SOME REMARKS
ON THE
USE OF NITRAT OF SILVER,
FOR THE DETECTION OF
MINUTE PORTIONS OF ARSENIC.

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IN the interesting account of the poisonous effects of arsenic, presented to the Society by Dr. Roget, and published in the second volume of the Medico-Chirurgical Transactions *, the author has recommended, for the detection of this poison, a test which I pointed out to him, and which, from a variety of experiments which we tried together, with a view to ascertain its comparative merits, we were induced to consider as the most effectual of all the tests hitherto used for that purpose. The method consists simply in adding in succession, to

* I take this opportunity of stating, at Dr. Roget's request, that the patient, whose case he there related, completely recovered her health, and has remained well ever since.

the fluid suspected to contain arsenic, minute quantities of solutions of ammonia and of nitrat of silver ; by which means, if the smallest quantity of arsenic be present, a dense yellow precipitate will be produced.

All the particulars respecting this mode of detection having been fully stated by Dr. Roget, with such references to former writers on the subject as the case required, it would be quite superfluous to enter into any further detail on this head. My object in resuming the subject, the practical importance of which need not be pointed out, is to communicate to the Society the result of an inquiry which I have made on the nature of the yellow precipitate, the appearance of which is assumed as denoting the presence of arsenic ; and to answer some objections which have been made against this test by Mr. Sylvester, of Derby, in a paper on metallic poisons, recently published in Nicholson's Journal. *

The yellow compound in question has the following properties :

If, after being well washed with distilled water, it be suffered to stand for some time in an open vessel, it gradually passes to a brown colour ; but

* Nicholson's Journal for December, 1812. Vol. xxxiii. p. 306.

it does not, like nitrat of silver, become black on continuing this exposure.

It is readily soluble in dilute nitric acid. It also dissolves on adding an excess of ammonia at the moment of its formation ; but after it has been separated and dried, it is no longer sensibly soluble in ammonia.

If a small quantity of this precipitate be exposed to the heat of a lamp on a slip of laminated platina, a white smoke arises from it, and the silver is partly reduced. The perfect reduction of the silver, in the form of a globule, is readily effected by mixing a little carbonaceous matter with the precipitate, or by placing it upon a piece of charcoal and applying the blow-pipe. The vapour which rises, has, in this case, the peculiar arsenical smell.

And again, if the yellow precipitate alone be inclosed in a tube, and exposed to the heat of a lamp, the white smoke condenses on the cold part of the tube in minute octohedral crystals of arsenious acid. But if a little pulverized charcoal and dried alkali be mixed with this sublimed matter, and heat again applied, the arsenic is deposited on the tube in the form of a brilliant metallic incrustation.

It appears, therefore, that the precipitate in question is a combination of white arsenic (arsenious acid) and silver, or an arsenite of silver ; and

it is inferred that its formation, when ammonia and nitrat of silver are added to a mixture containing arsenious acid, is owing to a double elective decomposition of the arsenite of ammonia, by the nitrat of silver, in consequence of which arsenite of silver is formed, and separates as an insoluble precipitate from the nitrat of ammonia which remains in the solution. The addition of ammonia is necessary, because arsenious acid alone cannot decompose nitrat of silver; but in Fowler's solution, in which the arsenic is already combined with an alkali, the decomposition takes place at once, without any addition of ammonia. The fixed alkalies, therefore, can answer a similar purpose; but ammonia has this advantage, that it does not, when added singly, decompose nitrat of silver, a circumstance which, in using the fixed alkalies, might occasion some confusion.*

With regard to Mr. Sylvester's objection, I shall, previous to my offering any remarks upon it, state

* It is necessary, as Dr. Roget has observed in the paper already quoted, that the quantity of ammonia should not be too large; for in that case the precipitate is redissolved. But, even then, it may be made to re-appear, by the addition of nitric acid in sufficient quantity to saturate the alkali. In this case, however, the precipitate is not permanent, owing, I find, to its being soluble in the nitrat of ammonia which is formed in the process. Carbonat of ammonia has also the property of producing and redissolving the precipitate. A considerable excess of ammonia can likewise redissolve muriat of silver.

The fixed alkalies in excess have not the power of redissolving the arsenical precipitate.

it in his own words. "If ever muriatic acid be present," says this gentleman, "the test is then wholly useless, as a muriat of silver will be immediately formed, and the yellow compound, said to be so unequivocal in its indication of arsenic, of course be prevented from appearing."

This difficulty, however, though applying in some degree to the process in question, and well deserving to be noticed, will be found to have been greatly over-rated; and there are such easy and obvious means by which it can be entirely removed, that it can make no solid objection to the utility of the test.

There cannot be the least doubt, as Mr. S. observes, but that whenever nitrat of silver is added to a solution containing muriatic acid, a precipitate of muriat of silver must be the consequence. But if the nitrat of silver be added in excess, the arsenite of silver is also thrown down by the intervention of ammonia, and a mixed precipitate of luna cornea and arsenite of silver is obtained, which partakes more or less of the yellow colour of the latter, according to the proportion of the two salts.

If to this dubious precipitate a few drops of dilute nitric acid be added, the arsenite of silver is instantly dissolved, and the muriat of silver, which is insoluble, immediately resumes its peculiar den-

sity and whiteness. If a little ammonia be now added to the clear fluid, the yellow precipitate appears in the most distinct manner, and becomes even more characteristic from a comparison with the white precipitate, the appearance of which differs from this in every respect.

By this method, I believe that every objection, to the test will be removed ; and in order to anticipate all danger of ambiguity on this head, I would propose to operate at once in the following manner:

To the suspected fluid, previously filtered, add, first, a little dilute nitric acid, and, afterwards, nitrat of silver, till it shall cease to produce any precipitate. The muriatic acid being thus removed, whilst the arsenious acid (if any, and in whatever state) remains in the fluid, the addition of ammonia will instantly produce the yellow precipitate in its characteristic form. It is hardly necessary to add, that the quantity of ammonia must be sufficient to saturate any excess of nitric acid which the solution may contain.*

* Some further remarks on this test, which the author of this communication considers as important, will be found in a note at the end of volume vi. of these Transactions, just published.—(Dec. 1815.)