

**Two cases of fatal poisoning by arsenious acid : with remarks on the solubility of that poison in water and other menstrua / by Mr. Alfred S. Taylor.**

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TWO CASES  
OF FATAL  
**POISONING BY ARSENIOUS ACID:**

WITH REMARKS ON  
THE SOLUBILITY OF THAT POISON, IN WATER  
AND OTHER MENSTRUUA.

BY MR. ALFRED S. TAYLOR.

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OF  
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CASE 1.

A FEMALE, aged 25, was admitted into Guy's Hospital, May 17, 1836, under the care of Mr. Cooper, suffering from symptoms of poisoning by arsenic.

It appears, that, about four o'clock in the afternoon of that day, she had taken a quantity of arsenic; which, from her description, must have amounted to about forty grains. She procured it in a small lump; reduced it to a coarse powder, which she then loosely mixed with water; and in that state she swallowed it. In about an hour afterwards she became very ill, and vomited: she had pain in the stomach, great thirst, and a sense of constriction in the throat. A medical practitioner, who was called in, administered emetics and mucilaginous drinks, from which she experienced some relief. She became worse in the course of an hour or two, and was subsequently brought to the Hospital. This was about eleven o'clock in the evening, and, therefore, about seven hours after she had taken the poison. She was then labouring under the following symptoms:—the countenance was pale and anxious; the extremities were cold; there was occasional vomiting; *great thirst*; and the tongue was moist, but very red: *the pain in the stomach was not great, and not increased by pressure*: the pulse was 134, very irregular, but rather full: there was no pain in the head; and her mental faculties were unimpaired.

As she had, previously to her admission, taken emetics, which had acted freely, it was not thought necessary to resort to any further exhibition of them. A saponaceous



mixture, consisting of equal parts of oil and lime-water, was, however, thrown into the stomach, by means of the stomach-pump. This was for the purpose of enveloping any residuary particles of poison, and sheathing the coats of the organ from their influence. The stomach was first well washed out with this mixture; and then about three ounces of it, mixed with forty drops of tincture of opium, were injected into the organ, and allowed to remain there.

She was seen the following morning, at half-past one: she then complained of great thirst, but there was no increase of pain in the stomach. Her tongue was dry, and red: her extremities had become warm: there was no pain in the head. The heart was acting rapidly, but feebly; the pulse being about 132, small and feeble. After this, she obtained some rest for about an hour and a half; but she then became extremely restless, repeatedly calling for liquids. The thirst continued unabated until her death, which took place at a quarter past seven in the morning, a little more than *fifteen hours* after having taken the poison. Just before her death, her parents came to see her: she was then very restless, but perfectly *sensible*. She had sat up in bed, and was in the act of drinking; when she suddenly had a slight convulsive fit, and almost instantly died.

The body was examined by Mr. King about eight hours after death. The thoracic viscera presented no appearances calling for notice; but the lining membrane of the bronchiæ was rather dark in colour, and congested.

On opening the abdomen, and exposing the cavity of the stomach, this organ was found to contain a dirty yellow-coloured liquid, somewhat tenacious, and holding, diffused through it, opaque grains of a white matter, evidently arsenic. Particles of the same substance, enveloped in mucus, were found scattered over the surface of the mucous membrane, in different parts. The appearances presented by the stomach, when seen and examined shortly after its removal, were as follows\*. The mucous membrane was very rugose,

\* A wax model of the stomach, representing very perfectly the morbid changes observed in it, has been made by Mr. Town. It is placed in the Museum, and numbered 2772<sup>c</sup>.



especially at the larger extremity and inferior portion. The edges of the rugæ were, for the most part, vascular; whilst, in the intervening depressions, there were here and there dark-coloured patches of blood, extravasated beneath the mucous membrane. There was great vascularity of the membrane in the upper part of the organ; and there were three distinct lines, of a vermilion redness (the colour having become a little more intense by exposure), running parallel to each other, for nearly the whole of the interspace between the pyloric and the cardiac orifices. These lines terminated in a well-defined margin of redness, situated at the junction of the cardia with the œsophagus.

The most striking morbid changes, however, in the stomach existed near the larger curvature, towards the pyloric extremity. Here there was a large prominent oval patch of thickened membrane, about three inches in length, and two inches in breadth. This patch was, in the first instance, covered with a dense layer of opaque mucus, with difficulty separable, containing small granules of arsenic diffused in a white pasty mass. When the surface was washed, it was seen to be of a yellowish colour in the centre; and it was surrounded by a dark margin, as of extravasated blood. At this part, the coats of the stomach were at least three-quarters of an inch in thickness. There was no trace of ulceration or corrosion in any part of the mucous membrane. The peritoneal coat was slightly injected.

In the report of the examination, it is stated that the small intestines contained a great quantity of viscid mucus, tinged with bile. The duodenum was but slightly vascular; but the jejunum was in a high state of inflammation, in circumscribed patches, these portions of the mucous membrane being covered with an easily separable layer of mucus. The lining membrane of the last twelve inches of the ileum, as well as that of the cæcum, was slightly inflamed. The rest of the intestinal canal, with the other organs of the abdomen, presented no abnormal appearances. From the condition of the uterus and its appendages, there was reason to suspect that impregnation had recently taken place.

The head was not examined.

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This case appears to me to be worthy of attention, in several points of view. The time at which the symptoms commenced, after the poison had been swallowed, was about the ordinary period; namely, *an hour*. The most remarkable circumstance, in their history, is, the general absence of pain throughout the progress of the case. It is true, that, in the first instance, there was pain in the stomach; but this soon abated, and did not afterwards return to any perceptible extent. In the generality of cases of poisoning by arsenic, pain is one of the most striking symptoms, especially in those in which the post-mortem inspection reveals such extensive changes in the stomach as were met with in this instance. In arsenical poisoning, also, the pain is commonly excruciating; being compared by the patient to a fire burning within the body\*. It is, generally, much aggravated on pressure; and goes on increasing in intensity, with only occasional remissions, until the time of death: but here, these features were entirely wanting. Several instances are on record, in which this symptom of poisoning by arsenic has been absent; and we ought, therefore, in suspected cases, to be prepared for such an anomaly. Dr. Christison mentions an instance of this kind; and others are reported by Orfila†. In general, where the pain in the abdomen is slight, death takes place much more speedily; and the post-mortem changes are much less extensive than in the case before us. Dr. Christison has formed a separate group of these cases, constituting his second variety of poisoning by arsenic, in which symptoms of cerebral disturbance are often manifested. Here, however, it is to be observed, the mental faculties remained unimpaired till the last; and neither comatose symptoms nor convulsions manifested themselves during the progress of the case.

One of the most prominent symptoms under which the deceased laboured was the *extreme thirst*, which she in vain endeavoured to assuage by having constant recourse to liquids. I have noticed the presence of this symptom, to a

\* Christison on Poisons, 217.

† Toxicologie Générale, Tome I. 384, 388, 397.



similar extent, in three other cases which have fallen under my observation. It certainly is not always present in arsenical poisoning; but, at the same time, I think too little notice has been taken of it by British toxicologists. One of our best writers on toxicology, Dr. Christison, mentions this symptom only in a cursory manner\*. Continental medical jurists, however, attach full importance to this sign†; and Prof. Martini looks upon it, when conjoined with dryness and constriction of the fauces, as affording the most certain evidence of irritant poisoning‡. The other symptoms require no particular remark.

The treatment pursued was perhaps the best which, under the circumstances, could have been applied. The viscid mixture of oil and lime-water was well adapted to sheathe the coats of the stomach; and certainly, by more effectually enveloping and retaining the undissolved portions of the poison, to facilitate its removal by the stomach-pump, from the cavity of the organ. Lime-water has been proposed as a chemical antidote in poisoning by arsenic; but in the case before us, its mechanical operation, mixed with oil, was alone relied on. Lime, it is true, will combine with arsenious acid, and form an arsenite; but this arsenite is easily redissolved, either by a slight excess of the poison, or by the presence of a small quantity of acid, such as that which is ordinarily contained within the stomach. Besides, the arsenite of lime thus formed, like the other arsenites which are insoluble in water, is capable of acting deleteriously; so that the alleged antidotal powers of lime-water are now generally exploded.

Another point of interest, in a case of poisoning by arsenic, is the period at which death takes place. In that before us, the deceased died within the average period; which may be taken at from *six to twenty-four hours* after the ingestion of the poison, when the dose has been large. Many cases do not prove fatal until from twenty-four to

\* Op. Cit. 216.

† Heuke's Lehrbuch der gerichtl. Medicin, 441. Vide also Meckel. Lehrb. der g. M. 216. Niemann's Taschenbuch d. S. A. 440.

‡ Introduzione alla Medicina Legale, Vol. II. 330.



forty-eight hours ; while, in some instances, the patient is destroyed in less than six hours. Taking the most severe cases of arsenical poisoning, however—of which this was one—the above may be assumed as the average period within which death will ensue. This question of the time at which arsenic proves fatal is, perhaps, not so interesting in a physiological, as in a medico-legal point of view ; but it is one for which a practitioner must be prepared. In a trial that took place at the Lewes Assizes, Autumn 1826, which is referred to by Dr. Christison\*, the fact of the prisoners' guilt, of which the moral evidence left but little doubt, rested almost entirely upon the decision of this question. The deceased, it appears, died within *three hours* after the only meal at which the prisoners could have administered the poison (arsenic) to him : and one of the witnesses for the defence is reported to have assigned, among other reasons, why the deceased had not died from poison, that arsenic never destroys life within so short a period as three hours. Dr. Christison very properly censures so dogmatical an opinion ; and adduces many cases, to shew that life may be very rapidly destroyed by this poison. The shortest case, quoted by him from a German writer, proved fatal in *three hours*. There are numerous instances on record, in which life has been destroyed in from three to six hours after the taking of the poison : and I find an instance, reported by Meckel, in which death followed in *two hours and a half*†. A case of probable poisoning by arsenic is mentioned by Remer, which proved fatal within *half an hour* after the ingestion of the poison‡. Setting aside the last case referred to, we see that arsenic may destroy life within a very short period of time ; although it is comparatively rare to find it proving fatal in less than six hours.

In looking over the post-mortem appearances, we find the chief seat of mischief, as usual, in the stomach. The extreme degree to which inflammation of the mucous membrane of this organ had advanced, within the short period of fifteen hours, is, however, worthy of remark. The local

\* On Poisons, p. 220.

† Lehrbuch der gerichtlichen Medicin, 218.

‡ Metzger System der gerichtlichen Arzneiwissenschaft, 256.



irritant action of the poison was here most strongly manifested; but there was neither ulceration nor gangrene. The effusion of dark blood beneath the mucous tunic has, perhaps, often given rise to the supposition of the existence of gangrenous spots in the stomach, in cases of arsenical poisoning. These patches of extravasation existed here chiefly in the interspaces of the rugæ, as well as around the raised oval portion of the stomach, at the pyloric extremity. The coats of the viscus were much thickened in the last-mentioned situation; a condition which does not appear to be very unfrequent; and perhaps, on the whole, is a much more common morbid change from arsenic, than perforation. Metzger met with this thickened state of the coats of the stomach\*; and Pyl reports a case, in which the parietes of the viscus had twice their usual thickness†.

Lastly, it remains for me to describe the plan pursued for the identification of the poison. The confession made by the deceased, as well as the nature of the symptoms, left but little doubt that arsenic had been taken: but a case is always rendered more satisfactory when, to these sources of evidence, we can add the certainty commonly derivable from chemical analysis.

Knowing that the poison had been swallowed in the state of a coarse powder, I considered it not unlikely that some undissolved particles might exist in the contents of the stomach. The liquid found in this organ was of a yellowish colour, and of thick gruelly consistency, containing, diffused through it, lumps of coagulated matter. A portion of this liquid was diluted with warm distilled water, placed in a glass vessel tapering to a point at the bottom, and then violently shaken. After waiting a minute, the liquid was rapidly poured off into a dish; and at the bottom of the glass, numerous hard masses, apparently of arsenious acid, slightly discoloured, were found. These were picked out, dried, and heated with black flux; when several well-defined rings of metallic arsenic were obtained. This process of separating arsenious acid, by its great specific gravity, I have often found to answer, where the viscosity of the liquid, con-

\* Metzger System der gerichtlichen Arzneiwissenschaft, 256.

† Aufsätze und Beobachtungen, I. 58.

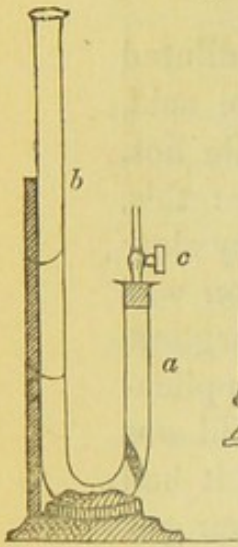


taining it, had been removed by the addition of distilled water. In this way, the examiner may frequently save himself a great deal of trouble and research.

Another portion of the contents of the stomach, diluted with distilled water, and well acidulated with acetic acid, was now boiled for two hours. It was filtered, while hot, through fine muslin, and afterwards through paper: this, owing to the abundance of organic matter, was a very slow process. The liquid obtained by this second filtration was still turbid; but it contained comparatively little organic matter, although sufficient to prevent entirely the application of the silver and copper tests. The filtered liquid was now divided into two portions. Into the first, after it had been acidulated with acetic acid, sulphuretted hydrogen gas was passed, to saturation: a golden-yellow coloured compound was speedily formed, which slowly subsided, after boiling the solution to drive off any excess of the gas. The precipitate thus obtained was proved to be sesquisulphuret of arsenic: 1st, by its insolubility in the mineral acids; 2dly, by its perfect solubility in strong liquor ammoniæ; and, 3dly, by its yielding a ring of metallic arsenic, when slowly heated with four times its weight of black flux. The precipitated sesquisulphuret was combined with a portion of extraneous matter; but I have never found this an obstacle to the determination of its true chemical characters, except when the foreign matter has been in unusually large quantity. The sesquisulphuret is not so easily reduced to the metallic state as arsenious acid: it requires a larger quantity of flux; and it is, perhaps, better to use a lower heat, and to apply it more slowly, than in the case of arsenious acid.

The second portion of filtered liquid, having been slightly reduced in bulk by evaporation, was now treated with an excess of alcohol, and introduced into the ingenious apparatus which had been then but recently proposed, by Mr. Marsh of Woolwich, for the detection of minute quantities of arsenic. The principle of this discovery is, to generate hydrogen gas slowly in the midst of a liquid containing any arsenious or arsenic acid, or any of the soluble salts formed by the union of these acids with bases. In all of these instances, the nascent hydrogen combines with the *metallic arsenic*, resulting from the decomposition of the acid or salt;





and forms a gas well known as the arseniuretted hydrogen. This gas is generated under the pressure of a column of water, in a glass tube bent upon itself; so that the two legs (*a*, *b*), one of which is only half the length of the other, are parallel. The shorter leg (*a*) is provided with a stop-cock (*c*); and it is in this leg that the gas is produced, by dropping a piece of metallic zinc into the suspected poisonous liquid previously acidulated with sulphuric acid. When the arseniuretted hydrogen has collected so as to fill the shorter leg of the tube, it is allowed to escape from the stop-cock; and at this moment, if a lighted taper be applied, it will burn with a dull white flame: and if, at the same instant, a plate of clean glass be brought over the flame, a circular stain of metallic arsenic is formed upon it; whilst the combustion of the hydrogen, at the same time, produces a ring of aqueous vapour around the metallic stain. In some instances, the quantity of arsenic deposited in the metallic state is such, that a perfect leaf of the metal may be raised from the surface of the glass\*.

In the case before us, upwards of twenty crusts of metallic arsenic were produced from about three drachms of the filtered liquid, treated with alcohol. The object of using

\* Several objections have been urged against the use of this, which may be called, the "Hydrogen Test." They may be reduced to two: 1. That arsenic is sometimes contained in the sulphuric acid of commerce, and often in metallic zinc.—This objection is at once removed, by trying the experiment, in the first instance, with zinc, sulphuric acid, and distilled water:—if arsenic be present in either of the bodies, a stain will be left on a plate of glass, in burning the gas: if not, there will be merely a deposit of pure water. In the former case, purer materials must be sought for; and these it will not commonly be difficult to find. 2. Other bodies may combine with hydrogen, and, during combustion, be deposited on glass. The plain and obvious answer to this objection is this: Let the sublimate be treated with dilute nitric acid, and then allow a current of sulphuretted hydrogen gas to pass over it. If the sublimate be arsenic, the yellow sesquisulphuret will be immediately produced, soluble in Liquor Ammoniae. This corroborative experiment must suffice to remove all doubt respecting the nature of the sublimate. I have found this test effectual in cases where the sulphuretted hydrogen gas has failed to indicate the least trace of arsenious acid. During the last six months, I have performed many experiments with this apparatus, both on artificial mixtures, and on the contents of stomachs of persons poisoned by arsenic. In respect to its delicacy, I have obtained sublimate from  $\frac{1}{100}$  gr. of arsenious acid, diffused in 45,000 parts of water.

$\frac{1}{45,000}$

Douglas & Flaudin say  $\frac{1}{100000}$  the part  
 stains begin to appear at  $\frac{1}{200000}$ .

$\frac{1}{3}$  45000 parts



alcohol, is to prevent the frothing of the liquid within the tube, which, in a mixture containing organic matter, is very likely to occur; and when this does occur, it interferes with the free escape and combustion of the gas. The precise nature of the sublimate was determined by the corroborative experiment mentioned in the note.

The contents of a portion of the jejunum, which had been insulated for the purpose of examination, were now submitted to analysis by the same processes, and with equally satisfactory results. The hydrogen test shewed that arsenic was abundantly present in the fluids of this part of the alimentary canal.

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CASE 2.\*

This was also the case of a female, aged 22, who was admitted Sept. 3, 1836, at nine o'clock in the evening. She was reported to have taken, an hour before her admission, an ounce of arsenious acid, in consequence of some disappointment. Ineffectual attempts had already been made to induce her to take emetics; but vomiting had occurred from the action of the poison. When admitted, the surface was cold; her pulse was small and quick; and the matters ejected from the stomach by vomiting, consisted chiefly of mucus, slightly streaked with blood. The stomach-pump was immediately applied, and the stomach well washed out. Albumen was then exhibited, followed by an emetic of the sulphate of zinc; and, in order to keep up the action of the stomach, warm water was freely administered at intervals. During this time, violent diarrhœa supervened, from the effect of the poison.

At twelve o'clock P.M., three hours after her admission, the following were the symptoms:—coldness of the surface; depression of the countenance; restlessness; lividity of the lips; glaziness of the eyes; a rapid, feeble, and irregular pulse; pain in the abdomen, materially increased by pressure, especially in the epigastric region; occasional vomiting of mucus tinged with blood; the respiration was somewhat accelerated, and accompanied by frequent sighing. The

\* For the substance of this report I am indebted to Mr. James Godfrey.



diarrhœa had at this time ceased, and there was a slight tendency to coma.

She was seen again about four hours afterwards, when all the above symptoms had rather increased, and she was affected with cramps in the legs. At eight o'clock on the 4th, vomiting had ceased; the pulse at the wrist was imperceptible; the symptoms of coma had increased; but she was still very restless. At ten o'clock, this restlessness subsided; she became quiet; the action of the heart was failing; the respiration was laborious; and she died at one o'clock, about *seventeen* hours after having taken the poison.

The inspection of the body took place twenty-six hours after death; and the following were the principal appearances. The mucous membrane of the stomach was highly inflamed throughout, and was in many parts *ulcerated*. The rugæ of the membrane were not very numerous, but their summits were especially the seat of inflammation and ulceration. No *arsenic* was found in the stomach, nor were there any solid matters present.

The mucous membrane of the duodenum was much inflamed, and there were also considerable patches of inflammation and ulceration on that of the ileum. The mucous membrane of the colon was slightly injected, as well as that of the rectum; but there was no trace of poison to be discovered in the last-mentioned portion of the intestinal canal. The œsophagus was likewise inflamed, and the lining membrane of the larynx and trachea was highly injected. The uterus exhibited evidence of existing menstruation.

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The history of this case does not differ from that generally detailed of the most severe forms of poisoning by arsenic. There is but little peculiarity in the progress of the symptoms, or in the post-mortem appearances. There was certainly an absence of thirst, in which respect this case differs from the preceding; and there was also a *tendency to coma*, indicating the remote effect of this poison upon the brain. This symptom, however, as indeed it has been generally remarked by toxicologists, did not make its appearance until the violent irritation in the alimentary canal had, in



great part, subsided. Death took place within the average period of time.

The summits of the rugæ in the stomach were in this, as in the former case, especially inflamed. This is what I believe to be very common, where the mucous membrane is at all inflamed. It appears to proceed from these prominent portions of the membrane, coming more directly in contact with the particles of the poison. There was, however, one appearance here, which was not observed in Case 1; namely, extensive ulceration of the mucous coat. My own observation, in the few cases in which I have had an opportunity of making a post-mortem examination, agrees with that of Dr. Christison; namely, that ulceration is not a very common morbid change from poisoning by arsenic\*. Dr. Christison remarks, that "death frequently takes place, before that process *can be established*:" and says, that, "for the most part, it is hardly to be looked for, unless the patient has survived nearly *two days*." We may observe, however, that the inflammation produced by an irritant poison, like arsenic, does not follow exactly the same laws as that which is termed 'healthy inflammation,' in surgery. The action of the poison is specific. The inflammatory condition of the stomach may be more rapidly induced, and the consequences of that inflammation more speedily manifested. Although, then, ulceration of the stomach, as an effect of arsenical poisoning, is not common, yet this case proves, that the process may be certainly perfectly established, both in this organ as well as in the intestines, when the poison has operated fatally within so short a period as *seventeen hours*.

There is another point worthy of remark in the account of the inspection; namely, that not a trace of the poison could be discovered in the stomach. This is to be regarded as the more singular, when it is considered that *an ounce* of the powder was taken; that the deceased lived only seventeen hours; and that the arsenious acid, of all poisons, is most liable to become enveloped in mucus, and locked up within the folds of the mucous membrane. One

\* On Poisons, 247.



or two cases are recorded by Dr. Christison somewhat similar, in relation to this point\*. The fact appears to me readily to admit of explanation, from the abundant vomiting, and from the diarrhœa, with which the deceased was affected; by either or both of which, it is well known, a mineral poison may be readily expelled from the body. It must also be borne in mind, that the stomach was well washed out with the stomach-pump: and this fact of the absence of the poison from the cavity of the organ after death, may perhaps be here adduced, to shew that that instrument may be sometimes very efficaciously employed in cases of arsenical poisoning. The result of this case will also enable a practitioner to give a decided answer to a question sometimes put in a Court of Law—"Whether the non-discovery of poison in the stomach, *when death has speedily taken place*, should be regarded as a proof that the individual has not been poisoned?" The records of medical experience will furnish a few such cases as this; but the more they are accumulated, the more satisfactory does medical evidence, founded upon them, become. Ulceration of the mucous membrane of the intestines is not very commonly seen in cases of poisoning by arsenic, except when a fatal result has been for some time deferred. In this instance, there were patches of ulceration in the ileum, especially around the seats of the glandulæ aggregatæ.

This case also shews to us how very extensively the mucous membranes of the body may be affected by the action of arsenic. The lining membrane of the larynx and trachea †, that of the œsophagus, and indeed of nearly the whole course of the alimentary canal to the rectum, was, in places, more or less injected, inflamed, or ulcerated. The changes in the rectum were but slight: they did not amount to ulceration.

Arsenic has been observed, in some instances, to have a singular effect on the menstrual function. Schweickhard met with a fatal case of poisoning by arsenic, in which the

\* On Poisons, 49, 249.

† An inflammatory redness of the air-passages is said to be somewhat rare, as an effect of poisoning by arsenic.



secretion, after having ceased eight days, was suddenly restored. On making an inspection of the body, the organs of generation were found inflamed. A precisely similar case occurred to Hasenest\*. In the instance before us, it does not appear that there took place any increased secretion from the effects of the poison.

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That arsenic was the substance which the deceased had taken, was proved by an analysis of some of the matter which she had vomited on her admission, conducted by Mr. Godfrey. This gentleman, however, kindly furnished me with two portions of liquid which had been removed from the stomach of the deceased, by the stomach-pump, at two different periods before her death. The process of analysis pursued with respect to these, was as follows:—The first liquid examined, appeared to consist of nothing more than water, with small brownish-coloured masses loosely diffused through it, which, when the vessel was agitated, and then allowed to stand, rapidly sank to the bottom. This liquid was filtered, and the undissolved residue collected and dried. The residue, when heated with black flux, yielded an abundant sublimate of metallic arsenic. The filtered liquid gave but a very faint re-action with the tests for arsenic. There was evidently but a very minute portion of poison dissolved in it.

The second liquid, which was next submitted to analysis, amounted to about two ounces: it was opaque, frothy, and viscid, containing, suspended in it, numerous flakes of coagulated albumen. After dilution with distilled water, it was treated with acetic acid, and boiled for about two hours; the waste by evaporation being made up. It was then filtered, and divided into two portions. Into one, sulphuretted hydrogen gas was passed for some time; which gave rise to a very copious white precipitate, indicating the presence of a salt of zinc. Accordingly, a portion, on being submitted to further analysis, was found to contain a very

\* Meckel, *Lehrbuch der gerichtlichen Medicin*, 217.



large quantity of the sulphate of zinc. The precipitate formed by sulphuretted hydrogen had no tinge of yellow: consequently, it might have been inferred that arsenic was not present. But on a part of the filtered liquid being submitted to the action of the "hydrogen test," sublimes of metallic arsenic were obtained. These, it is true, were extremely slight: one of them, when tried, was not ponderable in a balance turning with the hundredth of a grain. The quantity obtained, however, was sufficient to shew that arsenic was really present; which, without the application of Mr. Marsh's apparatus, I do not think it would have been possible for an experimentalist to have declared.

Neither the copper nor the silver test was employed in this investigation. Indeed, I have long acted on the principle of never employing these tests, except when operating upon a clear solution of the poison, in which there is certainly no organic matter, nor any foreign salt, alkaline or metallic. The common alkaline and earthy salts do not in the least interfere with the action of sulphuretted hydrogen gas on arsenious acid; but their presence materially counteracts or modifies the effects of the copper and silver reagents. Thus, muriate of soda is very likely to be found in the human stomach, mixed with arsenic: this salt not only destroys the action of the silver test, but renders that of the copper ambiguous. Very complicated directions are given by some writers for the purpose of removing this substance from a mixture of arsenious acid containing it, before the application of the tests in question: but there is no necessity whatever for following these directions; since, setting aside the valuable application of the hydrogen test, the action of sulphuretted hydrogen, with the subsequent reduction of the precipitated sulphuret, must furnish the practitioner with such evidence, that the seeking for further corroborative re-actions would only be a work of supererogation. I have found that the presence of a very minute portion of arsenious acid, dissolved in a large quantity of a saturated solution of muriate of soda, was detected by sulphuretted hydrogen, with the same facility as if it had been dissolved in water.

There is one case in which the sulphuretted hydrogen may fail; and we have an exemplification of it in the chemical



analysis just given; namely, where a metallic salt is mixed up with the contents of the stomach, in cases of arsenical poisoning. The sulphates of copper and zinc, and tartarized antimony, are so frequently resorted to as emetics, that the practitioner ought to be prepared for occasional ambiguity, in the re-action of sulphuretted hydrogen. In the second case reported, sulphate of zinc had been given; and nothing but a sulphuret of that metal could be obtained, in operating on the contents with sulphuretted hydrogen gas. So, if a compound poison were ever exhibited or taken—as, for instance, a mixture of arsenic and corrosive sublimate—the process of analysis might be seriously embarrassed, unless the operator were prepared with a knowledge of the effects of sulphuretted hydrogen on particular metallic salts. In admitting, however, that the results of the application of sulphuretted hydrogen are not always clear and satisfactory, we must remember, that we have now in our hands a means of demonstrating the presence of arsenic, in whatever state of admixture with other substances it may be. By the use of the hydrogen apparatus, the smallest quantities of arsenious acid, when mixed up with corrosive sublimate, sulphate of zinc, sulphate of copper, tartarized antimony, or other metallic poisons, in large proportions, may be detected with the same facility and certainty, as if those salts were absent.

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REMARKS ON THE SOLUBILITY OF ARSENIOS ACID IN WATER AND  
OTHER MENSTRUUA.

The solubility of arsenic in water at different temperatures has been variously stated. In general, chemists and medical jurists have relied upon the results, obtained by M. Guibourt; but it seems to me, that these results have been somewhat hastily adopted. The action of water on arsenious acid is, in some respects, peculiar. Under any circumstances, the affinity between the two bodies is extremely slight: at *low* temperatures, even when they are allowed to remain in contact many hours and the vessel is frequently agitated, but a very minute portion of the poison is dissolved: at *high* temperatures, *i. e.* when boiling water is poured on the poison, and allowed to cool over it, the quan-



tity dissolved, although greater than in the preceding cases, is extremely small; and much less than the quantity retained in a cold saturated solution, prepared by boiling together, for several hours, the arsenic and water. When a solution is made by gradually adding arsenious acid to water kept boiling for an hour, the proportion taken up is greater as the boiling continues, at least for the first half hour. On removing the vessel from the fire, and allowing it to stand for a few minutes only, a considerable imperfectly-crystalline deposit takes place: this deposit rapidly increases as the liquid cools, so that about one-half of the arsenic falls down in octohedral crystals, after the lapse of seventy-two hours. The mere admixture of arsenic and boiling water is not then sufficient, as in the case of most soluble bodies, to bring about a combination: it is necessary that the poison should be for some time boiled in water, before perfect solution can be effected: the mere application of a heat of  $212^{\circ}$ , with subsequent cooling, is ineffectual for this purpose.

Several explanations have been offered, to account for this seeming anomaly in the phenomena of solution. Fischer, a German chemist, conceived, that during the process of boiling, the arsenious acid underwent some change; although he confessed that he was unable to discover any difference in the composition of the crystals which were separated on cooling\*. He imagined that one portion of the arsenious acid might surrender a part of its oxygen to another portion, by which the latter would acquire a higher degree of acidification, and be rendered more soluble; while the de-oxidized portion would become, in the same ratio, less soluble. It is, indeed, stated by him, that the arsenious acid, separated by crystallization from a boiling saturated solution on cooling, has only one-twentieth of the solubility of this substance, as it is ordinarily met with. He also notices the change of colour which the arsenic undergoes; and considers this, as affording evidence of the process of ebullition having brought about some chemical change in

\* Remer's Lehrbuch der Polizeilich-gerichtlichen Chemie, 2<sup>te</sup> Band, p. 714.



this body. With regard to the impaired solubility of the crystallized arsenious acid procured in the manner above stated, so far from obtaining the extraordinary result mentioned by this chemist, I have not been able to observe any other difference, when the crystals had been previously reduced to powder, than that the boiling required to be kept up for a longer period. It appears to me, that the force of cohesion in the crystalline particles is the main obstacle to the free solution of this substance, under these circumstances. The change of colour in arsenious acid—for the crystals have invariably a dusky brown or yellowish colour—is perhaps easily explicable, on the principle, that the arrangement of the particles is different in the crystalline and amorphous states.

That the increased solubility of arsenious acid by long boiling is not due to any transference of oxygen from one portion to another\*, is, I think, evident, from numerous circumstances:—1. There is no difference in the chemical composition of the crystals and of the amorphous powder. 2. A portion of the clear solution (procured by long boiling), evaporated to dryness, leaves a residue, which, when heated on platina to about 400°, by means of a spirit-lamp, is entirely volatilized. Now any portion of arsenic acid, existing in this residue, would be at once discovered, by its remaining fixed at the temperature which a spirit-lamp is capable of affording. 3. The dried residue, obtained in the manner just stated, is in no respect deliquescent; while the arsenic acid speedily passes to the liquid state, when exposed to air. 4. The nitrate of silver gives no precipitate with the clear solution of arsenious acid after boiling and filtration, (when the two solutions are in a highly concentrated state, there is a milkiness produced;) while this re-agent throws down the smallest quantity of arsenic acid, if mixed with arsenious acid, of a *brick-red* colour. Arsenious acid, then, does not undergo, during ebullition, any chemical change, by which its degree of acidification becomes altered. We know that the effect of heat, in rendering solids more soluble in water, is due to this agent increasing the force of affinity between the

\* Brande's Manual of Chemistry, Vol. II. 114.



solid and the liquid. With some bodies—and arsenious acid is a direct instance of this—it is necessary that the heat *should be for some time applied*, in order that the affinity of water for this body should be raised to its maximum degree.

Before proceeding to detail my own experiments on the solubility of this poison in water, I shall quote the observations of other experimentalists; reducing them, for the sake of comparison, to one standard; and always presuming, unless the contrary be expressed, that a thousand parts of water have been used\*.

*Klaproth.*

This chemist was one of the first who experimented on the subject: according to him,

1000 parts of water, at 60°	dissolve of arsenious acid	2. 5	or $\frac{1}{400}$ .
1000 . . . . .	212° . . . . .	77.75	or $\frac{1}{13}$ .

By this, it appears that arsenious acid is thirty times more soluble in boiling, than in temperate water. Klaproth further observed, that one thousand parts of the boiling solution, after having stood three days, retained only thirty parts of arsenious acid, about  $\frac{1}{33}$  — or twelve times as much, as was taken up by water *at the same temperature*, without boiling†.

*Bucholz.*

Bucholz confirmed, in some respects, Klaproth's experiments. He was also the first chemist who described a difference in the solubility of the varieties of arsenious acid; and he found that, *cæteris paribus*, more arsenic, proportionally, was dissolved, when a large quantity was introduced into water at once, than when a small quantity only was present. This experimentalist determined, with regard to the solubility of arsenious acid, that,

1000 parts of water, at 50°	dissolve . .	15	or $\frac{1}{66}$ .
1000 . . . . .	at 65° . . . . .	20	or $\frac{1}{50}$ .
1000 . . . . .	at 140° . . . . .	45.4	or $\frac{1}{22}$ .
1000 . . . . .	at 212° . . . . .	81	or $\frac{1}{13}$ .

The result, with regard to boiling water, differs but little from that obtained by Klaproth: but there is a material difference relative to the solvent power of temperate water,

\* 1000 gr. of water correspond to two fluid ounces of the measure here used; but two fluid ounces of the new pharmacopœial measure are equal to 875 gr.

† Beiträge zur chemischen Kenntniss der Mineralkörper. *Berlin*, 1815.



which can only be partially explained away, by supposing that Bucholz is speaking of the quantity of arsenic retained at that temperature, after the liquid has been boiled\*.

*Fischer.*

Fischer proved how much ambiguity was connected with this subject, by demonstrating, that, even when the quantities of arsenic and water were taken in the ratio of the solubility of the former, or when even a less proportion of arsenic had been taken, it was not always possible to effect a perfect solution. He states, that at ordinary temperatures he could not procure a stronger solution, than that indicated by the respective quantities below. In digesting one part of arsenious acid in eighty parts of water, he found that the solvent did not take up more than one ninetieth of its weight †. Thus,

80 parts water, at 60°, dissolve . . .	$\frac{1}{90}$
160 . . . . .	$\frac{1}{180}$
240 . . . . .	$\frac{1}{270}$
1000 . . . . .	$\frac{1}{1200}$

*Remer.*

This writer remarks, that most experimentalists have found arsenic to be soluble in eighty parts of cold, and in fifteen parts of boiling water. He has, however, brought together the results of several observers, in order to shew the discrepancy which exists ‡:—

Hahnemann found that 1000 parts water, at 96°, dissolved 10.4 or	$\frac{1}{96}$ .
Spielmann . . . . . 50° . . .	10.4 or $\frac{1}{96}$ .
De la Métherie . . . . . 212° . . .	41.6 or $\frac{1}{24}$ .
Beaumé . . . . . 212° . . .	15.6 or $\frac{1}{64}$ .
Vogel . . . . . 212° . . .	16.6 or $\frac{1}{60}$ .
Navier . . . . . 212° . . .	12.5 or $\frac{1}{80}$ .
Nasse . . . . . 212° . . .	5. or $\frac{1}{200}$ .

In one of the most recent German works on Chemistry, Professor Von Jacquin of Vienna merely quotes the experiments of Guibourt, which will be hereafter given §.

\* Remer's *Polizeilich-gerichtlichen Chemie*, 2<sup>ter</sup> Band, 715.

† Berzelius *Traité de Chimie*, T. II. p. 429.

‡ *Op. cit. loc. cit.*

§ *Grundzüge der allgemeinen und medicinischen Chemie*, 1<sup>ter</sup> Band, 271. *Wien*, 1836.



*La Grange* \*.

1000 parts water, at 60°, dissolve . . .	41.6 or $\frac{1}{24}$ .
1000 . . . . . 212° . . . . .	66.6 or $\frac{1}{15}$ .

*Berzelius*.

Berzelius's remarks upon this subject are very few. He somewhat vaguely states, that when a solution of arsenious acid is about to crystallize, it contains from  $\frac{1}{12}$  to  $\frac{1}{13}$  of its weight of arsenic dissolved. According to this, therefore,

1000 parts water, cooled from 212°, dissolve 80 parts.

This distinguished chemist chiefly relies upon the experiments of Guibourt †.

*Dumas*

states the observations of Guibourt

*Despretz*

gives, for the solubility of arsenious acid in cold water,  $\frac{1}{26}$ ; and adds, it is much more soluble in hot water. According to this,

1000 parts water, at 60°, dissolve 50 parts, or  $\frac{1}{20}$ .

Although it is not stated, it is possible that this chemist is speaking of a solution which has been boiled and allowed to cool. It has been already observed, that cold water will not dissolve a quantity, which water cooled from long boiling with arsenious acid will readily retain §.

Orfila || and Devergie ¶ quote the experiments of Guibourt; and Bouchardat \*\* quotes the remarks of Berzelius.

Thénard, after having stated Guibourt's experiments, observes, that a solution of arsenic is easily procured by boiling it in water. On cooling, a portion is precipitated

\* Henry's Elements of Experimental Chemistry, Vol. II. 51.

† *Traité de Chimie*, II. 430.

‡ *Traité de Chimie, appliquée aux Arts*, I. 355.

§ *Elémens de Chimie*, I. 252.

|| *Elémens de Chimie*, I. 559.

¶ *Médecine Légale*, II. 716.

\*\* *Cours de Chimie Elémentaire*, I. 193.



in *tetrahedral* crystals, nearly opaque. The solution, according to him, has no action on vegetable blue colours\*.

This last observation must have been made from the employment of a kind of litmus paper, not very susceptible of slight acid re-action.

*Guibourt.*

The results obtained by this experimentalist are detailed in most works on Chemistry and Medical Jurisprudence: a very complete account of them will be found in the treatises of Berzelius and Dumas. Guibourt noticed a difference in the solubility of the opaque and transparent varieties of arsenious acid, as also a difference in their specific gravities. With regard to the latter point, he found the specific gravity of the opaque kind (common arsenic) to be 3.699; while that of the transparent variety was 3.7385. He states, that the opaque is much more soluble than the transparent variety;—that the latter alone has an acid reaction in solution; while the former possesses the property of rendering reddened litmus paper, blue; a circumstance which he considered to be owing to its containing ammonia, although he could not detect that alkali in it. His results, with respect to the solubility of the opaque variety of arsenic, are as follows:—

1000 parts water, at 60°, dissolve . . . . .	12.5 or $\frac{1}{80}$ .
1000 . . . . . 212° . . . . .	114.7 or $\frac{1}{8}$ .
1000 . . . . . 212° cooled to 60°, retain	29. or $\frac{1}{34}$ .

So far as I have been able to ascertain, no English chemist has yet made a series of experiments on this subject.

Mr. Brande †, Dr. Paris ‡, and Dr. A. T. Thompson §, give

\* *Traité de Chimie*, II. 361. Thénard describes the crystals as opaque; but this must have arisen from his having confined his observations to the semi-crystalline mass, which is rapidly deposited from a boiling concentrated solution, on its beginning to cool. With regard to the form of the crystals, Thénard, and a few other chemists, state them to be tetrahedral: but by far the greater number of experimentalists describe them as octohedral. In examining the crystalline deposit with high and common magnifying powers, the crystals have always appeared to me to have the form of octohedra. Brande states, that both octohedral and tetrahedral crystals are deposited.

† *Manual of Chemistry*, II. 114.

‡ *Medical Jurisprudence*, II. 215.

§ *London Dispensatory*, 171.



the results of Klaproth. Dr. Henry\*, those of Bucholz and La Grange. Drs. Turner† and Christison‡, those of Klaproth and Guibourt; while Dr. Ure§ takes the experiments of Guibourt for temperate water, and those of Klaproth for water at 212°. In another part of his paper, however, this latter chemist says, that,

1000 parts water, at 60°, dissolve . . .	3.	or $\frac{1}{333}$ .
1000 . . . . . 212° . . . . .	72.	or $\frac{1}{14}$ nearly.
1000 . . . . . 212° cooled, retain 30.		or $\frac{1}{33}$ .

These results differ but slightly from those of Klaproth.

### Summary of Results.

#### 1.

One thousand parts of temperate water dissolve, of their weight of arsenious acid, according to—

<i>Despretz,</i>	<i>La Grange,</i>	<i>Bucholz,</i>	<i>Guibourt,</i>	<i>Hahnemann,</i>
$\frac{1}{20}$	$\frac{1}{20}$	$\frac{1}{50}$	$\frac{1}{80}$	$\frac{1}{96}$
	<i>Spielmann,</i>	<i>Ure,</i>	<i>Klaproth,</i>	<i>Fischer,</i>
	$\frac{1}{96}$	$\frac{1}{333}$	$\frac{1}{400}$	$\frac{1}{1200}$

The results of some of these experimentalists were probably obtained by boiling the water on arsenious acid, allowing the solution to cool, and then estimating the quantity dissolved; while those of others were probably deduced from the actual digestion of the poison in cold water. It is perhaps in this way, that we may reconcile the enormous difference between the statements of Despretz and Fischer; the former making arsenic sixty times more soluble than the latter.

#### 2.

One thousand parts of boiling water dissolve, of their weight of arsenious acid, according to

<i>Guibourt,</i>	<i>Bucholz,</i>	<i>Klaproth,</i>	<i>Ure,</i>	<i>La Grange,</i>	<i>De la Métherie,</i>
$\frac{1}{8}$	$\frac{1}{12}$	$\frac{1}{13}$	$\frac{1}{14}$	$\frac{1}{15}$	$\frac{1}{24}$
	<i>Vogel,</i>	<i>Beaumé,</i>	<i>Navier,</i>	<i>Nasse,</i>	
	$\frac{1}{60}$	$\frac{1}{64}$	$\frac{1}{80}$	$\frac{1}{200}$ .	

The differences in this table may perhaps be explained, by supposing that a heat of 212° may have been applied for

\* Elements of Chemistry, II. 51.    † Elements of Chemistry, 531.

‡ Treatise on Poisons, 177.    § Chemical Dictionary—Acid Arsenious.



different periods of time; as also, that specimens of arsenious acid, probably varying considerably in their degree of ~~solu-~~ *purity* ~~bility~~, may have been employed.

It was the discovery of these very different results, respecting the solubility of arsenic by men of well-known authority as chemists, that first induced me to endeavour to ascertain which statement was borne out by experiment.

In relation to specific gravity, I found that of a mass of arsenious acid which had been kept four years, and was perfectly *opaque*—presenting, when fractured, a slightly crystalline structure—to be 3.529. Having procured a recently-prepared specimen, perfectly *transparent*, but of a slightly-yellowish tinge, I tried its specific gravity, and found it to be 3.798.

Arsenious acid, it may be remarked, is soluble in water, oils, and alcohol. Water is its most common solvent: and it is, therefore, of its solubility in this menstruum that I shall first proceed to speak. The water employed in the experiments mentioned below, was the common water of the Hospital; which is the Thames water, filtered. It contains, comparatively, little foreign matter. A given measure of this water weighed 752.7 gr.; while the same measure of recently distilled water weighed 752 gr. Its specific gravity will, therefore, be 1.00093. Distilled water was not employed in these experiments, since I had a medico-legal object in view: in no case of criminal poisoning, is it likely that distilled water will be used by the suicide or murderer. In the course of many experiments, however, there did not appear to me to be the least appreciable difference in the solvent power of water over arsenious acid, whether distilled, or common river-water filtered, was employed.

#### EXP. 1.

Twenty grains of opaque arsenious acid, reduced to a fine powder, were placed in a clean glass vessel, and eight fluid ounces of *boiling water* were poured on. A portion of the powder collected into small lumps, which floated, and, even after violent agitation, adhered to the sides of the vessel; while another portion sank to the bottom. The vessel remained covered *seventy-two hours*; the contents being



frequently agitated, to ensure perfect contact and admixture. The water was then carefully filtered, and the filter dried. The residuary undissolved powder weighed 10.46 gr. Therefore,

$$20 - 10.46 = 9.54 \text{ gr. dissolved by } f\bar{3} \text{ viij. or } (500 \times 8) \text{ 4000 gr. water,}$$

$$\text{and } 4000 \div 9.54 = 419; \text{ as also, } 9.54 \div 4 = 2.385 \text{ gr.}$$

Hence,

$$1000 \text{ parts water at } 212^\circ, \text{ dissolved } \dots \dots 2.385 \text{ pts. or } \frac{1}{119}.$$

### EXP. 2.

A similar experiment was performed; and the residuary powder obtained on the filter, weighed 9.27 gr. Therefore,

$$20 - 9.27 = 10.73, \text{ dissolved by } f\bar{3} \text{ viij. or } (500 \times 8) \text{ 4000 gr. water;}$$

$$\text{and } 4000 \div 10.73 = 372; \text{ as also, } 10.73 \div 4 = 2.6825 \text{ gr.}$$

Hence,

$$1000 \text{ parts water at } 212^\circ, \text{ dissolved } \dots \dots 2.6825 \text{ gr. or } \frac{1}{372}.$$

Twenty-five grains of each of these solutions, filtered, were now evaporated to dryness, at a low temperature; and .06 gr. were obtained as the mean weight of the residue of several successive evaporations of Exp. 1.; and .07 as the mean for Exp. 2; results which come as near to the proportions above ascertained, as could be well expected, considering that distilled water was not employed.

The mean of the Exps. 1 and 2 will be the following: 1000 gr. of boiling water, allowed to cool, and remain 72 hours (with frequent agitation), on 20 gr. arsenious acid, will dissolve 2.53 gr., or about  $\frac{1}{395}$  of their weight.

### EXP. 3.

Two ounces of water were kept *gently* boiling for *an hour*, the waste by evaporation being made up; and while boiling, finely powdered arsenious acid, in small quantities at a time, was gradually added, from a previously weighed quantity. No further portion was added, until that which had been previously added, was dissolved. The result was, that,

$$1000 \text{ gr. of water (} f\bar{3} \text{ij.) dissolved } \dots \dots 31.5 \text{ gr. or } \frac{1}{32}.$$

This solution was placed aside for 72 hours; and at the end of that time, it was found to have deposited in brown octohedral crystals, 14.5 gr.; and  $31.5 - 14.5 = 17$  gr. Hence, 1000 grains water ( $f\bar{3} \text{ij.}$ ) held dissolved, on perfect cooling, 17 grains, or  $\frac{1}{58}$ .

Twenty-five grains of the cold solution were slowly evaporated to dryness; and the mean of several evaporations



gave .41 gr. as a residue, which is a little below the proportion as above ascertained.

## EXP. 4.

Two ounces of water were kept *violently* boiling for an hour, the waste by evaporation being made up; and arsenious acid was gradually added from a weighed quantity, as before. It was then found, that

1000 gr. of water had dissolved . . . . 46.3 or  $\frac{1}{21}$ .

From this solution, there were deposited in crystals, after 72 hours, 21.6 gr. and  $46.3 - 21.6 = 24.7$  gr.

1000 gr. water held dissolved, on perfect cooling, 24.7 gr. or  $\frac{1}{40}$ .

Twenty-five grains of the cold solution, evaporated, left .55 gr., rather less than the proportion deduced from the weight of the undissolved residue.

## EXP. 5.

In this experiment, four ounces of water were kept *violently* boiling for *half an hour*; arsenious acid being added, as before, from a weighed quantity. 89 gr. were dissolved. Hence,

1000 gr. water dissolved ( $89 \div 2$ ) . . . . 44.5 gr. or about  $\frac{1}{22}$ .

The mean of Exps. 3, 4, and 5, will be the following:

1000 gr. of boiling water dissolve . . . . 40.76 gr. or  $\frac{1}{24}$ .

The *rapidity* of boiling will make a considerable difference in the quantity dissolved, as will be seen on comparing Exps. 3 and 4. Indeed, water which boils violently will dissolve as much arsenic in half an hour, as water kept gently boiling will dissolve in an hour. All other circumstances being equal, the *length of time* during which the boiling continues will assuredly make a difference in the quantity of the poison taken up.

## EXP. 6.

Arsenious acid, in fine powder, was boiled for several hours to saturation, in two separate quantities of water. These solutions were, after filtration, kept apart; and allowed to stand for *six months*, in well-stoppered bottles. A very abundant crop of octohedral crystals, lining the whole interior of the bottle, was deposited in each case. After this



lapse of time, twenty-five grains of the filtered solution (A) were evaporated to dryness; and the solid residue weighed .7 grains. Hence,

1000 gr. of the solution contained  $40 \times .7 = 28$  gr. or  $\frac{1}{35}$ .

Twenty-five grains of (B) left, as a solid residue, .6 gr. Hence,

1000 gr. held dissolved  $40 \times .6 = 24$  gr. or nearly  $\frac{1}{42}$ .

The mean of these two experiments will be as follows:

1000 gr. of a saturated solution, after six months standing, held dissolved, 26 gr. or  $\frac{1}{38}$ .

In closing these remarks on the solubility of arsenic in *boiling* water, I shall subjoin the results of some experiments on the recently-prepared, or transparent, arsenious acid: and I am the more desirous of doing this, since the statements of Guibourt, relative to the transparent being *less soluble* than the opaque variety, are not supported by them. In a medico-legal point of view, the question of a difference of solubility in these varieties of arsenious acid is not, perhaps, of much importance; since the pure transparent arsenic is with difficulty obtainable, and is rarely sold by druggists.

#### EXP. 7.

A perfectly *transparent* and recently-prepared mass of arsenious acid was finely pulverized; and a weighed quantity of the powder was gradually added to two fluid ounces of water, kept *violently* boiling for *an hour*, the waste by evaporation being made up. Forty-six grains were dissolved.

1000 gr. water dissolved . . . . 46 gr. or <sup>about</sup> ~~nearly~~  $\frac{1}{21}$ .

From this solution there were deposited in crystals, after 48 hours, 27.3 gr. and  $46 - 27.3 = 18.7$ .

1000 gr. water held dissolved, on perfect cooling . . . . 18.7 gr. or  $\frac{1}{53}$ .

#### EXP. 8.

In this experiment, four ounces of water were kept boiling for *an hour*, and pulverized *transparent* arsenic was gradually added. There were dissolved 95.1 gr. Hence,

1000 gr. water dissolved  $(95.1 \div 2)$  . . . . 47.55, or  $\frac{1}{21}$ .

From this solution there were deposited, in crystals, after 48 hours, 68.3 gr. Hence,  $95.1 - 68.3 = 26.8 \div 2 = 13.4$  gr. 8.2 gr

1000 grains of water, held dissolved, on perfect cooling, 13.4 grains, or  $\frac{1}{74}$ .



The results of these experiments shew, that there is certainly *not always* the difference in the degree of solubility of these two varieties of arsenic, which M. Guibourt suspected; and which, upon his authority, is to be found stated in many chemical and medico-legal works. The quantity dissolved of either variety, under similar circumstances, according to these experiments, may be regarded, for all practical purposes, as the same.

In cases of criminal poisoning, it occasionally happens that *cold* or *temperate water* is used as the solvent for this poison, and a witness is expected to state the degree of its solvent powers. The consideration of this, led to the performance of the following additional experiments.

EXP. 9.

Eight fluid ounces of *temperate* water were poured upon twenty grains of the pulverized opaque arsenic, in a clean glass vessel. The powder immediately collected in lumps, which partly floated, and partly remained at the bottom of the vessel. A slight film of powder formed by repulsion on the surface of the water. The vessel was covered over, and allowed to stand 72 hours, having been first well agitated. The liquid was filtered, and the filter carefully dried. The residuary undissolved powder weighed 16 gr. And,  $20 - 16 = 4$ . Hence,

1000 gr. water (f $\bar{z}$ ij.), dissolved . . . . 1 gr. or  $\frac{1}{1000}$ .

Twenty-five grains of the filtered solution, evaporated, left .03 gr.; which is nearly equal to the proportion above determined from the undissolved residue.

EXP. 10.

Another experiment was performed, which only differed from the preceding in the circumstance of the vessel having been *frequently agitated*. The undissolved powder left on the filter, after drying, weighed 11.5 gr., and  $20 - 11.5 = 8.5$  gr. Hence,

1000 gr. water (f $\bar{z}$ ij.), dissolved . . . . ~~(0.51)~~ 2.125 or  $\frac{1}{470}$ . 8.5  $\div$  4 =

Twenty-five grains of the filtered solution were evaporated; and left not quite .06 gr., a proportion rather larger than that above deduced.

*8.5  $\div$  4 = 2.125*



It follows, from these experiments, that very nearly the same quantity of arsenious acid is taken up by hot water allowed to cool, and cold water poured on this substance in powder; provided the vessel, containing the cold water, be frequently agitated. They also shew the necessity for a continued application of heat, in order that the poison should be dissolved in any considerable quantity. It is a curious, and hitherto an unexplained fact, that water should retain so much more of this poison, as from ten to twenty times the quantity, when *perfectly cooled* from a boiling saturated solution, than it will take up at common temperatures without heat. It would seem to indicate, that heat must excite some permanently powerful affinity, between the particles of arsenious acid and water, which did not previously exist.

We see, then, that trivial circumstances may bring about material differences, in the results of experiments on the solubility of this poison;—a subject, which calls for the serious attention of medical jurists. Our legal authorities cannot stop to inquire into the causes of the differences among experimentalists. They expect that the witness, who is summoned before them to give professional evidence in a case of criminal poisoning, should be prepared to answer some such questions as the following:—

Is there any difference in the degree of solubility of the different varieties of arsenic?

To what degree is arsenic soluble in hot water?

To what degree does it become more soluble by long boiling?

What quantity is held dissolved, when a boiling solution has perfectly cooled?

To what degree is arsenic soluble in cold water?

The act of malice, on the part of a prisoner, is often to be inferred or disproved by the quantity of poison held in solution in a liquid: and an instance has occurred, within the last few years, in which a man was acquitted of the crime of a wilful attempt to poison, because the quantity dissolved was insufficient to cause serious consequences.



This, then, is a point to which a judicial inquiry may tend, in a case of "attempted poisoning"; which, it may be remarked, involves the same punishment by our law as the actual perpetration of murder by poisoning. The question put to a medical jurist may be:—Is the quantity of a solution of arsenic, which a party may have administered, sufficient to cause serious symptoms, or to bring about a fatal result?

In the case of Nairne and Ogilvie\*, who were tried at Edinburgh, in 1765, for murder by poisoning, the medical witness, Dr. Scott, who appeared in the defence, was particularly questioned, by the prisoner's counsel, respecting the solubility of arsenic. He is stated to have said, "that he has made sundry experiments on arsenic—that he knows *it will not dissolve in warm water*—and that the common arsenic, that is to be met with in the shops, although pretty finely powdered, *falls to the bottom* of a vessel with water, almost *instantaneously*." Dr. Smith, in commenting upon this evidence, observes: "We are too much addicted, even now, to talk of arsenic, as if it were soluble with the same readiness as sugar†." But even admitting the existence of exaggerated views on the solubility of the poison, this cannot excuse the very incorrect statement in the above evidence; namely, that arsenic is insoluble in warm water. Dr. Scott also affirmed, what experiment will shew to be a popular error, namely, that the pulverized poison almost instantaneously sinks to the bottom of a vessel of water: (*vide* Exp. 1 and 9). This error, it is of more importance to notice than may at first sight appear, as I shall presently endeavour to shew. Arsenious acid, it is true, is more than three and a half times heavier than water, but, like magnesia, and other finely-powdered substances which are of greater specific gravity than that liquid, a portion of it will float from repulsion; and, indeed, it is somewhat difficult to cause the powder entirely to sink. This fact was long ago observed by Dr. Addington, who gave evidence, in 1752, on the trial of Miss Blandy for

\* State Trials.

† Analysis of Medical Evidence: Appendix.



poisoning her father with arsenic\*. In his evidence respecting the nature of the powder (arsenic) which he had been required to examine, he states: "Part of it swims on the surface of cold water, like a pale sulphureous film; but the greater part sinks to the bottom, and remains there undissolved." The floating or sinking of this poison becomes a question of importance, when a quantity of it has been mixed with a large quantity of water, and the upper stratum only of the fluid has been swallowed. In the case of Bodle, who was lately tried for the murder of his grandfather by poisoning him with arsenic, the defence was partly made to rest upon a point of this nature†. It was alleged against the prisoner, that he had put arsenic in powder into a large kettle of water, which had been placed to boil on the fire, for the purpose of making coffee for the deceased's breakfast. The prisoner, in his defence, which, I understand, was written for him by an accomplished barrister—and which indeed bears about it marks of the greatest ability and ingenuity—was made to say: "I am informed, that to have put arsenic into the kettle, would have been a very doubtful mode of administering it; and that its weight would have caused the greater portion of it to *sink to the bottom of the water*. It was stated, indeed, before the coroner, that it was only upon the presumption that the boiling of the water would cause the arsenic to rise from the bottom, that the possibility of arsenic being poured from the kettle was admitted. But although, in making tea, the water is used in a boiling state, it is not necessarily so in preparing coffee. The coffee has again to be boiled; and therefore it is of no importance that boiling water should be poured on it. In point of fact, boiling water is seldom so used." In relation to this part of the prisoner's defence, however, I may observe, that so far from a doubtful, it would have been a very *certain* mode of administering the poison. A portion of arsenic, notwithstanding its supposed weight—certainly sufficient when poured off to destroy life—might have floated, whether the water were hot or cold. The possibility of the poison having been poured from the kettle, being made to rest

\* State Trials.

† Home Circuit, Maidstone, December 1833.



upon the presumption that the boiling of the water would alone cause the arsenic to rise from the bottom, furnishes an appropriate illustration of the danger of attempting to prove too much. If the water had boiled, so as to have produced this effect, then it becomes probable that sufficient poison would have been dissolved, to give rise to fatal consequences. But in the defence, it is attempted to be shewn, that the water did not boil, from the fact of boiling water not being commonly required for the making of coffee. Here, then, the inference would be, not that all the poison would have sunk by its weight, but that sufficient would have floated, and have remained on the upper stratum of water, to allow of a fatal dose being poured off. There was no evidence to shew that the poison, in this case, was administered through the medium of water in the kettle; but it appears to me that the reasons assigned in the defence, for its not having been so administered, are, medically speaking, wholly unfounded.

It very commonly happens, that those who take, or criminally administer, arsenic, mix the substance loosely with water, and swallow it in this state. This was the manner in which it was taken in the two fatal cases reported. In some instances, however, murderers display great diabolical ingenuity. A case was tried at Mayence, in March 1835, in which the evidence clearly proved, that the prisoners had poisoned the deceased and several persons previously, by administering arsenic in a saturated solution in water. One of them confessed that she had boiled the poison in water, allowed it to cool, filtered the solution, and then administered it, by small quantities at a time, in wine, milk, gruel and other liquids. On one of these occasions, the poison operated with fatal rapidity—a circumstance which led to the detection of the crime. As might have been anticipated, not a trace of arsenic could be discovered, on analyzing the contents of the viscera of those who had perished in this manner.

The solubility of arsenious acid, in liquids containing organic matter, sometimes forms a subject of inquiry in our courts of law. A suicide generally selects *water*, as the menstruum for dissolving the poison;—a murderer, in most



cases, selects some liquid article of food, probably for the purpose of more effectually lulling suspicion, by concealing the *supposed* taste of the poison\*. Tea, coffee, brandy, or gruel, is thus very often made a vehicle for the administration of arsenic. No certain opinion can be expressed respecting the solvent powers of gruel, broth, or liquids of a similarly viscid nature. These last-named menstrua *mechanically suspend* the particles of arsenic, exactly in proportion to their viscosity; and thus a very powerful dose of poison may be administered in a small quantity of liquid. But few experiments have been performed on the solubility of arsenic in organic liquids. Hahnemann found that water impregnated with mucus or milk dissolved the poison with difficulty. Dr. Christison states generally, that the solubility of arsenic is much impaired by the presence of organic matter. According to this gentleman, a cup of tea left beside the fire, at a temperature of  $200^{\circ}$ , for half an hour, upon two grains of arsenic, did not entirely dissolve even that small quantity†. This, however, gives us but a very imperfect notion of the solvent power of the liquid, since the quantity of tea which the cup contained, is not stated. In consequence of finding no satisfactory statements on this subject, the following experiments were performed.

#### Exp. 11.

Eight fluid ounces of *tea, with milk and sugar*, at a temperature of about  $170^{\circ}$ , were poured on twenty grains of opaque arsenious acid in fine powder. The mixture became instantly turbid, and the greater part of the poison sank to the bottom of the vessel. The tea was well agitated, and allowed to remain, with the vessel covered, seventy-two hours. It was then filtered—a process which occupied a

\* It is generally imagined that arsenic has an acrid, caustic taste: it is so stated in numerous chemical and medico-legal works; but it is pretty certain, that arsenic, which possesses such a taste, cannot be pure. I have not been able to perceive any other than a faintly sweetish taste, as described by Christison; and the annals of criminal poisoning plainly shew that, in nine cases out of ten, the poison has been swallowed without producing any peculiar sensation on the tongue.

† On Poisons, p. 177.



whole day. The filter was well dried; and the undissolved powder left on it, separated and weighed. Allowing for the admixture of a small quantity of foreign matter, the undissolved arsenic weighed, as nearly as could be estimated, 15.5 gr. Hence  $20 - 15.5 = 4.5$  gr. dissolved by eight ounces of tea, and  $(4.5 \div 8 = .5625)$  rather more than  $\frac{1}{2}$  gr. to each ounce of the liquid.

For very obvious reasons, no comparison of solubility, from the *weight* of the solvent, can here be instituted. We can only judge by employing a measured quantity of the solvent: and it is this standard, indeed, which it is alone requisite to follow, for practical purposes.

#### EXP. 12.

Eight ounces of *coffee, with milk and sugar*, at a temperature of  $160^{\circ}$ , were poured on twenty grains of arsenic. The mixture was well agitated, and allowed to remain covered seventy-two hours. It was then filtered, but the liquid was more than four days in passing through; and the large quantity of organic matter, left on the filter, completely obscured the undissolved arsenic. The coffee in this case, when filtered, was so weakly impregnated with arsenic, that half an ounce of it, acidulated with acetic acid, and treated with sulphuretted hydrogen gas for half an hour, gave no arsenical re-action whatever. The hydrogen test indicated the presence of arsenic in very minute proportion.

#### EXP. 13.

Eight ounces of *coffee*, boiled and clarified, but without milk and sugar, were poured, at a temperature of  $170^{\circ}$ , on twenty grains of the poison. The mixture was frequently agitated, allowed to stand seventy-two hours, and then filtered. The filter was dried; the residuary powder found on it—which was but little impregnated with organic matter—was then placed in a balance, and found to weigh, making full allowance for combined impurity, 11 gr. Hence  $20 - 11 = 9$  gr. dissolved by eight ounces of coffee; or  $(9 \div 8 = 1.125$  gr.) rather more than a grain to each ounce of the solvent.



## EXP. 14.

Two ounces of common *brandy* were poured on twenty grains of arsenious acid. Not a particle of the powder floated, but the whole remained at the bottom of the vessel. The mixture was frequently agitated during seventy-two hours. It was then filtered, and the filter slowly dried. The undissolved residuary powder, allowing for a slight impregnation with organic matter, weighed 17.3 gr. Hence  $20 - 17.3 = 2.7$  gr. dissolved by two ounces of brandy; or  $(2.7 \div 2 = 1.35)$  about one grain and three-tenths to the ounce\*.

## EXP. 15.

Eight ounces of cold *porter* were poured on twenty grains of arsenious acid. The mixture was allowed to remain for the same period as in the preceding experiments, with frequent agitation: it was then filtered. The undissolved residuary powder weighed 16 gr. Hence  $20 - 16 = 4$  gr. dissolved by eight ounces of porter; or  $(4 \div 8 = .5)$  one half grain to each ounce of solvent.

The above experiments were repeated several times, without any material difference in the results.

From the whole of these experiments, I may perhaps be permitted to draw the following conclusions:—

1. That hot water, allowed to cool from  $212^{\circ}$  on this poison, dissolves less than  $\frac{1}{400}$  of its weight, or about  $1\frac{1}{4}$  grains to each ounce of water.

2. That water, boiled for an hour on this substance, dissolves  $\frac{1}{24}$  of its weight, or rather more than 20 grains to each ounce.

3. That this water (2), on perfect cooling, does not retain more than about  $\frac{1}{40}$  of its weight, or 12 grains to the ounce.

4. That water boiled on arsenious acid to the most perfect

\* According to Mr. Brande (*loc. cit.*), 1000 parts of *alcohol* at  $60^{\circ}$  dissolve 12.5 gr. arsenious acid, or about  $\frac{1}{80}$ . I have found that two fluid ounces of cold alcohol, digested for ten days on 20 grs. of arsenious acid, dissolved 4.5 grs. The organic matter contained in brandy, may interfere with the solvent powers of the alcohol.



state of saturation, after having stood six months, holds dissolved about  $\frac{1}{38}$  of its weight, or 13 grains to the ounce.

5. That there is no observable difference in the solubility of the *transparent* and *opaque* varieties of arsenious acid.

6. That water at ordinary temperatures will dissolve from about  $\frac{1}{1000}$  to  $\frac{1}{500}$  of its weight, or from  $\frac{1}{2}$  grain to 1 grain to each ounce of solvent, according to circumstances.

7. That the presence of *organic matter* in a liquid is an obstacle to the solution of this poison. Thus hot tea, and cold porter, will not take up more than about  $\frac{1}{2}$  grain to the ounce; while hot coffee and cold brandy, do not dissolve more than a grain to the ounce.

There are two points of practical importance, which these experiments suggest in relation to the analysis of organic liquids suspected to contain arsenic, especially when the liquids have been obtained from the stomach or intestines: 1st, To dilute the liquid considerably with water; and, 2dly, to boil the liquid thus diluted for at least two or three hours. By attending to the first point, we in a great degree destroy the effect of organic matter in impairing the solubility of the poison; and by the second, we insure the solution of every portion of poison which may be present.



state of solution after having stood six months. Solids dissolved about 1/2 of its weight or 15 grains in the ether. That there is no appreciable difference in the solubility of the compound and other varieties of arsenious acid. That water at ordinary temperatures will dissolve from about 1/2 to 1 of its weight or from 1/2 grain to 1 grain in each ounce of ether according to circumstances. That the presence of organic matter in a liquid is an obstacle to the solution of the poison. Thus hot tea and cold water will not take up more than about 1/2 grain in the ounce, while hot coffee and cold brandy do not dissolve more than a grain in the ounce.

There are two points of practical importance which these experiments suggest in relation to the analysis of organic liquids and tests to certain arsenic, especially when the liquid has been obtained from the stomach or intestines: 1. To dilute the liquid considerably with water, and allow to boil the liquid that diluted for at least two or three hours. By referring to the first point, we in a great degree destroy the effect of organic matter in impeding the solubility of the poison; and by the second, we insure the solution of every portion of poison which may be present.