

Separation of arsenic : From the Transactions of the Society of Arts. Vol. LI. The large gold medal was presented to Mr. James Marsh, of the Royal Arsenal, Woolwich, for his method of separating small quantities of arsenic from substances with which it may have been mixed. / [By James Marsh].

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SEPARATION OF ARSENIC.

FROM THE TRANSACTIONS OF THE SOCIETY OF ARTS.

VOL. LI.

The LARGE GOLD MEDAL was presented to MR. JAMES MARSH, of the Royal Arsenal, Woolwich, for his Method of separating Small Quantities of Arsenic from Substances with which it may have been mixed.

NOTWITHSTANDING the improved methods that have of late been invented of detecting the presence of small quantities of arsenic in the food, in the contents of the stomach, and mixed with various other animal and vegetable matters, a process was still wanting for separating it expeditiously and commodiously, and presenting it in a pure unequivocal form for examination by the appropriate tests. Such a process should be capable of detecting arsenic not only in its usual state of white arsenic or arsenious acid, but likewise in that of arsenic acid and of all the compound salts formed by the union of either of these acids with alkaline substances. It ought, also, to exhibit the arsenic in its reguline or metallic state, free from the ambiguity which is sometimes caused by the use of carbonaceous reducing fluxes. It appeared to me, that these objects might be attained by presenting to the arsenic hydrogen gas in its nascent state: the first action of which would be to deoxygenate the arsenic; and the next, to combine with the arsenic, thus deoxygenated, into

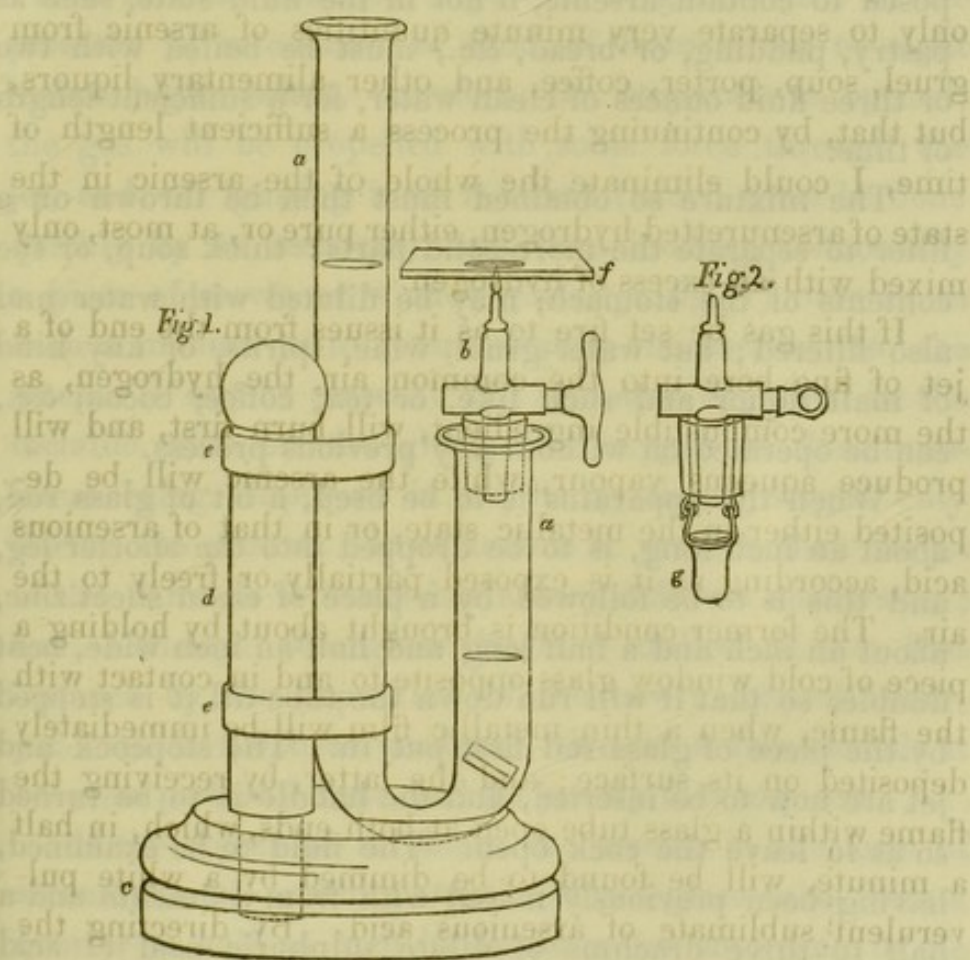
the well-known gas called arsenuretted hydrogen. Being thus brought to the gaseous state, the arsenic would spontaneously (so to speak) separate itself from the liquor in which it was before dissolved, and might be collected for examination by means of any common gas apparatus; thus avoiding the trouble, difficulty, and ambiguity of clarification and other processes whereby liquors, suspected of containing arsenic, are prepared for the exhibition of the usual tests, or of evaporation and deflagration which are sometimes had recourse to in order to separate the arsenic from the organic substances with which it may have been mixed.

I had the satisfaction of finding, on trial, that my anticipations were realized; and that I was thus able, not only to separate very minute quantities of arsenic from gruel, soup, porter, coffee, and other alimentary liquors, but that, by continuing the process a sufficient length of time, I could eliminate the whole of the arsenic in the state of arsenuretted hydrogen, either pure or, at most, only mixed with an excess of hydrogen.

If this gas be set fire to as it issues from the end of a jet of fine bore into the common air, the hydrogen, as the more combustible ingredient, will burn first, and will produce aqueous vapour, while the arsenic will be deposited either in the metallic state, or in that of arsenious acid, according as it is exposed partially or freely to the air. The former condition is brought about by holding a piece of cold window glass opposite to and in contact with the flame, when a thin metallic film will be immediately deposited on its surface; and the latter, by receiving the flame within a glass tube open at both ends, which, in half a minute, will be found to be dimmed by a white pulverulent sublimate of arsenious acid. By directing the

flame obliquely within side of the tube, it strikes against the glass and deposits the arsenic partly in the metallic state. In this case, if the tube, while still warm, be held to the nose, that peculiar odour, somewhat resembling garlic, which is one of the characteristic tests of arsenic, will be perceived. Arsenuretted hydrogen itself has precisely the same odour, but considerable caution should be used in smelling to it, as every cubic inch contains about a quarter of a grain of arsenic.

The requisite apparatus is as simple as possible; being a glass tube open at both ends, and about three quarters of an inch in its internal diameter. It is bent into the form of a syphon (*aa*, fig. 1), the shorter leg being about



five inches, and the longer about eight inches in length. A stop-cock *b*, ending in a jet of fine bore, passes tightly through a hole made in the axis of a soft and sound cork, which fits air-tight into the opening of the lower bend of the tube, and may be further secured, if requisite, by a little common turpentine lute. To fix the apparatus, when in use, in an upright position, a hole is made in the wooden block *c* for the reception of the lower part of the pillar *d*, and a groove is cut in the top of the same block to receive the bend of the tube *a a*. Two elastic slips *e e*, cut from the neck of a common bottle of India rubber, keep the tube firm in its place.

The matter to be submitted to examination, and supposed to contain arsenic, if not in the fluid state, such as pastry, pudding, or bread, &c., must be boiled with two or three fluid ounces of clean water, for a sufficient length of time.

The mixture so obtained must then be thrown on a filter to separate the more solid parts: thick soup, or the contents of the stomach, may be diluted with water and also filtered; but water-gruel, wine, spirits, or any kind of malt liquor and such like, or tea, coffee, cocoa, &c., can be operated on without any previous process.

When the apparatus is to be used, a bit of glass rod, about an inch long, is to be dropped into the shorter leg, and this is to be followed by a piece of clean sheet zinc, about an inch and a half long and half an inch wide, bent double, so that it will run down the tube till it is stopped by the piece of glass rod first put in. The stopcock and jet are now to be inserted, and the handle is to be turned so as to leave the cock open. The fluid to be examined, having been previously mixed with from a drachm and a half to three drachms of dilute sulphuric acid (1 acid

and 7 water), is to be poured into the long leg, till it stands in the short one about a quarter of an inch below the bottom of the cork. Bubbles of gas will soon be seen to rise from the zinc, which are pure hydrogen if no arsenic be present; but, if the liquor holds arsenic in any form in solution, the gas will be arsenuretted hydrogen. The first portions are to be allowed to escape, in order that they may carry with them the small quantity of common air left in the apparatus; after which the cock is to be closed, and the gas will be found to accumulate in the shorter leg, driving the fluid up the longer one, till the liquor has descended in the short leg below the piece of zinc, when all further production of gas will cease. There is thus obtained a portion of gas subject to the pressure of a column of fluid of from seven to eight inches high: when, therefore, the stop-cock is opened, the gas will be propelled with some force through the jet, and, on igniting it as it issues (which must be done quickly by an assistant), and then holding horizontally a piece of crown or window-glass (*f*, fig. 1) over it, in such a manner as to retard slightly the combustion, the arsenic (if any be present) will be found deposited in the metallic state on the glass; the oxygen of the atmosphere being employed in oxydizing the hydrogen only during the process. If no arsenic be present, then the jet of the flame as it issues has a very different appearance; and, although the glass becomes dulled in the first instance by the deposition of the newly formed water, yet such is the heat produced, that in a few seconds it becomes perfectly clear, and frequently flies to pieces.

If the object be to obtain the arsenic in the form of arsenious acid, or white arsenic, then a glass tube, from a quarter to half an inch in diameter (or according to the

size of the jet of flame), and eight or ten inches in length, is to be held vertically over the burning jet of gas, in such a manner that the gas may undergo perfect combustion, and that the arsenic combined with it may become sufficiently oxydized; the tube will thus, with proper care, become lined with arsenious acid in proportion to the quantity originally contained in the mixture.

When the glass tube is held at an angle of about forty-five degrees over the jet of flame, three very good indications of the presence of arsenic may be obtained at one operation; viz. metallic arsenic will be found deposited in the tube at the part nearest where the flame impinges,—white arsenic or arsenious acid at a short distance from it,—and the garlic smell can be readily detected at either end of the tube in which the experiment has been made.

As the gas produced during the operation is consumed, the acid mixture falls into the short limb of the tube, and is thus again brought into contact with the zinc, in consequence of which a fresh supply is soon obtained. This gas, if submitted to either of the processes before described, will give fresh indications of the presence of the arsenic which the mixture may have originally contained; and it will be easily perceived that the process may be repeated as often as may be required, at the will of the operator, till no further proofs can be obtained.

When certain mixed or compound liquors are operated on in this apparatus, a great quantity of froth is thrown up into the tube, which may cause a little embarrassment by choking the jet. I have found this effect to take place most with the contents of the stomach, with wine,

porter, tea, coffee, or soup, and, indeed, with all mucilaginous and albuminous mixtures. The means I adopt to prevent this effect from taking place, or, at least, for checking it in a great measure, is to grease or oil the interior of the short limb of the apparatus before introducing the substance to be examined, or to put a few drops of alcohol or sweet-oil on its surface previously to introducing the stopcock and its appendages. I have, however, found, if the tube be ever so full of froth in the first instance, that, in an hour or two, if left to itself, the bubbles burst, and the interior of the tube becomes clear without at all affecting the results.

In cases where only a small quantity of the matter to be examined can be obtained, I have found a great convenience in using the small glass bucket (*g*, fig. 2). Under such circumstances, the bent glass tube may be filled up to within an inch of the short end with common water, so as to allow room for the glass bucket, which must be attached to the cork, &c. by means of a little platina wire; a bit or two of zinc is to be dropped into the bucket, with a small portion of the matter to be examined, and three or four drops of diluted sulphuric acid (acid 2, water 14); and the whole is then to be introduced into the mouth of the short limb of the tube. The production of gas under this arrangement is much slower, and, of course, requires more time to fill the tube, than in the former case; but the mode of operating is precisely the same. Indeed, it is of great advantage, when the quantity of arsenic present is very minute, not to allow the hydrogen to be evolved too quickly, in order to give it time to take up the arsenic.

A slender glass funnel will be found of service when as much as a table-spoonful, or even a tea-spoonful of

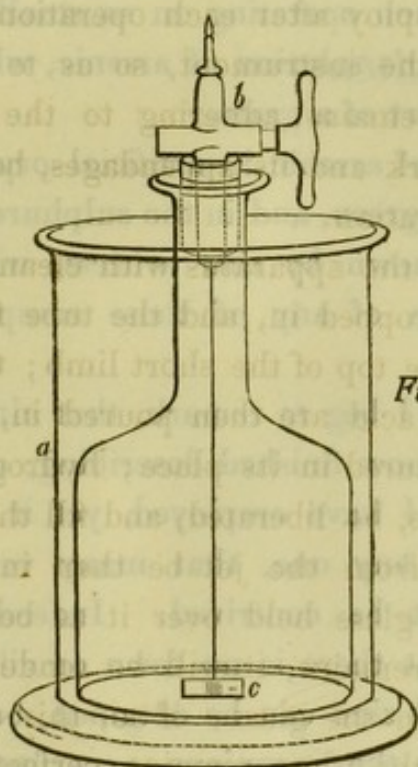
matter, can be obtained for examination. In this case, the tube is to be partly filled with common water, leaving a sufficient space for the substance to be examined; a piece of zinc is to be suspended from the cork by a thread or wire, so as to hang in the axis of the tube; and the fluid to be operated on, having previously been mixed with dilute sulphuric acid, is then to be poured through the funnel carefully, so as to surround the zinc, avoiding, as far as possible, to mix it with the water below, and the stopcock and its appendages are to be replaced in the mouth of the tube; the production of the gas then goes on as before stated, and the mode of manipulating with it is exactly the same as described in the foregoing part of this paper.

It will be necessary for me, in this place, to explain the methods I employ after each operation, to determine the integrity of the instrument, so as to satisfy myself that no arsenic remains adhering to the inside of the tube, or to the cork and its appendages, before I employ it for another operation.

After washing the apparatus with clean water, a piece of zinc may be dropped in, and the tube filled to within half an inch of the top of the short limb; two drachms of diluted sulphuric acid are then poured in, and the stopcock and cork secured in its place; hydrogen gas will in this case, as before, be liberated, and fill the tube. If the gas as it issues from the jet be then inflamed, and a piece of window glass held over it as before described, and any arsenic remains, it will be rendered evident by being deposited on the glass; if so, this operation must be repeated till the glass remains perfectly clean, after having been exposed to the action of the gas.

When I have had an opportunity of working with so

large a quantity of mixture as from two to four pints (imperial measure), I then have employed the instrument (fig. 3), which is, indeed, but a slight modification of one of the instantaneous light apparatuses, now so well known and used for obtaining fire by the aid of a stream of hydrogen gas thrown on spongy platinum. It will, therefore, be of importance only for me to describe the alteration which I make when I employ it for the purpose of detecting arsenic. In the first place, I must observe, that the outer vessel *a*, which I use, holds full four pints, and that the jet of the stopcock is vertical, and its orifice is twice or three times larger than in the instrument as generally made for sale, and also that there is a thread or wire attached to the cork of the stopcock *b*, for suspending a piece of zinc *c*, within the bell-glass



With an instrument of this description, I have operated on one grain of arsenic in twenty-eight thousand

grains of water (or four imperial pints), and have obtained, therefrom, upwards of one hundred distinct metallic arsenical crusts.

Similar results have been obtained with perfect success from three pints of very thick soup, the same quantity of port wine, porter, gruel, tea, coffee, &c. &c.

It must, however, be understood, that the process was allowed to proceed but slowly, and that it required several days before the mixture used ceased to give indication of the presence of arsenic, and, also, a much larger portion of zinc and sulphuric acid was employed from time to time, than when working with the small bent tube apparatus, in consequence of the large quantity of matter operated on under this arrangement.

With the small apparatus, I have obtained distinct metallic crusts, when operating on so small a quantity as one drop of Fowler's solution of arsenic, which only contains one-120th part of a grain.

The presence of arsenic in artificial orpiment and realgar, in Scheele's green, and in the sulphuret of antimony, may be readily shewn by this process, when not more than half a grain of any of those compounds is employed.

In conclusion, I beg to remark, that although the instruments I have now finished describing, are the form I prefer to all that I have employed, yet it must be perfectly evident to any one, that many very simple arrangements might be contrived. Indeed, I may say unequivocally, that there is no town or village in which sulphuric acid and zinc can be obtained, but every house would furnish to the ingenious experimentalist ample means for his purpose; for, a two-ounce phial, with a cork and piece of tobacco-pipe, or a bladder, with the same

arrangement fixed to its mouth, might, in cases of extreme necessity, be employed with success, as I have repeatedly done for this purpose.

The only ambiguity that can possibly arise in the mode of operating above described, arises from the circumstance, that some samples of the zinc of commerce themselves contain arsenic; and such, when acted on by dilute sulphuric acid give out arsenuretted hydrogen. It is, therefore, necessary for the operator to be certain of the purity of the zinc which he employs, and this is easily done by putting a bit of it into the apparatus, with only some dilute sulphuric acid; the gas thus obtained is to be set fire to as it issues from the jet; and if no metallic film is deposited on the bit of flat glass, and no white sublimate within the open tube, the zinc may be regarded as in a fit state for use.

JAMES MARSH.

