

Observations on Reinsch's test for arsenic / by William Odling.

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Dr. Taylor
with Dr. Odling's correction

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OBSERVATIONS
ON
REINSCH'S TEST FOR ARSENIC.

BY WILLIAM ODLING, M.B., F.C.S.

I BELIEVE that all British toxicologists are fully agreed upon the merits of Reinsch's process for the detection of arsenic. Its delicacy, its freedom from fallacy, the facility and rapidity of its application, and the non-requirement of any special form of apparatus, are advantages sufficiently obvious. The tedious and complicated processes, with their elaborate forms of apparatus, which are from time to time described in foreign periodicals, are rather interesting as specimens of perverted ingenuity, than useful as improved means for the detection of the poison.

If, in the performance of Reinsch's test, the grey metallic deposit upon copper yields a crystalline sublimate which, when treated with nitric and hydrochloric acids and evaporated to dryness, leaves a residue giving a brick-dust coloured precipitate with nitrate of silver, its arsenical nature is indubitable,—there is no fallacy whatever. Should the deposit be not possessed of these characters, the suspected substance must be further examined for the presence of antimony, bismuth, sulphur, &c.

But supposing that we are unable to obtain any characteristic deposit upon the copper, are we justified in affirming the absence of arsenic in the substance under examination? Is it not possible that our want of success may be due to the insufficient delicacy of the process, or to some unavoidable loss in its performance, or to the existence of the arsenic in some particular form of combination not amenable to the action of the test? I propose to consider these three points seriatim.

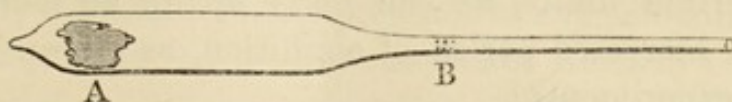
Delicacy of Reinsch's process.—Dr. Taylor has very clearly pointed out, that in considering the delicacy of any test, we

must have regard, firstly, to the smallest quantity of the poison that can be satisfactorily determined under favorable conditions ; secondly, to the effect of dilution, and other circumstances, in interfering with the determination of this quantity. As regards the former inquiry, I have repeatedly found, in confirmation of Dr. Rainey's experiments, that $\frac{1}{1000}$ th of a grain of arsenious acid will give, in succession, a deposit upon copper gauze, an obvious crystalline sublimate, and a brick-dust coloured precipitate of arseniate of silver. When the test is performed in the ordinary manner, but with less than $\frac{1}{1000}$ th of a grain of arsenious acid, the production of a crystalline sublimate, and brick-dust precipitate, is unsatisfactory ; though the deposit upon copper may be obtained from much smaller quantities.

Nevertheless, the practical application of Reinsch's test is not absolutely limited to the detection of $\frac{1}{1000}$ th of a grain of arsenious acid, as shown by the following experiment.

The $\frac{1}{5000}$ th part of a grain of arsenious acid was dissolved in a mixture of three fluid drachms of water with one fluid drachm of hydrochloric acid, sp.gr. 1.16. A small piece of Dr. Taylor's fine copper gauze was introduced, and the whole boiled in a long-necked flask. In the course of ten minutes, a decided discoloration of the copper was produced. The ebullition was continued for half an hour, by which time there was a very obvious deposit. The copper was then removed, washed, and dried. Thus, $\frac{1}{5000}$ th of a grain of arsenic was clearly perceptible in the state of metal ; but in order to render it visible in the state of crystalline arsenious acid, it was necessary that the sublimate should be confined to the smallest possible space, and not be spread over the entire circumference of an ordinary-sized reduction-tube. An appropriate subliming tube was made as follows : A piece of clear, hard, German tubing, a couple of inches long, with a bore of about one eighth of an inch in diameter, was drawn out at one end, so as to form an almost capillary termination of about an inch in length. The piece of coated gauze was folded up, and introduced at the other extremity of the tube, which was then sealed by the blowpipe ; care being taken to keep the copper as far removed as possible from the heated extremity. After cooling, the copper was tilted back to the sealed extremity, and the heat of a spirit-lamp applied to the whole body of the tube, commencing at the open capillary

shoulder, and proceeding backwards to the copper. By this means, the arsenicum was volatilized from the copper, which

FIG. 1.¹

resumed its normal appearance, and on examining the capillary termination of the tube, a delicate glistening ring was observable. This, when examined microscopically, with a quarter-inch object-glass, presented a most characteristic appearance. The triangular facets of the crystals, with here and there well-marked octahedra and tetrahedra, truncated and otherwise, were perfectly recognisable. Any further examination was quite unnecessary; but to render the experiment as perfect as possible, a minute quantity of sulphide of ammonium was introduced into the capillary tube, so as to reach the deposit. Heat was then very cautiously applied, and a bright yellow ring of orpiment obtained, which could be sublimed up and down the capillary tube.

The above experiment, which I have frequently repeated, shows that $\frac{1}{5000}$ th of a grain of arsenious acid can be positively determined by Reinsch's process, and may be obtained, successively, as a metallic deposit, a crystalline sublimate, and a yellow sulphuret. This degree of delicacy, though, from the statements of others, and in accordance with my own observation, inferior to that of Marsh's process, is more than sufficient for every practical purpose. Moreover, I believe that even it does not constitute the limit of applicability of the test.

In the performance of these minute experiments, it is extremely important that the hydrochloric acid employed should be perfectly pure. It should always be tested, not only for arsenic, but also for nitric acid or free chlorine. I have found many specimens of miscalled pure hydrochloric acid, which bleached sulphate of indigo; and, only within this last week, by employing unwittingly an acid of this description, was

¹ Fig. 1 is a somewhat enlarged representation of the above-described subliming tube. *A* indicates the copper gauze; *B*, the crystalline sublimate.

much embarrassed in not obtaining such delicate results as heretofore.

The effect of dilution, in interfering with the detection of the poison, is, I believe, not so great as is generally supposed. Within certain limits, we can make up for an increased dilution by an increased period of ebullition, as shown by the two following experiments :

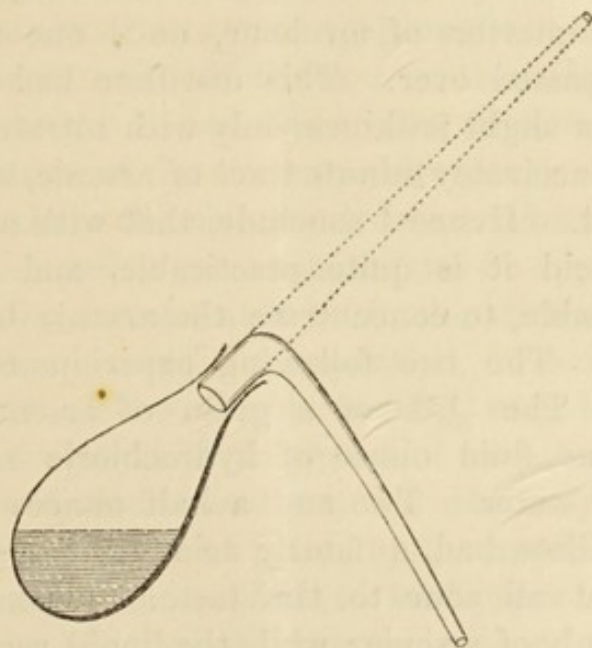
One measure of hydrochloric acid was mixed with four measures of water. In the first experiment, the $\frac{1}{1000}$ th of a grain of arsenious acid was added to an ounce of the mixture, the whole boiled, and a piece of copper foil, exposing one square inch of surface, introduced into the boiling liquid. In the course of five minutes there was a decided discoloration ; in a quarter of an hour, a deposit through which the copper colour could be only faintly perceived ; and in twenty minutes, a well-marked, characteristic, steel-coloured deposit. Even then, however, the whole of the arsenic was not abstracted from the liquid ; for on removing the foil, and replacing it by a very small piece of gauze, and continuing the ebullition for half an hour longer, a further deposition of arsenicum took place.¹

In the second experiment, the $\frac{1}{1000}$ th of a grain of arsenious acid was added to five ounces of the acid mixture, the whole boiled, and another piece of foil, exposing the same amount of surface, introduced. After one hour's ebullition, the colour of this piece of copper foil approximated to that which the first piece presented, after a quarter of an hour. Reckoning an ounce of the dilute hydrochloric acid to weigh 450 grains, the dilution in this last case amounted to 2,250,000 times, or the arsenious acid formed considerably less than one two-millionth part of the whole, and yet gave a decided deposit. By boiling a small piece of copper gauze, for half an hour, in five ounces of dilute hydrochloric acid, containing $\frac{1}{1000}$ th of a grain of arsenious acid, a very characteristic deposit was formed, from which the crystalline sublimate and brick-dust precipitate were readily obtained. I find that arsenicum is deposited with greater facility upon copper gauze than upon foil, and is less liable to be rubbed off. This want of adherence to the copper foil becomes a source of some little difficulty, when the ebulli-

¹ This incomplete separation of arsenic after twenty minutes' ebullition is opposed to some results obtained by Dr. Maclagan.

tion has been protracted. The non-adherence of a deposit is no evidence of its non-arsenical nature. It is a circumstance that occurs frequently when, the arsenic being in minute quantity, the ebullition has been protracted, or the hydrochloric acid not sufficiently diluted, or in the presence of any oxidizing agent.

Loss in the process.—The great merits of Reinsch's test are, that it necessitates no appreciable loss, and that it allows the whole of the arsenic present to be concentrated upon a small surface. It has, however, been urged as an objection to the process, that during the ebullition with hydrochloric acid, a portion of the arsenic is volatilized in the state of terchloride. The fact is indubitable, but the objection is one of no practical validity. When the arsenic is in large quantity, a slight loss is of no consequence; and when it is in small quantity, the loss is quite inappreciable. Moreover, the alleged loss may always be avoided by performing the ebullition in a retort or alembic.

FIG. 2.¹

The amount of arsenic that may be volatilized during the evaporation of strong hydrochloric acid is very great. At the suggestion of my friend Mr. Scanlan, I have, on one occasion, availed myself of this property for the detection of absorbed

¹ Fig. 2 represents a very convenient alembic for making decoctions of suspected viscera. When the straight tube is substituted for the bent neck, the greater portion of the vapours originally formed become condensed, and flow back again into the liquid.

arsenic in the stomach of a dog. The viscus was cut up into small pieces, placed in an alembic, and drenched with strong hydrochloric acid. The heat of a sand bath was then applied, and the distillation continued to dryness. Arsenic was very abundantly detected in the distillate, but the residuum was not by any means free from the poison. Altogether, the process did not present any advantages to compensate for the increased trouble attending it.

In proportion to the dilution of the hydrochloric acid, so is the diminution of the quantity of arsenic which volatilizes during the evaporation. The presence of animal matter, moreover, retards the volatilization, both of the hydrochloric acid and of the arsenic. One half of a dog's stomach, free from arsenic, was cut into small pieces, and put into a pint alembic, containing two fluid ounces of dilute hydrochloric acid, made in the proportion of one volume of acid to nine of water. The one tenth of a grain of arsenious acid was then added, and the whole boiled. The ebullition was continued for rather less than three quarters of an hour, until one fluid ounce of distillate had passed over. This distillate had a faintly acid reaction, gave a slight milkiness only with nitrate of silver, and yielded an inconceivably minute trace of arsenic, when examined by Marsh's test. Hence I conclude, that with a much diluted hydrochloric acid it is quite practicable, and may in some cases be advisable, to concentrate the arsenic by evaporation of the liquid. The two following experiments lead to the same result. The $\frac{1}{500}$ th of a grain of arsenious acid was mixed with one fluid ounce of hydrochloric acid, and four fluid ounces of water. Two and a half ounces were distilled off. The distillate had a faintly acid reaction to test paper, but was not at all sour to the taste. It contained a very minute trace only of arsenic; while the liquid remaining in the retort gave a full steel-coloured deposit to two square inches of copper surface. In the next experiment, the same quantity of liquid, with the same proportions of water, acid, and arsenic, was evaporated down to one half its bulk in an open dish. This experiment differs somewhat from the previous one. During the evaporation of a liquid in a retort, any of the least volatile vapours, in this case the arsenical, which may form throughout the process, become condensed in the upper part of

the retort, and flow back again into the liquid; whereas in a dish, vapours once formed are entirely lost. But here likewise the residue of the evaporation gave a full steel-coloured deposit to two square inches of copper surface, showing that no appreciable amount of arsenic had been lost by volatilization; inasmuch as, according to the experiments of Dr. Rainey, which I can fully confirm, a quantity of arsenious acid, much less than the $\frac{1}{500}$ th of a grain, will not give a characteristic coating to two square inches of copper surface.

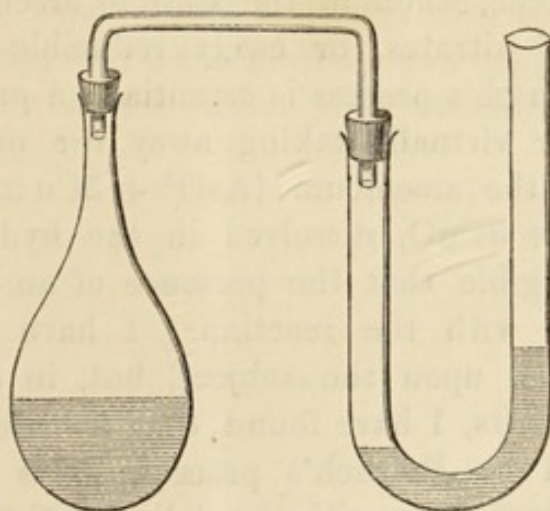
Insoluble condition of the arsenic.—Reinsch's process is usually said to be applicable only to such arsenical compounds as are soluble in dilute hydrochloric acid. Now, the tersulphuret of arsenic, or sulph-arsenious acid, AsS_3 , is always represented as being scarcely at all soluble in concentrated, and quite insoluble in dilute, hydrochloric acid. But it is not unfrequent, in medico-legal investigations, to find considerable quantities of arsenic in the state of tersulphuret. In many cases, the yellow-coloured patches of orpiment present themselves, to a greater or less extent, throughout the whole of the alimentary canal, and constitute a well-marked *post-mortem* sign of the poison. In some instances of arsenical poisoning, the decomposition of the tissues is altogether *sui generis*; but in every case where the ordinary decomposition has commenced, even though the yellow colour should not be apparent, a certain proportion of the arsenic must be in the state of tersulphuret; and in cases of advanced decomposition, it is not improbable, that the whole of the arsenic present may be in that condition. The evolution of sulphuret of ammonium during the decomposition of animal matters, is a generally admitted fact, and one readily capable of proof, by the application of a piece of red litmus paper and a piece of lead paper to the mouth of the bottle or jar containing the putrid viscera. Moreover, on the addition of dilute hydrochloric acid to the decomposing tissues, as in the performance of Reinsch's test, sulphuretted hydrogen gas is given off freely. The quantities of sulphuret of ammonium, or sulphuretted hydrogen, developed by a decomposing viscus, are frequently more than sufficient to convert the whole of the arsenic present into the state of orpiment,—into a form said to be insoluble in dilute hydrochloric acid. If, under these circumstances, we were to make and filter our

dilute hydrochloric decoction of the viscus, it is clear that none of the arsenic ought to be dissolved,—that the whole of it would remain upon the filtering paper, along with the débris of the tissue. That such is not the case, however, I have repeatedly assured myself by experiment. I have invariably found the whole of the arsenic to exist in the clear filtered acid decoction; or in other words, the whole of it was in a condition suitable for recognition by Reinsch's test. I will detail an experiment. I took a portion of the duodenal end of the small intestine of a man who had died poisoned by arsenic. The yellow patches of sulphuret of arsenic were numerous and characteristic. After preservation for four days in a tall jar, I found that considerable decomposition had taken place. On the application of a piece of moistened red litmus paper to the mouth of the jar, the blue colour was immediately restored. A piece of lead paper became speedily turned of a brown colour, and ultimately blackened. The viscus was then cut up into small pieces, transferred to an alembic, and a mixture of one fluid ounce of hydrochloric acid, sp. gr. 1.16, with four fluid ounces of water, poured upon it. The alembic was arranged in such a manner as to necessitate the flowing back of the distillate into the body of the vessel.¹ Heat was then applied, and the ebullition continued for one hour, after which the whole was allowed to cool. When cool, the mixture was thrown on to a filter. In the clear filtrate, arsenic was readily detected by Reinsch's process. The residuum upon the filtering paper was thoroughly washed, at first with cold water acidulated with hydrochloric acid, subsequently with cold water. It was then transferred to a flask, and treated with hydrochloric acid and chlorate of potash, according to the process of Fresenius and Von Babo, for the destruction of animal matter. By this means, any arsenic left in the original residuum would be converted into soluble arsenic acid. Filtration was again performed. The clear, pale yellow coloured filtrate was saturated with sulphurous acid gas, to reduce the arsenic acid into the state of arsenious, and then set aside in an open dish for twenty-four hours, by which time the sulphurous odour had entirely disappeared. Reinsch's and Marsh's tests were then applied, but by neither process could arsenic be detected; showing

¹ *Vide* fig. 2, and foot-note, page 293.

clearly, that despite the obvious and necessary existence of tersulphuret of arsenic in the tissue, the whole of the arsenic had been dissolved in the hydrochloric decoction. Dr. Geoghegan, in his elaborate paper on arsenical poisoning, seems to consider it advisable, for the detection of arsenic absorbed into the tissues, to employ Danger and Flandin's preliminary process of carbonization by sulphuric acid, before applying Reinsch's test. In my own experience, I have not found this proceeding requisite; I have always found the dilute hydrochloric acid decoction of the viscus quite sufficient for the detection of the poison. As I have before stated, this decoction might, if necessary, be concentrated by evaporation.

The above-described, and other corresponding results, induced me to examine more particularly the solubility of tersulphuret of arsenic in dilute hydrochloric acid. Arsenious acid was dissolved in dilute hydrochloric acid, much water then added, the liquid supersaturated with sulphuretted hydrogen, the yellow precipitate allowed to subside, collected on a filter, and thoroughly washed with cold water. Several successive portions of the precipitate were transferred to a Florence flask, connected, by means of a piece of glass tubing

FIG. 3.¹

bent twice at right angles, with a U tube, containing potash solution of lead. The precipitate was then boiled in mixtures

¹ Fig. 3 indicates the disposal of the apparatus. The sulphuretted hydrogen, liberated from the decomposition of the orpiment, is arrested in its passage through the lead solution contained in the U tube.

of one volume of hydrochloric acid with four of water ; of one volume with nine ; of one volume with nineteen ; and, finally, with pure water. In each case the results, indicating the decomposition of the sulphuret and the solution of the arsenic, were most marked. As soon as ebullition was arrived at, sulphuretted hydrogen was given off freely, and an abundant black precipitate was formed in the U tube. The most dilute acid acted equally well, if not better, than the stronger specimens ; while, with regard to pure water, the action was most powerful of all. In this case, the whole of the precipitate disappeared, forming a clear, colourless solution. The precipitate did not reappear upon cooling. When the ebullition had not been continued sufficiently long, the addition of a few drops of hydrochloric acid caused a slight yellow deposit of tersulphuret. After prolonged ebullition, this addition of hydrochloric acid to the liquid did not disturb its transparency. The liquid thus acidulated was readily precipitable by sulphuretted hydrogen ; as were each of the acid liquids in which the tersulphuret had been boiled. I obtained similar results, though not quite so readily, with some tersulphuret that had been dried in a water-bath, and also, though to a much less extent, with some pure sublimed tersulphuret.¹

It is said that Reinsch's test is scarcely applicable to the detection of arsenic, when in the state of arsenic acid,—or in the presence of nitrates, or easily reducible metallic salts. Seeing that Reinsch's process is essentially a process of reduction, the copper virtually taking away the oxygen formerly combined with the arsenicum ($\text{AsO}^3 + 3\text{Cu} = \text{As}$, deposited on the copper, $+ 3\text{CuO}$, dissolved in the hydrochloric acid), it is quite intelligible that the presence of an oxidizing agent should interfere with the reaction. I have not made any exact experiments upon the subject, but, in confirmation of Dr. Rainey's results, I have found that arsenic acid is not so readily detected by Reinsch's process, as is the arsenious ; although the interference with the delicacy of the test may, to a very great extent, be counteracted by an increased period of ebullition. Similarly, with regard to the presence of nitrate of potash, chlorate of potash, and perchloride of iron,—when

¹ Dr. Christison alludes to the solubility of orpiment in water, but not to anything like the above-described extent.

any one of these substances exists in large quantity in proportion to the amount of arsenic present, it is scarcely practicable to obtain the arsenical deposit upon the copper; but when they exist only in small proportion, and the absolute quantity of arsenic is not very minute, they constitute but slight impediments only to the test. I have found, indeed, that under these circumstances, the deposit of arsenicum adheres but very feebly to the copper, and can be easily rubbed off by the finger: this non-adherence is, I believe, only partially due to the necessarily prolonged ebullition, but chiefly to the surface of copper being, as it were, dissolved away from the arsenic at first thrown down upon it.

But in actual toxicological practice, we do not meet with difficulties of the above description. The only one likely to present itself, is that arising from the presence of perchloride of iron, formed by the action of the dilute hydrochloric acid upon the hydrated peroxide of iron administered as an antidote. In this case, however, the ferric preparation forces itself upon our attention, and by the passage of a current of sulphurous acid gas through the hydrochloric liquid, the difficulty can be at once removed.

I have not found the presence of mercurial salts to interfere with Reinsch's test, to the extent mentioned by Fresenius; inasmuch as the whole of the mercury, with the exception of a minute trace only, can be removed upon copper, prior to the ebullition of the liquid, when the arsenic is deposited as usual.

Arsenic dissolved

