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A Guide to the Detection of Poisons, Examination of Tea, Stains, Etc.

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Legal Chemistry.

A GUIDE TO THE DETECTION OF POISONS, EXAMINATION OF TEA, STAINS, ETC., AS APPLIED TO CHEMICAL JURISPRUDENCE.

TRANSLATED WITH ADDITIONS FROM THE FRENCH OF A. NAQUET, *Professor to the Faculty of Medicine of Paris*. BY J. P. BATTERSHALL, Nat. Sc. D., F.C.S. *SECOND EDITION, REVISED, WITH ADDITIONS.*

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Transcriber's Note: Obvious printer errors have been corrected. A list of all other changes can be found at the [end of the document](#). In the Appendix of the book, only the most obvious errors of punctuation were remedied.

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PREFACE.

The importance of exact chemical analysis in a great variety of cases which come before the courts is now fully recognized, and the translation of this excellent little book on Legal Chemistry, by one of the most distinguished French Chemists, will be appreciated by a large class of American readers who are not able to consult the original. While it is to be regretted that the author has not presented a much more complete work, there is an advantage in the compact form of this treatise which compensates, in some degree, for its brevity.

The translator has greatly increased the value of the book by a few additions and his copious index, and especially by the lists of works and memoirs which he has appended; and while he could have further increased its value by additions from other authors, we recognize the weight of the considerations which induced him to present it in the form given to it by the author. Some chapters will have very little

value in this country at this day, but the translator could not, with propriety, omit anything contained in the original.

C. F. Chandler.

PREFACE TO THE SECOND EDITION.

The principal change to note in this edition of the Legal Chemistry is the addition of a chapter on Tea and its Adulteration. The general interest at present evinced concerning this species of sophistication appeared to call for a simple and concise method of examination which would include the requisite tests without entering upon an exhaustive treatment of the subject. The translator's practical experience in the testing of tea at the United States Laboratory of this city has enabled him to make a few suggestions in this regard which, he trusts, may be of use to those interested in food-analysis. Numerous additions have also been made to the bibliographical appendix.

J. P. B.

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LEGAL CHEMISTRY.

The term Legal Chemistry is applied to that branch of the science which has for its office the solution of problems proposed in the interest of Justice. These most frequently relate to cases of poisoning. When the subject of the symptoms or anatomical lesions produced by the reception of a poison is under consideration, the services of a medical expert are resorted to; but when the presence or absence of a poison in the organs of a body, in the *egesta* of an invalid or elsewhere is to be demonstrated, recourse is had to the legal chemist. Investigations of this character require great practice in manipulation, and, however well the methods of analysis may be described in the works on the subject, there would be great danger of committing errors were the examination executed by an inexperienced person. The detection of poisons, although perhaps the most important, is not the only subject that may come within the province of the legal chemist; indeed, it would be somewhat difficult to define, *a priori*, the multitude of questions that might arise. In addition to cases of supposed poisoning, the following researches are most often required:

1. The examination of fire-arms.

2. The analysis of ashes, in cases where the destruction of a human body is suspected.

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3. The detection of alteration of writings, and of falsification of coins and precious alloys.

4. The analysis of alimentary substances.

5. The examination of stains produced by blood and by the spermatic fluid.

Each of these researches justly demands a more extended consideration than the limits of this work would permit. The several subjects will be treated as briefly as possible, and at the same time, so as to convey an exact idea of the methods employed, leaving to the expert the selection of the particular one adapted to the case under investigation. We will first mention the methods used in the search for toxic substances. The poisons employed for criminal purposes are sometimes met with in a free state, either in the stomach or intestines of the deceased person, or in the bottles discovered in the room of the criminal or the victim. Under these circumstances, it is only necessary to establish their identity by means of their chemical properties, as directed in the general treatises on chemistry, or by their botanical, or zoological character, in case a vegetable or animal poison, such as

cantharides, has been administered. Examinations of this class are extremely simple, the analysis of the substances found, confined to a few characteristic reactions, being a matter of no great difficulty. We will not here dwell longer upon this subject, inasmuch as the analytical methods used are identical with those employed in more complicated cases, with the sole difference that, instead of performing minute and laborious operations in order to extract the poisons from the organs in which they are contained, with a view of their subsequent identification, we proceed at once to establish their identity. The directions given in regard to complicated investigations apply, therefore, equally well to cases of a more simple nature. The detection of a poison

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mixed with the organic substances encountered in the stomach, or absorbed by, and intimately united with the tissues of the various organs is more difficult. If, however, other information than chemical can be obtained, indicating the poison supposed to be present, and the presence or absence of this one poison is the only thing to be determined, positive methods exist which admit of a speedy solution of the question. When, on the other hand, the chemical expert has not the advantage of extraneous information, but is simply asked,—whether the case be one of poisoning?—nothing being specified as to the nature of the poison used, the difficulty of his task is greatly increased. Up to the present time, the works on Toxicology have, it is true, given excellent special tests for the detection of particular poisons; but none have contained a reliable general method, which the chemical expert could use with the certainty of omitting nothing. Impressed with this need, we proposed, in 1859, in an inaugural dissertation then presented to the Faculty of Medicine, a general method, which, after some slight modifications, is now reproduced. The special methods which allow of the detection of various individual poisons will, however, first be indicated. In cases where the poison is mixed with organic matter, the latter must be removed as the first step in the investigation, as otherwise the reactions characteristic of the poison searched for would be obscured. When the poison itself is an organic substance, this separation is effected by processes modified according to the circumstances. If the detection or isolation of a metallic poison is to be accomplished, the most simple method consists in the destruction of the organic substances. The various methods for effecting this decomposition will now be described.

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I. METHODS OF DESTRUCTION OF THE ORGANIC SUBSTANCES. *BY MEANS OF NITRIC ACID.*

In order to destroy the organic matters by this process, a quantity of nitric acid equal to one and a half times the weight of the substances taken is heated in a porcelain evaporating dish, the amount of acid being increased to four or six times that of the organic substances if these comprise the brains or liver. As soon as the acid becomes warm, the suspected organs, which have previously been cut into pieces, are added in successive portions: the organs become rapidly disintegrated, brownish-red vapors being evolved. When all is brought into solution, the evaporation is completed and the carbonaceous residue obtained separated from

the dish and treated either with water, or with water acidulated with nitric acid, according to the nature of the poison supposed to be present.

Several objections to this method exist, the most serious of which is based upon the fact that the carbonaceous residue, containing, as it may, nitric acid, readily takes fire and may

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therefore be consumed, or projected from the vessel. This objection is a grave one, and is not always entirely removed by the continual stirring of the materials.

According to *M. Filhol*, the addition of 10 to 15 drops of sulphuric acid to the nitric acid taken obviates the difficulty; not having personally tested the question we cannot pronounce upon it. If it be the case, this process is an advantageous one, as it is not limited in its application, but can be used in the separation of all mineral poisons.

BY MEANS OF SULPHURIC ACID.

The organic matter to be decomposed is heated with about one-fifth of its weight of concentrated sulphuric acid, the complete solution of the materials being thus accomplished. The excess of acid is next removed by heating until a spongy carbonaceous mass remains. The further treatment of this residue depends upon the nature of the poison supposed to be present. If the sulphate of the suspected poison is a soluble and stable compound, the residue is directly treated with water; if, on the contrary, there is reason to think that the sulphate has suffered decomposition, the mass is taken up with dilute nitric acid; if, finally, the presence of arsenic is suspected, the residue is moistened with nitric acid, in order to convert this body into arsenic acid. The acid is afterwards removed by evaporation, the well pulverized residue boiled with distilled water, and the solution then filtered.

This method, when applied in the detection of arsenic, is objectionable in that the carbonaceous residue, in contact with sulphuric acid, almost invariably contains sulphurous acid, detected by means of permanganate of potassa. This acid, being reduced in the presence of hydrogen, would cause the formation of insoluble sulphide of arsenic, and in this way

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prevent the detection of small amounts of arsenic by the use of Marsh's apparatus.

M. Gaultier de Claubry, indeed, states that he has not been able to detect the presence of sulphurous acid in the carbonaceous residue; but one affirmative result would, in this case, outweigh twenty negative experiments. A further objection to this process consists in the fact that the materials to be destroyed almost always contain chlorides, which, in presence of sulphuric acid and an arsenical compound, might determine the formation of chloride of arsenic, a volatile body, and therefore one easily lost. This difficulty is doubtless of a less serious nature than the preceding, as the operation can be performed in a closed vessel provided with a receiver which admits of the condensation of the evolved vapors; but even then the process would be prolonged. The above method is still again objectionable on account of its too limited application, it being serviceable almost exclusively in cases where the poisoning has been caused by arsenic, for, if applied in other instances, a subsequent treatment would be necessary in order to redissolve the metal separated from its decomposed sulphate.

BY MEANS OF NITRATE OF POTASSA.

This method was formerly executed as follows: Nitrate of potassa was fused in a crucible, and the substances to be destroyed added in small portions to the fused mass. The organic matter soon acquired a pure white color; owing, however, to the imperfect admixture of the organic matter with the salt used for its decomposition, it was necessary to take a large excess of the latter.

The following process, suggested by *M. Orfila*, remedies this inconvenience: The organs are placed in an evaporating dish, together with one tenth of their weight of caustic potassa,

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and a quantity of water varying with the weight of the substances taken. An amount of nitrate of potassa equal to twice the weight of the organic matter is next added, and the mixture evaporated to dryness. The residue is then thrown by fragments into a Hessian crucible heated to redness, the portions first taken being allowed to become perfectly white before more is added.

Whichever process has been employed, the fused mass is decanted into a porcelain crucible, which has previously been heated in order to avoid danger of breakage. The portion remaining in the vessel is taken up by boiling with a small quantity of distilled water, and the solution so obtained likewise added to the crucible. The mass is then heated with sulphuric acid until all nitrous fumes are expelled, as these could give rise to an explosion, when, in the search for arsenic, the substance is introduced into Marsh's apparatus. As soon as the nitric acid is completely expelled, the liquid is allowed to cool; the greater portion of the sulphate of potassa formed now separating out in crystals. The fluid is next filtered and the crystalline salt remaining on the filter, washed, at first with a little distilled water, then with absolute alcohol, which is subsequently removed from the filtrate by boiling. This method is scarcely applicable otherwise than in the detection of arsenic, as in other instances the presence of a large amount of sulphate of potassa would be liable to affect the nicety of the reactions afterwards used. Its application, even in the search for arsenic, is not to be strongly recommended; on the contrary, the separation of the potassa salt by filtration is indispensable, as otherwise a double salt of zinc and potassium, which might be formed, being deposited upon the zinc used in Marsh's apparatus, would prevent the disengagement of hydrogen, and every chemist

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is too well aware of the difficulty of thoroughly washing a precipitate, not to fear the possible loss of arsenic by this operation.

BY MEANS OF POTASSA AND NITRATE OF LIME.

In this method the organic materials are heated with water and 10 to 15 per cent. of caustic potassa. As soon as disintegration is completed, nitrate of lime is added, and the mixture evaporated to dryness. A glowing coal is then placed upon the carbonaceous residue obtained: the mass, undergoing combustion, leaves a perfectly white residue. This residue dissolves in hydrochloric acid to a clear fluid which is then examined for poisons.

The above process possesses the undeniable advantage of completely destroying the organic substances, at the same time avoiding the introduction of sulphate of potassa, the presence of which impairs the usefulness of the preceding method; but

it necessitates the presence of numerous foreign bodies in the substance to be analysed, and this should be avoided. The *absolute purity* of reagents is not always to be attained, and the results of an analysis are the more certain, in proportion as they are less numerous and more easily purified.

BY MEANS OF POTASSA AND NITRIC ACID.

It has been proposed, instead of using nitrate of lime, to dissolve the organic matter in potassa and then saturate the fluid with nitric acid. This method is evidently more complicated than the simple treatment with nitrate of potassa, and possesses, moreover, no advantages over the latter process.

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BY MEANS OF CHLORATE OF POTASSA.

The organic materials are treated with an equal weight of pure hydrochloric acid, and water added, so as to form a clear pulp. This being accomplished, two grammes of chlorate of potassa are added to the mixture at intervals of about five minutes. The fluid is next filtered, and the insoluble residue remaining on the filter washed until the wash-water ceases to exhibit an acid reaction. The filtrate is then evaporated, an aqueous solution of sulphurous acid added, until the odor of this reagent remains distinctly perceptible, and the excess of the acid removed by boiling the solution for about an hour. The fluid is now adapted to further examination for arsenic, or other metallic poisons.

This method is one of the best in use, both chlorate of potassa and hydrochloric acid being reagents easily procured in a state of great purity; their use, however, is liable to the objection that they convert silver and lead into insoluble chlorides.

BY MEANS OF CHLORINE.

M. Jacquelain suggests, in the search for arsenic, the decomposition of the organic matters by means of a current of chlorine, and recommends the following process: The organic substances are bruised in a mortar and then macerated with water. The fluid so obtained, in which the organic matter is held suspended, is next placed in a flask into which a current of chlorine is passed until all the organic matter is deposited in colorless flakes on the bottom of the vessel. The flask is then well closed and allowed to stand for 24 hours, when the odor of the gas should still be perceptible. The fluid is now filtered, the filtrate concentrated by heating in a vessel which

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permits of the preservation of the volatile chloride of arsenic possibly present, and then examined for poisons.

This process fails to possess the degree of generality desirable, and presents the disadvantage of requiring considerable time for its execution.

BY MEANS OF AQUA REGIA.

This method is exceedingly simple: *Aqua regia* (a mixture of two parts of hydrochloric and one part of nitric acids) is placed in a tubular retort provided with a receiver, and the organic materials, which have previously been cut into small pieces, added; the reaction commences immediately; if it is not sufficiently active, it is accelerated by a gentle heat: lively effervescence now occurs, and the destruction of all non-oleaginous substances is soon accomplished. The latter substances alone are not immediately decomposed by *aqua regia*, which attacks them only after

prolonged action. As soon as the operation is concluded, the apparatus is removed from the fire and taken apart. The fluid condensed in the receiver is added to that remaining in the retort, and the whole thoroughly cooled in an open dish. The fatty matters now form a solid crust upon the surface of the fluid, which is removed and washed with distilled water, and, the washings being added to the rest of the solution, the latter is directly examined for metallic poisons. It is recommended by *Gaultier de Claubry*, in cases where the detection of arsenic is desired, to saturate and afterwards boil the suspected fluid with sulphuric acid, in order to remove the nitric and hydrochloric acids present.

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DIALYSIS.

The application of the dialytic method was first proposed by *Graham*. By its use we are enabled to distinguish between two large classes of bodies, viz., *colloids* and *crystalloids*. Albumen, gelatine, and analogous substances are typical of colloid bodies; crystalloid substances, on the other hand, are those that are capable of crystallization, either directly or in their compounds, or, in case they are fluids, would possess this property when brought to the solid state. Graham discovered that when an aqueous solution containing a mixture of colloid and crystalloid substances is placed in a vessel having for its bottom a piece of parchment or animal membrane, and this is immersed in a larger vessel filled with water, all of the crystalloids contained in the first vessel transverse the porous membrane and are to be found in the larger vessel, the colloid bodies being retained above the membrane. The organic matter to be eliminated in toxicological researches being colloids, and the poisons usually employed being crystalloids, the value of dialysis as a method of separation is evident. The process is executed as follows:

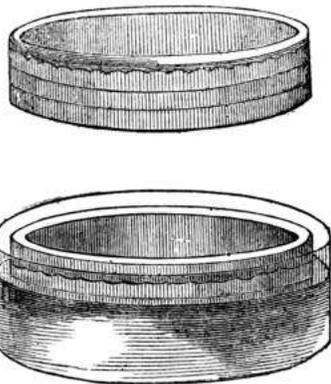


Fig. 1.



Fig. 2.

A wooden,—or better, a gutta-percha—cylinder (Fig. 1), 5 cubic centimetres in height and from 20 to 25 c. c. in diameter, is employed. A piece of moistened parchment is securely attached to one of the openings of the cylinder,

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which, upon drying, shrinks and completely closes the aperture. If its continuity becomes impaired, the pores of the membrane should be covered with the white of an egg which is subsequently coagulated by the application of heat. The organs previously cut into small pieces, or the materials found in the alimentary canal, etc., after having been allowed to digest for 24 hours in water at 32 °^[A]—or, in dilute acids, if the presence of an alkaloid is suspected,—are then placed in the upper vessel, which is termed the dialyser. The whole should form a layer not over 2 cubic centimetres in height. The dialyser is next placed in the larger vessel filled with distilled water. In about 24 hours three-quarters of the crystalloid substances present will have passed into the lower vessel. The solution is then evaporated over a water-bath, and submitted to analysis. The portion remaining in the dialyser is decomposed by one of the methods previously described, in order to effect the detection of any poisonous substances possibly present. Instead of the above apparatus, the one represented in Fig. 2 can be employed. The fluid under examination is placed in a bell-shaped jar, open at the top and closed below with a piece of parchment, which is then suspended in the centre of a larger vessel containing water. In other respects the operation is performed in the same manner as with the apparatus represented in Fig. 1.

II. DETECTION OF POISONS, THE PRESENCE OF WHICH IS SUSPECTED.

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DETECTION OF ARSENIC.

It is frequently required, in chemical jurisprudence, to institute a search for arsenic in the remains of a deceased person, whose death is supposed to have been caused by the reception of a poison. Under these circumstances the poison is mixed with a mass of substances which would obscure its characteristic properties, and it becomes necessary, in order to accomplish its identification, to isolate it, and then, by decisive reactions, determine its character. Three methods exist which permit of this result; they are:

1st. The method used prior to Marsh's test.

2nd. Marsh's test.

3rd. A method more recent than Marsh's, proposed by *M. Raspail*.

METHOD USED PRIOR TO MARSH'S TEST.



Fig. 3.

The materials supposed to contain arsenic are boiled in water which has been rendered strongly alkaline by the addition of pure potassa. The fluid is then filtered, an excess

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of hydrochloric acid added, and a current of sulphuretted hydrogen conducted through it. If arsenic be present in the suspected fluid, it is soon precipitated as a yellow sulphide. In dilute solutions the formation of the precipitate fails to take place immediately, and only a yellow coloration of the fluid is perceptible; upon slightly boiling the solution, however, the precipitation of the sulphide is soon induced. The precipitate is collected on a filter, well washed with boiling water, and

then removed, if present in a quantity sufficient to admit of this operation. It is next dissolved in ammonia,^[B] and the solution so obtained subsequently evaporated to dryness on a watch-glass. The residue of sulphide of arsenic is placed in a tube closed at one end containing nitrate of potassa in a state of fusion: it is decomposed by this treatment into a mixture of sulphate and arsenate of potassa, the reaction being completed in about fifteen minutes. The mixture is now dissolved in water, and lime water added to the solution: a precipitate of arsenate of lime is formed, which is separated from the fluid by filtration, dried, mixed with charcoal, and introduced into a second tube. A few pieces of charcoal are then placed in the tube adjoining the mixture and exposed to a red heat, the part of the tube containing the arsenical compound being also heated. By this operation the arsenic acid is reduced to arsenic, which is deposited upon the cold portion of the tube in the form of a metallic mirror. This mirror is then identified by subsequent reactions. The method just described is no longer in use, although the precipitation of the arsenic by sulphuretted hydrogen is still often resorted to in its separation from the other metals with which it may be mixed. The destruction of the organic sub

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stances is, however, accomplished by means of chlorate of potassa and hydrochloric acid. To insure the complete precipitation of the arsenic, it is advisable to conduct sulphuretted hydrogen through the solution, at a temperature of 70° for twelve hours, and then allow the fluid to remain in a

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moderately warm place, until the odor of the gas is no longer perceptible, the vessel being simply covered with a piece of paper. The precipitate is next freed from the other metals possibly present, as directed in the general method of analysis, collected on a filter, and dissolved in ammonia. The ammoniacal solution is evaporated on a watch crystal, as previously described, and the residuary sulphide reduced to metallic arsenic. This reduction is effected by a process somewhat different from the one previously mentioned: the residue is fused, in a current of carbonic acid gas, with a mixture of carbonate of soda and cyanide of potassium. The apparatus employed is represented in Fig. 3: *a*, is an apparatus producing a constant supply of carbonic acid. Upon opening Mohr's clamp, *g*, the gas passes into the flask *h*, which contains sulphuric acid; it is then conducted, by means of the tube *i*, into the reduction tube *k*, which has an interior diameter of 8 mm. This tube is represented, in half size, in Fig 4.



Fig. 4.

The reduction is performed as follows: The sulphide of arsenic is ground in a small mortar, previously warmed, together with 12 parts of a mixture consisting of 3 parts of carbonate of soda and 1 part of cyanide of potassium, both salts being perfectly dry. The powder thus obtained is placed upon a piece of paper rolled in the form of a gutter, and introduced into the reduction tube. The latter is then turned half round its axis, so as to cause the mixture to fall in *de* without soiling the other parts of the

tube. The paper is now withdrawn and the apparatus mounted. Upon opening the clamp *g*, and strongly heating the mixture by either the flame of a gas or an alcohol [21]

lamp, a mirror-like ring of metallic arsenic is deposited at *h*, if this poison be present in the substances under examination. When the coating is too minute to permit of perfect identification, it should be driven by heat to a thinner part of the tube; in this way it is rendered easily visible, being condensed upon a smaller space.

The above process possesses the advantage of not allowing arsenic to be confounded with any other body; it also permits of a quantitative estimation of the poison present. For this purpose, it is only necessary to previously weigh the watch-crystal, upon which the ammoniacal solution of sulphide of arsenic was evaporated, and to determine its increased weight after the evaporation; the difference of the two weighings multiplied by 0.8049, gives the corresponding weight of arsenious acid, and by 0.6098, the weight of the corresponding amount of metallic arsenic.

MARSH'S TEST.

Marsh's test is based upon the reduction of arsenious and arsenic acids by nascent hydrogen, and the subsequent transformation of these bodies into water and arsenetted hydrogen, a compound from which the arsenic can be readily isolated. When pure hydrogen is generated in a flask having two openings, one of which is provided with a perforated cork through which a safety-tube passes, the other with a tube bent at a right angle and drawn out to a small point at the free extremity, the evolved gas, if ignited, burns with a pale non-luminous flame. The air should be completely expelled from the apparatus before igniting the gas. Upon bringing a cold porcelain saucer in contact with the point of the flame, only water is formed. If, however, a small quantity of a solution containing

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arsenious or arsenic acids is introduced into the apparatus by means of the safety-tube, arsenetted hydrogen is produced. This gas burns with a bright flame, yielding fumes of arsenious acid. In case a large amount of the poison is present, it can be recognized by the appearance of the flame, and by inclining a glass tube towards it upon which a portion of the arsenious acid becomes deposited. These indications are, however, not distinguishable in presence of only a small amount of arsenic, and the following distinctive properties of the gas should be verified:

1st. At an elevated temperature it is decomposed into its two constituent elements.



Fig. 5.



Fig. 6.

2nd. The combustibility of the constituents differs: the arsenic being less combustible than the hydrogen, begins to burn only after the complete consumption of the latter body has taken place. For this reason the flame (Fig. 5) is composed of a dark portion *O* and a luminous portion *I*, which surrounds the first. The maximum temperature exists in *O* at the point of union of the two parts of the flame. Owing to an insufficient supply of oxygen, the complete combustion of the arsenic in this part

of the flame is impossible, and if it be intersected by the cold surface *AB*, that body is deposited as a brown spot, possessing a metallic lustre. The metallic deposit originates, therefore, from the decomposition of the arsenetted hydrogen by heat and from its incomplete combustion. If the spot is not large, it fails to exhibit a metallic lustre; an experienced chemist, however, will be able to identify it by the aid of proper tests. Spots are sometimes obtained when the substance

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under examination does not contain the least trace of arsenic. These may be caused by antimony or by a portion of the zinc salt in the generating flask being carried over by the gaseous current. This difficulty is remedied by giving the apparatus the form represented in Fig. 6. *A* is the flask in which the gas is generated. The delivery-tube *I* connects with a second tube *H*, filled with asbestos or cotton; this is united by means of a cork with a third tube *C*, made of Bohemian glass. The latter tube is quite long, and terminates in a jet at its free end, enclosed in tin-foil;^[C] it passes through the sheet-iron furnace *R*, supported upon *G*. The screen *D* protects the portion *DE* of the tube *C* from the heat. The gas disengaged is ignited at *E* and the porcelain dish *P* is held by the hand in contact with the flame. The apparatus being mounted, zinc, water and some sulphuric acid are placed in the

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generating flask,^[D] and the solution containing arsenious acid added: the evolution of gas commences immediately. The tube *H* serves to retain any liquids that may be held suspended. The gas then passes through the part *CD* of the tube *C*, which is heated by placing a few live coals upon the furnace *R*. The greater portion of the arsenetted hydrogen is decomposed here, and is deposited on the cold part of the tube, in a mirror-like ring. The small quantity of gas that escapes decomposition, if ignited at *E*, produces a metallic spot on the dish *P*. In order to determine that the spots are due to the presence of arsenic, and not produced by antimony, the following tests should be applied:

1. The color of the spots is distinctive: arsenical spots are brown and exhibit a metallic lustre, whereas those originating from antimony possess a black color, especially near their border. This difference is, however, not perceptible when the deposits have a large surface.
2. If the mirror be arsenical, it is readily volatilized from one part of the tube to another, when the latter is heated, and a current of hydrogen, or carbonic acid gas made to pass through it. Spots that are due to the presence of antimony are much less volatile.
3. If the tube is held in an inclined position so that a current of air traverses it, and the part containing the arsenical mirror heated, the arsenic oxidizes and arsenious acid is sublimed and deposited higher up in the tube in the form of a ring, which exhibits octahedral crystals when examined with a magnifying glass. This ring should be further tested as follows:

a. If it is dissolved in a drop of hydrochloric acid and a so

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lution of sulphuretted hydrogen added, a yellow precipitate of sulphide of arsenic is formed. This compound is soluble in ammonia and in alkaline sulphides, but insoluble in hydrochloric acid.

b. If the ring is dissolved in pure water and an ammoniacal solution of sulphate of copper added, a beautiful green precipitate ("*Scheele's green*"), consisting of arsenite of copper, is produced.

4. When produced by arsenic the spots are soluble in nitric acid, and upon evaporating the solution so obtained to dryness, a residue of arsenic acid, which is easily soluble in water, remains. If an ammoniacal solution of nitrate of silver is added to the aqueous solution of the residue, a brick-red precipitate is produced. Spots consisting of antimony give, when treated with nitric acid, a residue of an intermediate oxide, insoluble in water.

5. Upon treating the spots with a drop of solution of sulphide of ammonium, the sulphide of the metal present is formed: if sulphide of arsenic is produced its properties, as enumerated above, can be recognized. It may be added that the sulphide of antimony formed is soluble in hydrochloric acid, and possesses an orange red color, whereas sulphide of arsenic is yellow.

6. When spots originating from arsenic are treated with a solution of hypochlorite of soda (prepared by passing chlorine into solution of carbonate of soda), they are immediately dissolved; if, on the other hand, they are produced by antimony, they remain unaltered by this treatment.

Such are the properties exhibited by soluble compounds of arsenic when treated by Marsh's process; the following precautions are, however, necessary when this test is made use of in medico-legal examinations.

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1. If small white gritty particles, resembling arsenious acid, are discovered in the stomach or intestines, they are directly introduced into Marsh's apparatus. When this is not the case, the destruction of the organic matter is indispensable even though, instead of the organs themselves, the contents of the alimentary canal are taken. In the latter instance, the solids are separated from the fluids present by filtration, the solution evaporated to dryness and the residue united with the solid portion; the organic matter is then destroyed by one of the methods previously described. In the special case of arsenic, the separation of the poison from the accompanying organic materials can be accomplished by a process not yet mentioned which may prove to be of service. The suspected substances are distilled with common salt and concentrated sulphuric acid. By this operation the arsenic is converted into a volatile chloride which distils over. The poison is isolated by treating this compound with water, by which it is decomposed into hydrochloric and arsenious acids. We must give preference, however, to the method by means of chlorate of potassa and hydrochloric acid.

2. The solution having been obtained in a condition suitable for examination, the air is completely expelled from the apparatus by allowing the gas to evolve for some time, and the suspected fluid then introduced into the generating flask. Danger of explosion would be incurred were the gas ignited when mixed with air.^[E]

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3. It is indispensable, in applying this test, to have a second apparatus in which only the reagents necessary to generate hydrogen are placed: in this way, if no spots are now produced by the use of the second apparatus, it is certain that those obtained

when the first apparatus is employed do not originate from impurities present in the reagents used.

It has come under the author's observation, however, that a sheet of zinc sometimes contains arsenic in one part and not in another; in fact, the shavings of this metal, as purchased for laboratory use, are often taken from lots previously collected, and may therefore have been prepared from several different sheets. If this be the case, it is supposable that the zinc used in the second apparatus may be free from arsenic, whereas the metal with which the suspected solution is brought in contact may contain this poison; serious danger would then exist of finding indications of the presence of arsenic in materials that did not originally contain a trace of the metal. In order to obviate this important objection, which might possibly place a human life in jeopardy, we propose the following modifications: Pure mercury is distilled and its absolute purity established. As the metal is a fluid and is therefore homogeneous, it is evident if one portion be found pure, the entire mass is so. Sodium is then fused under oil of naphtha, in order to cause the complete admixture of its particles, and the purity of the fused metal in regard to arsenic tested. An amalgam is next prepared by uniting the mercury and sodium. This is eminently adapted to toxicological investigations: in order to generate a supply of very pure hydrogen, it is only necessary to place the amalgam in water kept slightly acid by the addition of a few drops

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of sulphuric acid, by means of which the disengagement of gas is rendered more energetic.^[F]

It should be borne in mind that the solution introduced into Marsh's apparatus must not contain organic substances, and that, in case their destruction has been accomplished by means of nitric acid all traces of this compound are to be removed. The sulphuric acid used should also be completely freed from nitrous vapors. According to *M. Blondeau*, nascent hydrogen in the presence of nitrous compounds converts the acids of arsenic not into arsenetted hydrogen (As H^3), but into the *solid* arsenide of hydrogen ($\text{As}^4 \text{H}^2$). This latter compound, upon which pure nascent hydrogen has no effect, is transformed into gaseous arsenetted hydrogen by the simultaneous action of nascent hydrogen and organic substances. These facts are of the greatest importance, for they might possibly cause a loss of arsenic when it is present, as well as determine its discovery when it is absent.

The first case is supposable: should traces of nitric acid remain in the solution, the arsenic would be transformed into solid arsenide of hydrogen and its detection rendered impossible. The second case may also occur: if the zinc placed in the apparatus contains arsenic, and the sulphuric acid used contains nitrous compounds, the evolved gas will fail to exhibit any evidence of the presence of arsenic, owing to the formation of the solid arsenide of hydrogen. Upon adding the suspected solution, which, perchance, may still contain organic substances, this arsenide is converted into arsenetted hydrogen, and the presence of arsenic will be detected, although the solution under examination was originally free from this metal.

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RASPAIL'S METHOD.

M. Raspail suggests the following method for detecting arsenic: The surface of a brass plate is rasped by filing. In this condition the plate may be regarded as an innumerable quantity of voltaic elements, formed by the juxtaposition of the molecules of zinc and copper. The suspected materials are boiled with caustic potassa, the solution filtered, a drop of the filtrate placed upon the brass plate, and a drop of chlorine water added. If the plate is then allowed to stand for a moment and the substance under examination contains arsenic, a mirror-like spot is soon deposited upon its surface. In order to avoid confounding this deposit with those produced by other metals, the substitution of granulated brass for the plate is in some cases advisable. The granulated metal is dipped successively in the suspected solution and in chlorine water. The granules retain a small quantity of the solutions and, owing to the action of the chlorine water, become covered with metallic spots, if arsenic be present. They are then dried, placed in a tube closed at one end, and exposed to the heat of an alcohol lamp. In case the spots are arsenical, the metal volatilizes and condenses in a ring upon the cold part of the tube, which is submitted to the tests previously described.

This method can hardly be of great service, inasmuch as

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it extracts the poison from but a very small portion of the solution containing it: we have not, however, personally tested its merits.^[G]

DETECTION OF ANTIMONY.

Strictly speaking the salts of antimony are more therapeutic than poisonous in their action. In fact they usually act as emetics and, under certain circumstances, may be taken in large doses without incurring serious results. There are instances, however, in which their action is truly toxic, and it becomes necessary to effect their detection in the organs

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of a body. It should be remarked that these salts, if absorbed, remain by a kind of predilection in the liver and spleen. A special examination of these organs should therefore be instituted, particularly if the fluids of the alimentary canal are not at hand, which is frequently the case when some time has elapsed before the investigation is undertaken.

The remarks made in the preceding article concerning the distinctive properties of arsenic and antimony need not be repeated here. The search for antimony is likewise executed by aid of Marsh's apparatus. We will confine ourselves to a description of a modification to this apparatus proposed by *MM. Flandin and Danger*, and employed in the separation of antimony and arsenic, when a mixture of these metals is under examination. Another process, by means of which we arrive at the same result with greater certainty and by the use of a less expensive apparatus, will then be mentioned. We will, however, first indicate the preferable method of destruction of the organic substances.

Were the decomposition performed by means of sulphuric acid, sulphate of antimony, a slightly soluble salt and one not well adapted to the subsequent treatment with nascent hydrogen, would be formed. In order to obtain the metal in a soluble state, the formation of a double tartrate of antimony and soda is desirable.

This may be accomplished in the following manner:

1. A cold mixture of nitrate of soda, sulphuric acid, and the suspected materials is prepared in the proportion of 25 grammes of the nitrate to 39 grammes of the acid, and 100 grammes of the substance under examination. This mixture is heated and evaporated to dryness, and the decomposition of the organic matter completed in the usual manner. The carbonaceous residue obtained is pulverized, and then boiled with a solution

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of tartaric acid. By this treatment the antimonate of soda present is converted into a double tartrate of antimony and soda, which is easily soluble in water. The solution is filtered and then introduced into Marsh's apparatus.

2. Another method consists in heating the substances under examination with one half of their weight of hydrochloric acid for six hours on a sand-bath, avoiding boiling. The temperature is then increased until the liquid is in a state of ebullition, and 15 to 20 grammes of chlorate of potassa, for every 100 grammes of the suspected matter taken, added in successive portions, so that a quarter of an hour is required for the operation. The liquid is next filtered, and the resinous matter remaining on the filter well washed with distilled water; the washings being added to the principal solution. A strip of polished tin is then immersed in the liquid: in presence of a large amount of antimony the tin becomes covered with a black incrustation: if but a minute quantity of the metal is contained, only a few blackish spots are perceptible. After the tin has remained immersed for 24 hours, it is withdrawn and placed in a flask together with an amount of hydrochloric acid sufficient for its solution in the cold. If, after several hours, blackish particles are still observed floating in the liquid, they can be dissolved in a few drops of *aqua regia*. The solution may then be directly introduced into Marsh's apparatus.

APPARATUS PROPOSED BY FLANDIN AND DANGER.



Fig. 7.

This apparatus consists of a wide necked jar *A* (Fig. 7) for the generation of the gas, the mouth of which is closed with a cork having two openings. The safety tube *S*, which is funnel-shaped at its upper extremity and has its lower end drawn out to a point, passes through one of these apertures;

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the other opening contains the small delivery tube *B*, open at both ends, and terminating in a point at its upper extremity: it is also provided with lateral openings, in order to prevent the solution being carried up to the flame. The second part of the apparatus is the condenser *C*, 0.03 metre in diameter, and 0.25 metre in length. This terminates at its lower extremity with a cone, and connects at the side with the tube *T*, slanting slightly downwards. In the interior of the condenser, the cooler *E* is contained, the lower end of which is nearly in contact with the sides of the opening *O*. The combustion tube *D*, 0.01 metre in diameter, is connected by means of a cork with the tube *T*; it is bent at right angles, and encloses the tube *B*, in

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