

ON THE DETECTION OF
IODINE,
 AND THE
 HYDRIODATE OF POTASH,

In Animal and Mineral Admixture.

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IODINE.

ALTHOUGH no case has hitherto been put upon record in which chemical evidence was required of poisoning by iodine or the hydriodate of potash, yet from the rapidly-increasing and general knowledge of their powers, and the virulent action they are capable of exerting, the subjoined observations may not eventually prove destitute of practical utility, especially since, in the latest publication on toxicology in existence, no directions at all are given for the detection of iodine, and the subject of hydriodate of potash is dismissed, in a manner which seems to me to admit of some qualification and much improvement. To remedy these deficiencies is my object in the ensuing remarks. I shall therefore consider,

First; The chemical properties of iodine as far as concerns their application to toxicological analysis.

Secondly; The difficulties which may present themselves to the exhibition of these properties, or tests, when the iodine is to be sought for in complex admixture; and,

Thirdly; The method by which these difficulties may be obviated.

1st. The physical or external characters of iodine are too well known to need description here; the chemical properties are peculiar and uncommon. Though when exposed to the open air at natural temperatures iodine undergoes slow and invisible evaporation, yet, if heat be suddenly applied in close vessels, it rapidly sublimates in rich violet vapours, and condenses in various forms, according to the quantity of materials, and the size of the apparatus that may be employed. Iodine is extremely soluble in alcohol, which it colours to an intense brown. It is also soluble, though with extreme difficulty, in water, being only capable of uniting with that fluid in the proportion of one to 7000 parts, and from this solution, when heated to the boiling point, the peculiar vapours of the iodine are disengaged. With the metals it unites in various proportions, producing coloured combinations, and from such of these iodides as are formed with the metals fixed at a red heat, the iodine is readily separated by raising their temperature to that

point. With hydrogen it unites by a very powerful affinity, and gives rise to the formation of hydriodic acid; so energetic is this attraction, that it enables iodine to decompose many substances which contain that element, such as the hydro. chloric, or muriatic acid, sulphuretted hydrogen, water, and many others. But of all the properties of iodine, its action upon starch is the most extraordinary and characteristic, producing a compound of an intensely blue colour, entirely insoluble in alcohol, but imperfectly in water, losing its colour when heated to the boiling point, and again regaining it if the fluid be suddenly cooled.

2dly. Of these properties, next to the exhibition of iodine itself, the action of starch affords the best evidence by which it can be distinguished; it acts in the proportion of one to 450,000, and on the blue fluid thus procured, the effects of alternate boiling and cooling may be perfectly exhibited; but amply and infinitely delicate as this indication is, yet when iodine is taken into the stomach, certain changes and actions frequently occur, which render its toxicological application often difficult, sometimes entirely impracticable. In the first place, it is liable (and apparently from the operation of many causes) to be rapidly converted into the hydriodic acid, and in this condition to be perfectly removed into the circulation and eliminated by the kidneys, salivary and cutaneous excretions, and in all probability, by the pulmonary exhalation also. This fact, as far as regards its excretion by the kidneys, has been perfectly established by the experiments instituted on diuretics by Drs. Wohlen and Stehberger; with respect to the actions which give rise to it, some speculations will be advanced, when the effects of amylaceous matter on iodine, in the intestinal canal, have been taken into consideration.

The second source of difficulty arises from the ready formation, in the alimentary canal, of a compound, consisting of iodine and albumen, totally insoluble in alcohol, and nearly so in water. As far as I am aware this compound has not yet attracted the attention of chemists; its nature, however, is susceptible of ready demonstration by adding the tincture of iodine to diluted white of egg or milk, or allowing solid iodine to remain in contact with the latter for some hours, when a yellow, pulverulent compound will be formed, which by exposure to a stream of sulphuretted hydrogen, is converted into hydriodic acid and concrete albumen.

The third obstacle to the detection of iodine is, the rapidity with which it unites with starch in every form in which it may present itself to it in the stomach or intestines. Such amylaceous matters may be present, perhaps administered as antidotes,

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but more usually in the form of different articles of diet, such as bread, potatoes, &c. I have found that the watery solution of iodine, and even the tincture itself, may be totally deprived of its iodine by standing over bread or potatoes, the blue iodide of starch being formed. Did this blue colour remain permanent in the contents of the stomach, as many have supposed it does, a test of the action of iodine would to a certain extent be afforded, but I have also found in dogs to whom iodine has been administered after a meal of potatoes (the œsophagus being subsequently tied), that when killed after the lapse of an hour or two, no traces of blue were perceptible, while on the contrary, the contents of the intestinal canal exhibited a reddish appearance. Further, these matters, when treated with fresh quantities of starch, gave no blue tint till nitric acid was added, when the whole mass instantly assumed an intense purple colour. Such were the results of three out of four experiments made with the iodine in tincture. Of two trials with the iodine in substance, *cæteris paribus*, one gave the blue colour on trituration with starch, the other did not. The supposed causes of this change of colour, I have preferred to allude to in the foot note, as they are, in some measure, hypothetical, and I am unwilling to encroach upon the practical bearings of the subject under consideration, by the advancement of any speculations which may admit of a difference of opinion.* Finally, another cause of

* The discoloration of the blue iodide of starch in the intestinal canal, appears to me to depend on the formation of hydriodic acid, which possesses no colouring effect on amylaceous matter. This conversion may depend on various causes, of which, I believe the action of free muriatic acid and sulphuretted hydrogen to be the principal, assisted materially by the degree of heat necessarily existing through the abdominal viscera. Both these acids decolorise the iodide of starch, out of the body, and in both cases the colour may be again restored by the addition of nitric or sulphuric acids, which I conceive to operate by imparting oxygen to the hydrogen of the hydriodic acid, and consequently setting iodine free. Again; that both muriatic acid and sulphuretted hydrogen may be present in the alimentary canal, I consider sufficiently proved by the researches of Dr. Prout, in the first instance, and by the ordinary chemical properties of intestinal status in the other. That hydriodic acid also is formed by boiling the iodide of starch, there is, I conceive, much reason to suspect, although no certain proof of the fact has yet been afforded; one strong circumstance at any rate is, that the iodide of starch decolorised by boiling, again becomes

difficulty exists, in the mechanical revolution of particles of iodine in the mucous fluids, on which it exerts no decomposing action, but which tend to prevent its solution in alcohol or water.

It will thus be perceived that several causes may operate in impeding the application of the starch test, infinitely delicate though it be, when these circumstances are not in operation. Besides, all these difficulties will be increased by the direct ratio of the time elapsing between the administration of the poison and the death of the patient; in fact, I feel convinced that in a vast majority of any fatal cases which may occur, no free iodine can be detected in the fluid contents of the stomach or intestines, neither can it be removed from them by water or alcohol. I believe, also, that the starch will very seldom, perhaps never, be directly applicable to the examination of the intestinal fluids, unless where, after the administration of the tincture in very large quantities, the vomited matters become the subject of analysis. A method of proceeding applicable to these difficult cases, becomes, therefore, absolutely necessary, and the following I can strongly and confidently recommend, as founded on the best known chemical properties of iodine, liable to no fallacy, and susceptible of the utmost delicacy in the indications it affords.

3dly. A trial test for free iodine should be always premised by the addition of a part of the suspected fluids to a solution of cold starch, when, if iodine be present, the blue colour will be struck, and the remainder of the fluid may be reserved for subsequent examination. Should this test afford no indications, the subsequent process may then be proceeded with. It is divisible into two parts, one applicable to the fluids, the second to the solid contents of the alimentary canal.

The first is extremely simple, and depends on the fact, that though free iodine be not immediately detected by starch in the fluids under examination, yet that hydriodic acid may nevertheless exist in them. A little of the fluid, therefore, after filtration, should be mixed with starch as before, and a few drops of sulphuric acid be then added,* when the blue tint will be struck, if an appreciable quantity of hydriodic acid be present. Should the test operate, the remaining fluid is to be reserved; if it do not.

blue, on the addition of nitric acid, which is precisely what occurs when hydriodic acid mixed with starch is similarly treated.

* The sulphuric acid is used here in preference to the nitric acid, because the latter causes a dark-green colour in any fluid containing bile, which can scarcely be distinguished from the blue of the iodide of starch.

it is no longer of any value, and our attention is next required to the solid substances remaining after the separation of the fluids by filtration.

These solid contents will usually consist of fibrin, casein, albumen, and starch—iodides of albumen and starch? Iodine mechanically involved in animal mucus? with other substances of less importance. To this mass a little cold starch paste should first be added, the entire should then be triturated together in a stone or glass mortar, next diffused through water, and, finally, a free current of sulphuretted hydrogen gas passed through the mixture for at least half an hour. By this process, any free iodine present will be first converted into the iodide of starch (if the quantity be considerable, the blue colour may be struck at this part of the process; for reasons, however, to be noticed in the sequel, this should not be considered sufficient), and by passing the sulphuretted hydrogen through the mixture, the iodides of albumen and starch will be converted into hydriodic acid. The fluid should now be filtered, and subsequently brought to the boiling point, in order to expel any excess of sulphuretted hydrogen. Finally, when cool, a small quantity of it should be treated with starch and sulphuric acid, and the remainder reserved for the second branch of the process, the object of which is to procure the iodine itself in its simple condition.

If any urine can be obtained, a small quantity of it is to be acted upon as directed in the case of the fluids of the stomach, and the remainder in like manner reserved. The serum of the blood should also be coagulated by boiling, the coagulum washed with water, and the fluid subjected to the same manipulation. The pericardial liquor is also to be similarly treated.

I shall proceed to the consideration of the hydriodate of potash, before I mention the ultimate process by which the iodine itself may be procured from these different fluids, which have already been found to answer to the starch as a trial test, since the same proceeding applies to the hydriodate also. Before I enter on this division of my subject, however, I may be allowed to observe, that I by no means insist on the necessity of searching for the iodine itself, after the colouring of starch has indicated its presence; on the contrary, as far as chemistry teaches us at present, the ulterior search is completely unnecessary; yet no matter how peculiar or striking a property of any substance may be, it is at the same time a logical and self-evident truth, that the substance itself affords in the aggregate of all its properties, evidence of a still more decisive and convincing nature. Under this impression, and feeling that every zealous

toxicologist must be anxious to obtain as perfect demonstration of the substance he investigates as his science is capable of affording him, I have not hesitated to seek for the best method by which iodine can be exhibited in its simple form, and this method will be found at the conclusion of the paper.

HYDRIODATE OF POTASH.

This important substance I propose to consider under the following heads:—

First; Its mode of preparation, and such of its chemical properties as are concerned in its toxicological relations.

Secondly; The tests recommended by the most eminent authorities for its detection in complex admixture.

Thirdly; The objections to the processes thus recommended, and

Fourthly; The method by which I propose to remedy these objections.

1st. The mode of preparing the hydriodate of potash adopted by the Dublin College, consists in the formation of hydriodic acid, in the first place, by passing a current of sulphuretted hydrogen gas through iodine suspended in water, and subsequently neutralizing the acid thus obtained by the carbonate of potash. It may also be prepared as Dr. Turner directs, by dissolving iodine in a hot solution of caustic potash, when water is decomposed, giving rise to the formation of iodic acid (iodine 1, oxygen 3), and hydriodic acid (iodine 1, hydrogen 1), and finally converting the iodic acid into hydriodic, by a current of sulphuretted hydrogen. As procured by either of these methods, the salt, when pure, is susceptible of perfect cubic crystallisation; it should have well-defined edges, be of a translucent, though rather milky colour, and be perfectly free from yellow stains. In this condition it is possessed of powerful medicinal activity, and is characterised by remarkable chemical peculiarities; it is extremely soluble in water,* and also in alcohol to a certain extent; in solution it is perfectly colourless and transparent, and exerts no action whatever upon starch; but if any substance capable of abstracting hydrogen be

* In most chemical works it is stated to be deliquescent; an assertion which, I believe, is not correct, as far as regards pure hydriodate of potash; at any rate, at the moment I write, a crystal of the hydriodate continues perfectly dry, after exposure to the air in a large apartment for seventeen days, on fourteen of which rain fell in great abundance. Some specimens, however, of what is called hydriodate of potash, will certainly deliquesce quickly enough, but simply on account of the carbonate of potash they contain.

brought in contact with it, such as nitric or sulphuric acid or chlorine, its colour becomes brown from the evolution of free iodine corresponding to the quantity of hydrogen it has lost, and the solution consequently acquires the power of forming the blue compound with starch.

With a solution of the chloride of platinum, hydriodate of potash causes a dark-brown precipitate; or, if the quantity be excessively minute, an intense port-wine colour, resulting in both cases from the formation of the iodide of platinum. With solutions of lead, such as the common acetate, nitrate, &c. it causes a canary-yellow precipitate, the iodide of lead; with the proto-salts of mercury, it forms the yellow proto-iodide; and with the per-salts, the carmine red per-iodide of mercury. In all these cases the action is simple, but requires to be remembered; it may be exemplified in the action which takes place when the acetate of lead is added to the hydriodate of potash; acetate of potash is first formed, and then the hydriodic acid reacts on the oxide of lead, the hydrogen of the former unites with the oxygen of the latter, producing water, while the simple iodine and the metal combine, and are precipitated as the yellow iodide of lead. Such are the properties of the hydriodate of potash, as far as relates to toxicological analysis. I have now to refer to the methods founded on these properties, by which the most recent writers propose to accomplish its detection in complicated mixtures.

2dly. In the 10th volume of the *Annales de Chimie*, a paper will be found by M. Devergie, in which the physiological and chemical relations of the hydriodate of potash are examined with reference to their toxicological bearings. In this composition much ability is doubtless displayed, and the author acquits himself with considerable credit on the several points he investigates; but, at the same time, he has, in the chemical details, omitted every notice of the most characteristic of all its properties, namely, the dye it is capable of imparting to starch under particular manipulation; he has also brought forward much matter of comparatively total unimportance. Further, an abbreviation of M. Devergie's observations constitutes the notice given by Dr. Christison of this subject in his recent publication. As this distinguished author supports the statements of the French toxicologist by the sanction of his entire approval, I shall take the liberty of quoting from Dr. Christison's work the passage to which I allude.

"In solution, the best tests of the hydriodate of potash are, sulphuric acid, corrosive sublimate, acetate of lead, and proto-nitrate of mercury. Sulphuric acid disengages the iodine, forming an orange-coloured solution;

corrosive sublimate forms a fine carmine-red precipitate, the iodide of mercury. Acetate of lead forms a fine yellow precipitate, the iodide of lead. Proto-nitrate of mercury throws down a yellow precipitate, the iodide of mercury. (By a misprint, this precipitate is termed 'carmine red' in Dr. Christison's text.) The corrosive sublimate is delicate enough to detect the hydriodate in 2000 parts of water, the sulphuric acid in 10,000 parts, acetate of lead in 18,000, and the nitrate of mercury in 60,000. Few of the ordinary organic fluids alter the action of the tests, unless they are much coloured. In that case, the best plan is to evaporate to dryness, and clear the residue by raising to the heat. The salt is not decomposed, and may be dissolved out by pure water, after which it may be subjected to its usual tests." In Devergie's paper, the solution of the chloride of platinum is also mentioned as a test for the hydriodate of potash: this Dr. Christison has altogether omitted.

3dly. I shall now, in the fewest words the subject can be expressed in, sum up the objections to which this mode of examination appears to me to be exposed. In the first place, even in a pure solution of pure hydriodate of potash, the sulphuric acid as a direct test is truly insignificant, and I pass it by the more briefly, as I have some reason to know that Dr. Christison himself does not now place much reliance either on its delicacy or decision. The next test, namely, the acetate of lead, is individually liable to the objection, that the chromate of potash produces the same effect. The per-muriate of mercury is also liable to this source of fallacy, that alkaline carbonates throw down a red precipitate, differing only in shade from the true precipitates with the hydriodate of potash. (As to the proto-nitrate, the water of this city, though remarkable for its purity, causes with it a yellow precipitate identical in appearance with the yellow proto-iodide of mercury.) In fine, of all the tests proposed by Devergie, the only one individually free from fallacy is the muriate of platinum,* which Dr. Christison omits, and the one which (according to the testimony of Dr. D. B. Reid in his Practical Chemistry, and corroborated by many other eminent observers) is infinitely the most delicate of all the metallic reagents. But further, whether in delicacy, simplicity, or facility of manipulation, all these tests yield to the indication afforded by starch, which, as before stated, suffers no change of colour in solutions of hydriodate, but be-

* Before adding the platinum test to urine, it should be acidulated with acetic acid, because the iodide of platinum is soluble in alkalis, especially in ammonia, to a considerable extent.

comes immediately blue, whenever the iodine is set free: thus, if starch be diffused through a suspected fluid, and still remain white, but immediately turn blue on the addition of sulphuric acid, the proof of the presence of hydriodic acid amounts to positive certainty, and requires no further corroboration. It acts also in the next to the infinite proportion of 1 to 200,000 parts. It is, to say the least of it, extremely strange, that such a simple, and almost palpable, test, should have been altogether overlooked by Devergie and Dr. Christison.

But all these objections to the metallic tests (except the muriate of platinum) become multiplied without end, when we consider them as applied to the adulterated salt, generally sold under the appellation of the hydriodate of potash. Of twenty-four specimens now in my possession, obtained indiscriminately from the leading establishments in this city, two only are pure! One of these is a beautiful specimen manufactured by Pelletier, of Paris; the other is inferior in appearance, though chemically pure, and was furnished by a celebrated London druggist. All the rest contain enormous quantities of carbonate of potash, muriate of soda, with, occasionally, the sulphate of soda also. In many of the impure specimens, more than one half are apparently carbonate of potash; and one of the most distinguished analytic chemists of the day, who took the trouble to make a quantitative examination of a suspected sample, has informed me that it contained of carbonate of potash, sixty-four per cent! Early in January last, my attention was first directed to this subject by the failure of my attempts to demonstrate Devergie's tests, as quoted by Dr. Christison, with a specimen I had recently procured. Soon after this occurred, a paper on the subject by Mr. Pereira, of London, was published in the London Medical and Physical Journal, in which he satisfactorily demonstrated the different adulterations above mentioned.

I will not here stop to inquire whether this mixture be accidental or designed; perhaps, indeed, the determination of the question belongs more appropriately to a court of justice than to the present investigation. Before I quit the subject, however, I beg leave most respectfully, but emphatically, to call the attention of practitioners to this adulteration; and to them I need not dwell on the manifest sources of fallacy and disappointment it may expose them to in the treatment of disease. They may readily ascertain the fact, as far as regards the carbonates, by dissolving a few grains of the suspected hydriodate in water, and adding a solution of the acetate of lead. If the salt be pure, a beautiful yellow precipitate will fall down; if adulterated with carbonates,

the precipitate will be altogether white, and when dried, soluble with effervescence in acetic acid.

I return to the effect of these adulterations on the application of the several reagents recommended by Devergie. With the exception of the muriate of platinum, it totally obscures them all. The acetate of lead is thrown down white instead of yellow; the proto-nitrate of mercury is thrown down white also by the muriates, and the per-salts of mercury are precipitated as the red carbonate of that metal. The muriate of platinum, of the metallic tests, is alone not interfered with, *except in the degree of delicacy of its operation*, because the sulphate, muriate, carbonate, and phosphate of that metal, are extremely soluble in water; the iodide, on the other hand, being very insoluble in that fluid. In this case the superior value of the starch test, applied as before mentioned, is entirely proved by the fact, that where even the muriate of platinum affords no indication of iodine, the starch and nitric acid will at once detect it.

The next point to be considered is, how far will the effect of these metallic reagents be influenced by the fluids of the intestinal tube, by the serum of the blood, or by the urine, since, from its rapid absorption into the circulation, the hydriodate must be sought for in the latter situations, and will very frequently be detected there, when none can be found in the contents of the alimentary canal. The question is easily decided with strictly animal fluids; the tests all act with little alteration; but neither the fluids of the abdominal viscera, the serum, nor, above all, the urine, can be regarded as pure animal fluids, as all these contain muriates and carbonates, and, the urine, sulphates and phosphates, sufficient to invalidate all, with the exception of the tests afforded by platinum and starch. On these tests, therefore, can we alone place our reliance in our examination of fluids suspected to contain iodine, either free or combined.

4thly. On these facts I propose to found a process by which, in the most complicated mineral fluids, the hydriodate of potash may be detected in the smallest proportion, and with the utmost certainty. This process consists of two parts, the first of which is merely the application of the starch and sulphuric acid to the suspected fluid as a *trial test*. The second part is the separating of iodine itself from any fluid in which the trial test has indicated its existence.

For this purpose the muriate of platinum should be dropped into the fluid; when, if the colour become immediately as deep as that of port-wine, the subsequent steps may be proceeded with at once; if not, the fluid must be reduced by evaporation to one half, and the muriate of platinum then added; the

iodide of platinum is now freely separated, but from its extreme firmness is apt to remain suspended in the liquid for an inconvenient length of time; neither can it be readily separated by the ordinary methods of filtration, without a great loss of the iodide on the filter itself, and some of it also escaping through the pores in the paper.

The coloured fluid, therefore, is to be agitated with about one-third of its volume of sulphuric ether in a stoppered phial, when any iodide of platinum present will be taken up by the ether, which, from its greater levity, soon rises to the surface of the fluid, and may be withdrawn by a small syphon or pipette. The ethereal solution thus procured is next to be evaporated to dryness, and a particle of the residue introduced into a glass-tube, sealed at one end, about six inches long, and the fourth of an inch in diameter. On applying heat the iodine is immediately sublimed, exhibiting beautifully its peculiar violet vapour, and condensing into black dendritic streaks about two inches from the mouth of the tube. If the part of the tube containing the iodine be now separated from the remainder, by cutting it across with a file, and a few drops of alcohol introduced, a brown tincture of iodine is immediately procured, the effects of which upon starch are next to be ascertained. By this process iodine may be reduced to the simple form, from one grain of the hydriodate of potash dissolved in six ounces of recent urine, which, on account of its numerous *mineral* ingredients, is the most complex fluid in which the hydriodate can ever present itself for investigation.*

This second part of the process also applies to the hydriodic acid prepared from the solid contents of the stomach, in the case of poisoning by free iodine. Little further remains for me now to add than to recommend in any case of poisoning by iodine, or the hydriodate of potash, that the examination of the urine should never be forgotten; and, if no urine can be procured in a fatal case, that the serum of the blood should be tested after conglutination; for if I may reason from the experiments of Wohlen and Stehberger, and from the examination of six dogs poisoned by myself, the iodine or hydriodate will, in a great majority of cases, be detected in these fluids, when it

has been sought in vain in the solids or fluids of the alimentary canal.

In conclusion, I trust I may be permitted to disclaim the most remote desire of starting captious objections to the views, or directions, of the authorities to which I have alluded in the preceding observations. My only wish, in truth, is, to increase, if possible, the accuracy which is so essential to toxicological analysis. If, therefore, in the preceding pages, I have succeeded in showing that any thing has been brought forward by them which is liable to objection, or that any point has been omitted which was of material importance to be retained, I have done enough, I hope, to escape the imputation, of presumptuously refusing to place implicit reliance on the tests which these distinguished individuals have proposed.

Edinburgh, 65, Lauriston Place,
July 13, 1830.

* The muriate of platinum is most readily prepared by dissolving *finely divided* metallic platinum in two parts of nitric and one of muriatic acid, evaporating the solution to dryness, and then dissolving the residuum in water. Platinum may be easily procured from the gunmaker's shops, and a very small quantity of it is sufficient for the preparation of the test.