently due to the action of arseniuretted hydrogen upon the nitrate of silver.

The two last experiments prove very conclusively, in my opinion, that when nitric acid checks the formation of a mirror of metallic arsenic, in Marsh's process, it does so, *not* by preventing the evolution of arseniuretted hydrogen, as M. Blondlot supposes. They show, moreover, how it is that mirrors of metallic arsenic are, under these circumstances, not obtained. When very dilute nitric acid acts upon metallic zinc, protoxide of nitrogen is evolved; if this gas be mixed with arseniuretted hydrogen, and the mixture of gases transmitted through a heated tube, the arseniuretted hydrogen will be oxidized, arsenious acid and water being formed as products. This is, doubtless, what occurs in all cases where dilute sulphuric acid containing a small quantity of nitric acid, acts upon zinc and an arsenical compound.

From the above experiments, we can legitimately deduce the following conclusions:—

1stly, When the acid used in Marsh's process contains a very small quantity of nitric acid, mirrors of metallic arsenic are obtained from extremely minute quantities of arsenic added to the apparatus; in other words, a trace of nitric acid present in the sulphuric acid in Marsh's process does not perceptibly interfere with the formation of mirrors of metallic arsenic.

2dly, When the acid used in Marsh's process contains a considerable percentage of nitric acid, the formation of mirrors is checked; the extent to which this occurs depending upon—(a) the proportion of nitric acid present in the sulphuric acid, (b) the quantity of arsenic present in the apparatus.

3dly, That under these circumstances the addition of an organic fluid to the apparatus does not promote the formation of mirrors.

4thly, That when nitric acid prevents the formation of mirrors of metallic arsenic in Marsh's process, it does not check the evolution of arseniuretted hydrogen, but prevents its being decomposed by heat into arsenic and hydrogen, by causing its oxidation; a ring of crystals of arsenious acid being, under these circumstances, formed inside the tube.

UNIVERSITY OF EDINBURGH, *October 1864.*

