

ON THE MODE OF DETECTING

NITRIC ACID,

*And the total inefficacy of the New Test
of decolorizing the*

SULPHATE OF INDIGO.

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HAVING been very recently engaged in a series of toxicological experiments, my attention was particularly arrested by the discovery of a glaring fallacy in one of the tests recommended by the most eminent authorities for the detection of this important poison.

On reference to the most recent works on chemistry and toxicology, and those justly considered to contain *standard* opinions on the subject (I will particularise Dr. Turner's Elements of Chemistry, and Dr. Christison's splendid Treatise on Poisons just published), a new test of the presence of ni-

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nate quantities of nitric acid in the diluted form, will be found advanced on the authority of Dr. Liebig, and its efficacy corroborated by these distinguished authors in the most positive and decided terms. As I consider the matter of no ordinary interest, I shall quote the passages from the above-mentioned works which contain the statement of the circumstances to be investigated in the following observations.

In page 232, last edition of Dr. Turner's Elements of Chemistry, the subjoined statement occurs:—"A new test of the presence of nitric acid has recently been proposed by Dr. Liebig; the liquid to be examined must be mixed with a sufficient quantity of a solution of the sulphate of indigo in sulphuric acid, for acquiring a distinct blue colour, a few drops of sulphuric acid added, and the mixture boiled. If a nitrate is present, the liquid will be bleached, or if the quantity is very small, rendered yellow; by this process, nitric acid may be detected, though diluted with 400 times its weight of water; or by adding a little muriate of soda to the liquid before applying heat, one-five-hundredth part of nitric acid may be discovered."

Again, on referring to page 120 of Dr. Christison's new work on poisons, we find the following passage:—"Nitric acid in its diluted state is not always so easily discovered as the other mineral acids, because it does not form with bases, any insoluble salt, or precipitate. Professor Liebig, however, has recently discovered a very characteristic and elegant test, provided the acid is not diluted with more than 400 parts of water; his test is taken from the effect of this acid on the sulphate of indigo. A solution of indigo in sulphuric acid is to be added to the suspected fluid, till it communicates a perceptible blue tint, care being taken not to make the tint too dark, particularly when the suspected fluid is presumed to contain but little nitric acid; a drop of sulphuric acid is next to be added, and the mixture being put into a glass tube, heat is to be applied till it boils; as soon as it reaches the point of ebullition, the blue colour is either destroyed altogether, so that a colourless liquid forms, or it gives place to a faint straw-yellow tint; the latter effect is remarked when the proportion of nitric acid is small, and the indigo tint rather deep."—Professor Christison then remarks on the test of neutralisation by the carbonate of potash, which he considers less delicate than Dr. Liebig's, and further adds, "Liebig's test is applicable to the nitrates as well as their acid. This is the most advisable method in a criminal case, Liebig's being made, in short, a trial test.

It is unnecessary to make further extracts in proof of the general faith in the validity of this process. In the very latest work on chemistry in existence (Mr. D. B. Reed's

Practical Elements), the same statement occurs, and reference is given to the original paper of Dr. Liebig in the *Annales de Chimie*, vol. 35, page 80, where in a memoir "Sur la substance amère produite par l'action de l'acide nitrique sur l'indigo, le saule, et l'aloes," the reader will find the original in French, of which Dr. Turner's statement is a literal translation.

Here, then, we are presented with the most unequivocal assertion, and testimony of the proof of the efficacy of this new method of detecting nitric acid; so positive, indeed, that it may appear presumptuous, if not absurd, to question the veracity of the statement. It will be remarked, however, that none of the authorities quoted, advance any explanation of the action which occurs in the decolorization of the fluid; the fact is asserted, but nothing more. Not having had Dr. Liebig's paper at hand when my attention was first directed to the subject, and being unwilling to advance the circumstance to the gentlemen attending my course of experiments without some explanation, I was led to institute some experiments for the purpose of ascertaining the nature of the decolorization, impressed with the idea that the test was valid, though unexplained.

The unexpected results which followed the inquiry, render it unnecessary for me to particularise the experiments which led me to suppose that the nitric acid was by no means essential to the decolorization of the fluid. I shall merely mention the facts, and subsequently add the requisite observations.

A few test tubes were filled to the same height with water, and the fluid tinted to the same depths of shade by the blue solution of indigo in sulphuric acid. Dr. Liebig's process with the nitric acid was performed on the first, and the colour was immediately discharged as he describes. To the fluid in a second tube, a few drops of sulphuric acid were added, as Dr. Turner desires in the process for nitric acid, and the colour, on the mixture reaching the boiling point, was discharged as effectually as in the first experiment. A third trial was made with muriatic acid alone in the same quantity, and the tint was again destroyed; and in a fourth experiment, two grains of the muriate of soda, with one minim of the sulphuric acid produced the same effect.

These experiments at once established the total inutility of Dr. Liebig's plan for detecting nitric acid, since the muriatic and sulphuric acids possessed equal decolorising power over the indigo solution. In order to corroborate the fact, I demonstrated it next day to nineteen gentlemen, candidates for the medical degree at the ensuing graduation, and all perfectly competent to form a correct estimate of the circumstances: not one of these gentlemen could distinguish the

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slightest difference of shade in the fluids, resulting from the four experiments just described.

It is true, that in a case of poisoning by a mineral acid, a fallacy of this kind can usually have but little influence on the issue of judicial investigation, or on the general efficacy of the medical testimony. So well marked are the morbid appearances which must present themselves in a fatal example; but without violating probability, it may be readily imagined that an inexperienced practitioner might confound the appearance of aphthæ in children with the effects of one of these corrosive agents, and under the influence of the suspicions which accidental coincidence or maternal solicitude will very frequently excite, be induced to apply Liebig's tests to the contents of the intestinal canal. In such a case, the "few drops of sulphuric acid" mentioned in Dr. Turner's Elements as a necessary ingredient in the process, or the single drop of sulphuric acid advised by Dr. Christison, along with the muriate of soda necessarily present in the stomach, would be amply sufficient to reduce the tint of the fluid to perfect transparency; and, under the present mistaken belief in the delicacy and characteristic nature of the test, sufficient evidence would be obtained to criminate an impeached individual. In addition to such a source of practical error, it is now notorious that the strong acids are administered with the intent to murder, almost exclusively to infant children or intoxicated persons, with whom the history of the occurrence must be necessarily incomplete; in case of a recovery too, the vomited matter may become the subject of analysis when the assistance of morbid appearances may be totally wanting.

It is a matter of trite remark, that it is easier to overturn a bad system than to establish a better; I trust, however, that in the present instance I may escape that imputation, as I feel convinced, that while I raise objections to Dr. Liebig's method, I can direct the attention of toxicologists to one free from every source of confusion; but before I proceed to its consideration, the circumstances under which nitric acid presents itself to the toxicological inquirer, demand a cursory observation. The analyst, then, will usually have to determine the nature of, 1st. The concentrated fluid remaining in the apartment, perhaps, unconsumed by a suicide, or forgotten by a murderer; 2nd. The stains on various articles of apparel; 3rd. The fluid mixed with the heterogeneous materials in the alimentary canal.

In the first case, various tests have been proposed to determine the presence of pure concentrated nitric acid, for example, the solution of gold leaf with muriatic acid, the evolution of nitrous fumes, by the deoxydis-

ing agency of the metals, such as copper, mercury, &c. On the gold leaf test it is unnecessary to dwell here; so many and generally admitted are the errors to which it is exposed; as to the action of the metals, this single test, though of considerable precision, is scarcely sufficient, in unpractical hands, to afford satisfactory evidence, if not supported by any more tangible demonstration.

In proof of the presence of the concentrated acid, there are three experiments, which appear to me perfectly free from fallacy, of extreme delicacy, and besides possessing the advantage of being preservable for exhibition or description on a criminal inquiry.

The *first* is the action of *morphia* on the nitric acid, being instantly turned yellow, and in a few seconds vermilion red, on the application of the smallest drop; the experiment may be beautifully shown, by placing a particle of morphia on a slip of white card, and allowing a minute drop of the suspected liquid to fall on it, from the extremity of a capillary tube. By sulphuric acid, morphia is slowly changed to a dirty black; by muriatic acid it is entirely unaffected. This fact I believe was first observed by M. Lassaignes and is mentioned by Mr. Children in his translation of Thenard.

The *second* experiment is the formation of the detonating cyanate of silver; for this purpose, add five minims of the suspected fluid to three of water, and ten of strong alcohol in a glass tube, and drop into the mixture a particle of silver the size of a pin's head; hold the tube near the fire till effervescence commences, and then restrain the action by pressing the point of the forefinger on its open extremity; if the fluid be nitric acid, in about three minutes, sometimes less, white flakes, like coagulated albumen, suddenly appear in the liquid, and subside as it cools; the tube should next be agitated, and its contents thrown on a filter about the size of a thimble, and allowed to dry in a warm place. A particle of the residuum thus obtained, detonates loudly when introduced into the flame of a candle or spirit lamp. In this process, nitrous ether is abundantly disengaged, affording excellent corroboration of the presence of nitric acid, by its flagrant and peculiar smell. From the above-mentioned proportions, I have repeatedly obtained twenty-eight loud detonations, by careful management. This test of nitric acid is quite decisive; for though other compounds of silver also fulminate, yet the mode of preparation, the materials employed, and the phenomena of the several actions, are so widely different, that no mistake can occur.

The *third* test for the concentrated acid, to which I would claim attention, is one, in

the manner, perfectly free from deception—I mean the formation of the nitrate of urea. The facility with which it can be applied, when morphia cannot be produced, is also another material argument in its favour. When urine is evaporated at a heat not exceeding 71° Fahrenheit, to the consistence of a thin syrup, the smallest drop of nitric acid immediately causes the formation of an abundant precipitate of yellowish scaly crystals, like little wheels, or radiations from a common centre; oxalic acid produces the same effect, but the action of oxalic acid on lime-water will, at once, discriminate between both re-agents.

I shall pass over the second head, or the recognition of stains on articles of apparel, as it may be merged in the consideration of the third section, namely, the method of detecting nitric acid in the impure diluted state, or, in other terms, mixed with the vegetable and animal matters co-existing in the intestinal canal.

The impure fluid, when removed for examination, principally consists of water, nitric acid, albumen, casein, fibrino, osmazome, and gelatin. Muriate of soda is invariably present; and sugar, spirits, and other accidental substances, are present, according to the circumstances of the case. To detect the poison in such a complicated state of admixture, Professor Christison recommends the neutralisation of the acid with the carbonate of potash, evaporation to dryness, re-solution of the extract in alcohol, evaporation again, and the examination of the nitrate of potash thus procured. The presence of that salt, he states, may be recognised by the effects on the indigo solution, and the deflagration which ensues, when it is inflamed with combustible matter.

Having succeeded, I think, in establishing the utter uselessness of the indigo test, the next point to be considered is, how can we conduct the neutralisation with the effect of obtaining the most abundant product of the nitrate? And, secondly, how is the constitution of the nitrate thus formed to be ascertained? I will not delay here, by reviewing the merits of other methods, but I will at once describe the plan by which I have always succeeded in obtaining the most satisfactory results, from the analysis and separation of the most complicated mixtures.

Before neutralisation. I pass the mixture through a filter of prepared paper, always observing the precaution of using a receiving vessel sufficiently capacious to contain the whole of the fluid filtering, in case of the breaking of the paper; by this means, a considerable quantity of coagulated albumen and casein is mechanically separated; the filtered solution now contains a large proportion of gelatin dissolved in the diluted nitric acid; to this I add an infusion of tan,

by which the gelatin is precipitated, and when the compound thus formed has subsided, I add the carbonate of potash, and neutralisation is effected, then boil for a quarter of an hour with animal charcoal, and filter again. By this manipulation I obtain a colourless fluid containing nitrate of potash, muriate of soda, and necessarily a little oxalate of potash, produced by the action of the nitric acid on the animal substances and accidental sugar; it also contains osmazome, and other substances of less importance; by cautiously evaporating to dryness, an amorphous mass is obtained, to which (according to its quantity) the annexed tests may with facility be applied, for the evidence afforded by deflagration is by no means a satisfactory proof of the nitrate of potash being present, since the chlorate, oxalate, and others, do the same; some more energetically, others less so.

1st. As a trial test, introduce about five grains of the mass into a small glass tube, with about ten minims of distilled water; heat the mixture in the flame of a spirit lamp, and when it boils, drop into it a grain of English morphia, and immediately touch the surface of the fluid with a glass rod moistened with sulphuric acid; if a nitrate be present, the mixture will instantly assume the colour of sherry wine.

2d. Introduce a drachm of the mass into a small retort capable of containing no more than two fl. ounces, with a neck twelve inches long and one-third of an inch in diameter; add an equal weight of strong sulphuric acid, and apply heat, condensing the product of the distillation in a little phial containing twenty drops of distilled water. Nitric acid will be procured in sufficient quantity to supply any or all of the tests I have advised, namely, the morphia, urea, and detouring silver, three times over, if sufficient economy be observed. I may add, that there is no difficulty in procuring from five grains of the nitrate of potash of the shops, as much pure nitric acid as is sufficient to show the morphia and urea tests in the most unequivocal manner.

I have thus given an outline of the process necessary to be pursued in the detection of this poison. It may perhaps be considered that I have dwelt too long on a subject, concerning which the ends of justice might be satisfied by a title of the investigation; yet I cannot but agree with Dr. Christison, when he observes, that "it is the duty of the medical jurist to supply not only satisfactory evidence, but also the best evidences which his science affords."

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