A manual of practical chemistry : the analysis of foods and the detection of poisons / A.W. Blyth.


via veritas vita

A MANUAL
OF
PRACTICAL CHEMISTRY.

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OF

PRACTICAL CHEMISTRY:

THE ANALYSIS OF FOODS

AND

THE DETECTION OF POISONS.

BY

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PREFACE.

THE following work consists of Two Parts—one devoted to the Analysis of the principal Articles of Diet in daily use; the other to the Detection and Estimation of Poisons, organic and inorganic.

In the First Portion, the author has endeavoured to give a clear and concise account of the composition of the various Foods and Beverages, with the best and most recent methods for the detection of any Adulteration. A few of the more important Legal Cases are detailed, where their bearing on the subject renders them helpful; and to every Article is appended a Bibliography of the works and papers consulted.

In the Second Portion, the arrangement of the *Organic Poisons* is simply that which suggests itself naturally in a methodical investigation — the more volatile Poisons, those that are obtained by processes of distillation, being considered first; and, in the second place, those extracted by alcoholic or ethereal solvents. The *Inorganic Poisons*, finally, are taken in the order in which they may most conveniently be sought.

The *Symptoms* produced by Poisons are only occasionally and briefly referred to, save in a few instances where the information furnished by the standard text-books seemed to require supplementing, or where recent cases have afforded new data. Under each head, however, will be found the *dose* likely to prove fatal to man and animals, with analyses of the chief technical, medical, veterinary, and patent compounds of the drug or poison in question. Due prominence is also given to the special points on which the evidence of the Expert will be looked for in Court.

The scope of the present work is, of course, essentially what its title implies; still, in several instances (*e.g.*, fousel oil, copper in vegetables, &c.), the medical, as well as the chemical, aspect of the subject under consideration has been freely discussed. This is more especially the case in the Article on "Milk," in which will be found its composition in health and disease, and an account (as complete as the limits of the work will allow) of the real or supposed propagation of various maladies by its agency.

In conclusion, the author trusts that the Manual will be found not only, and in reality, a *handy*-book of reference for professed Students of Chemistry, but suggestive also to Hygiènists, Medical Men, Veterinary Surgeons, and Pharmaceutists. To the best of his knowledge, there is no other work in the language covering precisely the same ground—a ground occupied in Continental Literature by such treatises as the "*Handbuch der Gerichtlichen Chemie*" of Sonnenschein, and others of a similar scope.

BARNSTAPLE,
December 5, 1878.

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FIRST DIVISION.

ANALYSIS OF FOODS.

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PART I.—INTRODUCTORY.

ASH — SUGAR — STARCHES.

THERE are but few substances inspected by the analyst in which it is not advisable to determine and examine the Ash; it will, therefore, save repetition to give at the outset the general course of procedure. As similar considerations apply to the chemically-allied substances, Sugar and Starch, they will now also be fully treated, and to this preliminary chapter the Reader is referred for details of processes mentioned throughout the work.

I.—ANALYSIS OF THE ASH OF ORGANIC SUBSTANCES.

§ 1. As a general rule, testing the ash for abnormal metals and alkaline earths is necessary, and more especially if the ash present any unusual character, whether in weight, colour, or solubility. Leaving for the present the *special* tests, the number and nature of the constituents which require to be determined for the purpose of the food analyst, vary according to the particular substance under examination, *e. g.*—

In all substances, *the percentage.*

In such fluids as milk, *the alkaline phosphates and the chlorides.*

In seeds, such as wheat, cocoa, &c., the total *phosphoric acid.*

In beer-ash, the amount of *common salt.*

In bread-ash, the presence or absence of *alumina.*

In tea-ash, the *alkalinity,* the *iron,* the *silica,* and proportion of *soluble* to *insoluble ash.*

In coffee-ash, likewise the proportion of soluble to insoluble ash, but the presence or absence of *silica* becomes also of importance.

From these illustrations (which might be multiplied) it follows that, for the purposes of the analyst, the general constitution of the ash will be sufficiently known when the following determinations have been made :—

(1.) The total percentage of ash.
(2.) The total percentage of ash soluble in water.
(3.) The total percentage of ash soluble in acid.
(4.) The alkalinity of the ash.
(5.) The percentage of chlorine.
(6.) The percentage of phosphoric acid.

(1.) *The Total Percentage of Ash.*—Of the various methods of estimating an ash, the simplest and most practical appears to be —to place a sufficient quantity of the substance to be burnt in a capacious platinum dish, and to consume at the lowest possible temperature by heating with a ring burner.* The quantity to be taken is regulated by the amount of ash in the substances. For example, flour, containing only ·7 per cent of ash, would give with 50 grms. ·35 ash, which is about as small a quantity as it is possible to work with conveniently, whilst in the case of coffee, tea, and cocoa, from 5 to 20 grms. is for most purposes ample.

(2.) *The Soluble Ash.*—The ash is boiled up two or three times with water in the same platinum dish; filtered, and the filtrate evaporated to dryness, heated to dull redness, and weighed.

(3.) *The Ash Soluble in Acid.*—The portion of ash insoluble in water is boiled up with HCl, and filtered from the sand; the latter is washed, dried, and weighed.

(4.) *The Alkalinity of the Ash.*—The solution in water from (2) is coloured with cochineal, and titrated with d. n. acid: the result may be usually expressed as potash.

(5.) *The Percentage of Chlorine.*—The determination of chlorine in the ash usually gives results too low, especially if the substance burnt is one like bread, of difficult combustion, or containing substances which decompose chlorides at a red heat. Notwithstanding this defect, in a series of ashes burnt under similar circumstances, the amount of chlorine found gives fair comparative results. Should there be any special necessity for

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* If the sulphuric acid in the ash is not to be determined, a wide glass tube (such as the chimney of a common paraffin lamp) adjusted over the dish, by its powerful up-draught greatly expedites the operation; but if the sulphuric acid is to be determined, the impure gas of commerce renders the results too high. It is, however, of course open to the analyst to make the gas pass through a proper absorption-apparatus, or to use as a fuel, alcohol.

an accurate determination of chlorine, no volatilisation will occur in the combustion of most articles of food, if they be not burnt to a complete ash, and if the charcoal be finely powdered and extracted with plenty of boiling water. The chlorine may be determined gravimetrically by nitrate of silver, or more conveniently by a standard solution of nitrate of silver, using as an indicator neutral chromate of potash. Should alkaline phosphates be present, they must be first removed by baryta water.

(6.) *The Phosphoric Acid.*—The usual method of determining phosphoric acid is to dissolve the ash in hydrochloric acid, evaporate to dryness, remove the silica, mix the acid filtrate with ammonia in excess, redissolve the precipitated earthy phosphates by acetic acid, filter off and estimate the insoluble phosphate of iron (and alumina, if present), precipitate the lime with oxalate of ammonia, and then in the fluid (free from lime and iron) precipitate the phosphoric acid, by the addition of ammonia and magnesian mixture.

The best method of determining *all the constituents* of an ordinary ash is, perhaps, as follows:—A sufficient quantity of the ash (from 5 to 10 grms.) is placed in a flask, about 25 cc. of water added, and saturated with CO_2; the liquid is now evaporated to dryness, heated with a small quantity of water to dissolve the alkaline salts—the solution is filtered through a small weighed filter—the filtrate evaporated to dryness, the saline residue treated with a small quantity of water, and the calcium sulphate which separates out filtered through a weighed filter, and estimated; the filtrate from this is put in a tared flask, made up to any convenient weight, and divided into five portions *by weight*, viz.—(1.) For CO_2, determined volumetrically by passing the gas into a solution of chloride of lime, and titrating the resulting carbonate with d. n. sulphuric acid. (2.) For the sulphuric acid, determined by chloride of barium. (3.) For the phosphoric acid, determined as magnesian pyrophosphate. (4.) For the chlorine, by precipitation as silver chloride. (5.) For the alkalies, by boiling in a platinum dish with slight excess of baryta water, filtering, getting rid of the excess of baryta by ammonia and ammonium carbonate, evaporating the filtrate to dryness, converting the alkalies into chlorides, and determining their relative proportion from their total weight and their content in chlorine. This completes the analysis of the *soluble* portion of the ash.

The *insoluble* will contain lime, magnesia, ferric oxide, alumina if present, silica, phosphoric, sulphuric, and carbonic acids.

The main portion of the insoluble ash is dissolved in nitric acid, freed from silica in the usual way, evaporated again to dryness in a porcelain basin, dilute nitric acid added until the bases are completely dissolved, and strong fuming nitric acid added, until the solution begins to be turbid from the separation of calcic nitrate. The turbidity is now destroyed by a few drops of dilute nitric acid, the solution warmed, and tinfoil added in small portions at a time, in weight about equal to the amount of ash taken. When the tin is fully oxidised, the solution is evaporated *nearly* to dryness, water is added, and the solution filtered; the phosphoric acid is retained in the precipitate—the bases are all in the filtrate. The precipitate is dissolved in strong potash solution, acidified with sulphuric acid, and freed from tin by hydric sulphide, concentrated to a small bulk, filtered if any further sulphide of tin separates, and the phosphoric acid determined by magnesia mixture and ammonia.*

The filtrate from the tin phosphate must be freed from lead (if the tin originally contained lead) by hydric sulphide, concentrated, the iron and alumina separated and determined by ammonia, the manganese separated as binoxide by bromine-water, the lime by oxalate of ammonia as oxalate, and the magnesia determined in the usual way as pyrophosphate.

A weighed portion of the insoluble ash must also be taken for the carbon dioxide, sulphuric acid, and sand. The carbon dioxide may be determined in a Geissler's carbonic acid flask, using HCl as the decomposing agent, and the two remaining constituents may be estimated in the resulting solution.

The process just given is not quite accurate with regard to the estimation of the alkalies; for Bunge† has shown that since the alkalies form insoluble compounds with the alkaline earths, a watery extract of the ash gives low results. For example, Bunge incinerated 300 cc. of cows' milk; from a watery extract of the ash he obtained

$$K_2O \cdot 5436, Na_2O \cdot 0700;$$

while from a subsequent nitric acid extract of the same ash,

$$K_2O \cdot 0937, Na_2O\ 0 \cdot 1162.$$

If chlorides of the alkalies be heated with tribasic phosphate of lime, the soda is specially likely to combine with the lime in insoluble combination—in far less proportion the potash.

Bunge recommends the following method:—The watery extract is decomposed with baryta water until a film forms on the surface of the solution, the mixture is warmed and filtered hot. The excess of baryta is got rid of by CO_2, subsequent warming,

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* Thorpe's "Quantitative Analysis." London, 1877.

† Liebig's *Annalen der Chimie u. Pharmacie.*

and filtration; the filtrate is evaporated in a platinum dish, the residue gently ignited, dissolved in a little water, filtered through a small filter, and evaporated with HCl in a small platinum dish. The chlorides are then ignited, weighed, and separated by platin chloride.

The hydrochloric or nitric solution of the insoluble portion of the ash is evaporated to dryness in a platinum dish, the residue again dissolved in a little of the acid and water, treated like the former with baryta water, and filtered hot. Ammonia and carbonate of ammonia are now added, the liquid filtered, and the filtrate evaporated in a platinum dish, and ignited at the lowest possible temperature. The residue still containing a trace of alkaline earth, is extracted with water, evaporated with oxalic acid, ignited again, taken up with water, filtered, evaporated in a small platinum dish, ignited again, dissolved in a little water, and lastly evaporated with HCl, and the alkaline salts separated by bichloride of platinum.

II.—ESTIMATION OF SUGAR.

§ 2. Sugar is estimated by chemical processes, by the specific gravity of the solution, by the estimation of the CO_2 evolved in alcoholic fermentation, and by certain physical processes.

It is only possible to estimate percentages of sugar (especially cane sugar) from the specific gravity of the solution when the fairly pure sugar is dissolved in pure water, so that this method is of but limited utility, and seldom employed by the analyst. The fermentation process is too tedious and inconvenient ever to come into general practice, and will therefore not be described.

(1.) *Chemical Processes depending upon the Precipitation of the Suboxide of Copper from a Copper Solution by Grape Sugar.*

The most general of the numerous processes under this head is that of Fehling, which requires a solution of cupric sulphate and Rochelle salt, alkalised by soda. 34·64 grms. of pure crystallised cupric sulphate, previously powdered, and pressed between blotting-paper, are dissolved in 200 cc. of distilled water; 174 grms. of Rochelle salt are dissolved in 400 cc. of a solution of pure caustic soda, specific gravity 1·14; the two solutions are now mixed and made up to 1 litre. Each cc. of the solution represents 5 mgrms. of anhydrous grape sugar, 7·46 mgrms. of milk sugar, ·03464 grm. of cupric sulphate, and ·01103 grm. of CuO. The liquid should be preserved in bottles protected from the light, and absorption of carbon dioxide from the air should be provided against.

On account of the slight instability of this solution, A. Soldaini has proposed the following:—416 grms. of potassium bicarbonate, 15 grms. of dry basic cupric carbonate, and 1,400 grms. of distilled water are heated together, the liquid being continually replaced; when the evolution of CO_2 has nearly ceased, the liquid is made up to its original volume with water, filtered, and concentrated down to 800 cc. Such a solution is not reduced by light or the carbonic dioxide of the air: it is unaltered by prolonged boiling, and may even be evaporated to dryness without decomposition. It is reduced by formic acid, laeoulose, glucose, and lactose, and can be used for quantitative purposes in the same way as Fehling's.

In either case a known volume of the copper solution (*e.g.*, 10 cc. of copper solution with 40 cc. of water) is placed in a white porcelain dish, heated to boiling, and the liquid to be examined (which must be so diluted as not to contain more than 1 per cent. of sugar) run into it from a burette, until the whole of the copper is separated as suboxide, as shown by the absence of blue colour. By allowing the precipitate to settle from time to time, the least trace of blue colour can be seen by inclining the dish, or if there be any uncertainty, a little can be filtered off and tested.

It is best in all cases to standardise the solution by grape sugar, or if milk is the object of research, by milk sugar, the latter reducing the copper solution in a different proportion. Cane sugar cannot be estimated in this way, since it does not reduce copper solution; by boiling with dilute acid it is, however, changed to inverted sugar, which reduces copper or mercury in exactly the same proportion as glucose.

Starch and starchy substances may be also changed into sugar by boiling for several hours with a dilute acid. The following is a convenient method:—Two or three strong assay flasks are taken, and in each is placed from ·5 to 1 grm. of the substance to be examined, with 50 to 60 cc. of decinormal sulphuric acid; the flasks are stoppered with caoutchouc corks, tied down with strong string, and capped with linen or canvas, and the whole suspended in a water bath and heated for from six to eight hours. At the end of four hours one of the flasks may be taken out, cooled, opened, and titrated; and at the end of six hours the second. If there is no marked increase in the amount of sugar between the first and the second, the operation is finished; but in any other case the third flask should be heated for another four hours before being examined. 100 parts of grape sugar = 90 of starch, therefore each cc. of Fehling's solution equals 4·5 mgrms. of starch.

(2.) *Volumetric Processes by the aid of Solutions of certain Salts of Mercury.*

Knapp's mercuric cyanide solution is made by dissolving 10 grms. of mercuric cyanide in about 600 cc. of water, then adding 100 cc. of caustic soda solution of specific gravity 1·145, and diluting to 1 litre. 40 cc. of the mercury solution are placed in a flask, heated to boiling, and the solution containing sugar run in gradually from a burette, four parts of mercuric cyanide being reduced to metallic mercury for every one part of anhydrous grape sugar (or, 3·174 parts of metallic mercury = 1 anhydrous grape sugar). The ending of the process is discovered by moistening filter-paper with the clear solution, and holding quite close to it a rod dipped in ammonium sulphide solution ; a *decided* brown coloration takes place if the mercury salt is in excess ; but if the colour is very faint, the operation is finished, for it appears to be impossible to decompose the whole salt, a trace always remaining, and for this reason the solution should be standardised with sugar.

A. Sacchse uses the following solution for the estimation of sugar: —18 grms. of pure dry mercuric iodide, and 25 grms. of potassic iodide are dissolved in water, a solution of 80 grms. of caustic potash is added, and the whole made up to 1 litre. 40 cc. of this solution [= 0·72 grm. HgI_2] are boiled in a basin, and the solution of grape sugar is run in, until the whole of the mercury is precipitated. The final point is determined by spotting a drop of the supernatant liquid on a white slab, and there bringing it into contact with a drop of a strongly alkaline solution of stannous chloride. The production of a brown colour shows the presence of unprecipitated mercury.

According to the author, this mercury solution acts in different ways toward inverted and grape sugar, whilst Fehling's solution has the same action on both. Hence by standardising the prepared mercury solution against grape sugar, and also against inverted sugar, and testing solutions of a mixed sugar under investigation both by Fehling's and by the mercury solution, it is possible by calculations, on the principles of indirect analysis, to determine the relative proportions of grape and inverted sugar simultaneously present in a liquid.

The above processes (and more especially the copper ones) only succeed satisfactorily when the liquid to be tested is pretty well devoid of colour. From certain very thick liquids it is best to extract the sugar by dialysis; but wines, beers, and similar fluids may be clarified by sugar of lead, or by adding a little milk of lime, and subsequent filtration through animal charcoal.

(3.) *Gravimetric Processes.*

The gravimetric processes are, upon the whole, more accurate than the volumetric, and more generally applicable. One of the best is that recently recommended by Dr. Pavy:—The ordinary Fehling's solution is boiled in slight excess with the substance containing glucose or lactose, the precipitate of suboxide of copper immediately collected on a filter made by packing the throat of a funnel with glass wool, the suboxide of copper dissolved by a little peroxide of hydrogen and a drop of nitric acid; and lastly, the copper deposited as copper on a tared piece of platinum foil by electrolysis, and weighed. The amount of copper found, multiplied by ·5678, gives its equivalent in glucose. Dr. Pavy recommends for the electrolysis the use of a constant battery, consisting of an outer cell charged with bichromate of potash dissolved to saturation in dilute sulphuric acid, an inner porous cell containing a little mercury at the bottom and filled up with water, and having in its centre an amalgamated zinc rod dipping into the mercury. In the outer cell are two carbon plates. However, any other battery will do, or an ordinary platinum dish may be coated with the copper, as described in the article on the estimation of Copper. The method is also applicable to the mercury processes just detailed, and either the excess of mercury cyanide in a solution, or the precipitated mercury, can be collected on gold foil or gold capsules.

It is also evident that the copper suboxide, instead of being weighed as copper or oxide, can be collected, washed, redissolved, and estimated volumetrically. One of the best methods under these particular circumstances is to collect as before on glass wool, dissolve, by the aid of a gentle heat, in a solution of pure ferric chloride with the addition of a little sulphuric acid, and then titrate the solution of cuprous chloride by a previously standardised solution of permanganate of potash.

(4.) *Physical Processes for the Determination of Sugar.*

The saccharimeters in use are numerous, but those only of Mitscherlich, Soleil, and Jellett will be described here. The polarising instrument of Mitscherlich is extremely simple. (See Fig. 1.)

It consists of a stationary Nicol's prism in *a*, a plano-convex lens in *b*, and a rotating Nicol's prism *c*. The first prism polarises the light, and the use of the second is to indicate the plane of the polarised ray coming from the first. The second prism is therefore set in a graduated circle *dd*, and is provided with an index *f*, and there is a handle *e*, which turns both prism and index. If the index be either at 0° or 180°, and an observer look through the tubes towards the source of light, the flame is seen divided by a vertical line into two equal parts; if now the tube, supplied with the instrument, be filled with the liquid to be examined, and interposed between the lens and the second prism, should it contain sugar or other polarising substance, the black stripe is no longer in the middle of the field, and the handle moving the index and prism must be turned until the black stripe is seen; or, if the stripe is broad and undefined, the prism is turned until the exact point is reached in which blue changes into red—the index at this point marking the amount of the polarisation by the scale and the direction; for if the index has to be turned to the right, the polarisation is +, or right-handed; if to the left −, or left-handed.

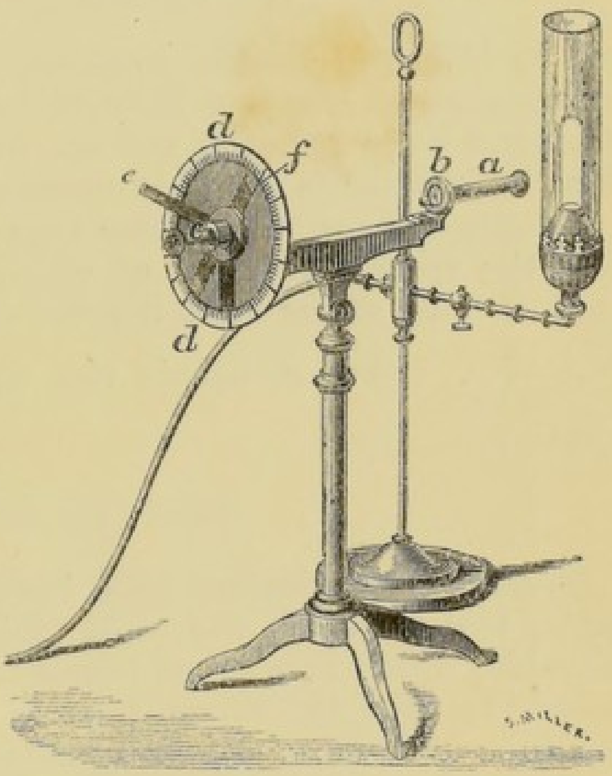


Fig. 1.

In order to make this quantitative, and to estimate the specific *rotation* of a sugar (*i.e.*, the number of degrees of rotation observed when 1 grm. of the sugar is dissolved in 1 cc. of fluid, and observed by yellow light through a tube 1 decimetre long), it is necessary to dissolve a known weight of the pure sugar in water; then if the length of the tube be known, and the temperature of the solution and the rotation be observed, all the necessary data are obtained. For example, let the rotation = a, the length of the tube in decimetres = 1, the weight of substance in 1 cc. of fluid = p, then the specific rotation for yellow light—

$$- \pm \frac{a}{p\,1} \qquad \text{or } (a)_j = \pm \frac{a}{p\,1}$$

the sign $(\alpha)_j$ being in use, signifying yellow light. Or, to take an actual example: 14·3 grms. of a substance dissolved in 100 cc. (·143 grm. in each cc.), and a 2 decimetre long tube filled with this liquid, the rotation on the scale being 16° to the right, then

$$\frac{16}{0{,}143\cdot 2} = 55\cdot 94,$$

and 55·94 is the specific rotation. The best source of light for accurate researches is a Bunsen burner, in the middle of which there is a little pellet of sodium held on a wire. This source of light in formulæ is usually indicated by $(\alpha)_D$.

Provided there be only one sugar in the fluid under investigation, the specific rotation of which is known, the weight of the sugar in 1 cc. of the fluid is estimated by the following formula: $P = \frac{\alpha}{(\alpha)\,1}$, where α equals the observed, and (α) the specific rotation.

Soleil's Saccharimeter.

Soleil's saccharimeter (*See Plate*) consists of three essential parts, two of which are fixed (Fig. 1), AB and CD, the other movable, which is inserted between B and C, and which is sometimes the tube BC 20 centimetres long (Fig. 2), and sometimes the tube B′C′ (Fig. 3), 22 centimetres long, furnished with a thermometer, T. These tubes are destined to contain the saccharine solutions, the value of which is to be determined.

The movable parts are—

(1.) The small movable tube D′D (Fig. 1), carrying the eye-piece, which focuses by drawing in and out.

(2.) The little button V (Fig. 4), serves to adjust the zero of the scale with the zero of the indicator.

(3.) The large milled screwhead on the vertical axis H (Fig. 1), by which is rendered uniform the tint observed.

(4.) The milled ring B (Figs. 1 and 2), by the aid of which they give to this same tint the colour which lends itself best to a precise valuation.

(5.) Lastly, the divided scale RR (Fig. 4), on which is read the number giving the richness of the sugar under examination.

The details of operating are as follows:—The lamp is adjusted so that its light traverses the axis. A tube similar to that which contains the saccharine solution is filled with pure water, and is adjusted in the place provided for it between the ocular and objective portion. Then applying the eye at D (Fig. 1), the tube DD′ is either pushed out or in, until the field is seen divided

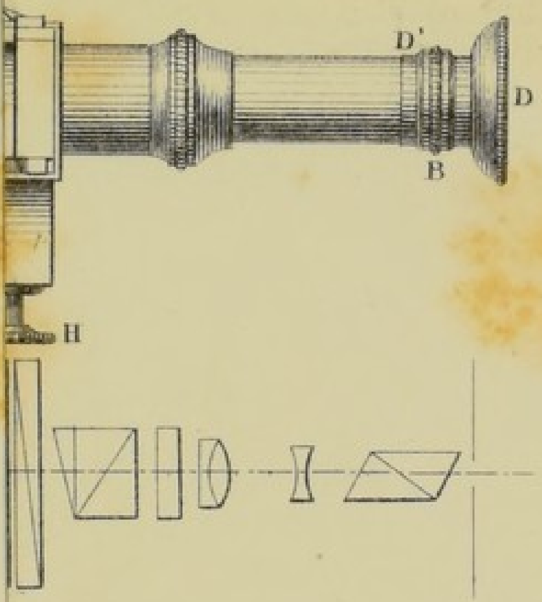


Fig. 2.

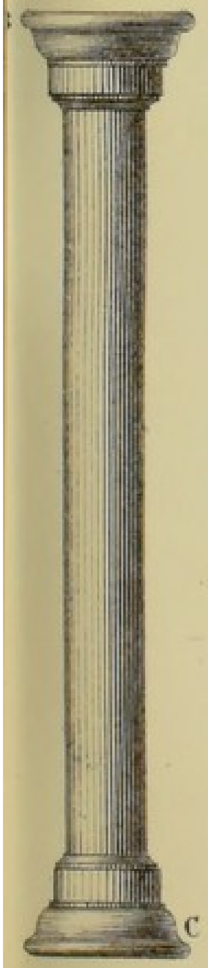
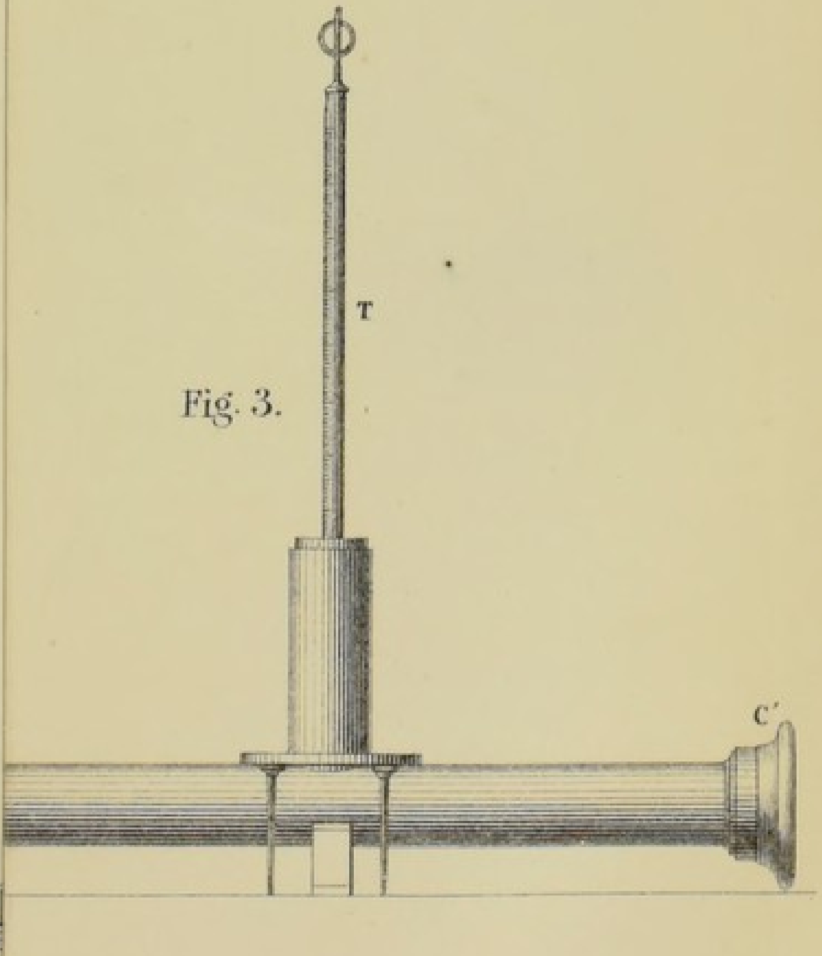


Fig. 3.



Vincent Brooks, Day & Son, Lith.

two equal halves, coloured with one and the same tint, or different tints separated from each other by a black line, h should be very sharply defined. If, as generally happens, wo half-discs have not the same tint or shade, the large ontal button H is turned either way until the desired result tained.

is not only necessary that the two half-discs should have same tint or colour, but in order to be extremely exact, that should be the one most sensible to the eye of the observer ; as all eyes are not equally sensible to the same tint, the er colour must be found by experiment.

he zero line on the scale must coincide exactly with the black of the indicator I (Fig. 4). If the coincidence is not perfect, ay be established by turning either way the little button ntil this is accomplished.

he instrument once adjusted, the examination of the sugar be commenced.

he tube BC, filled with the saccharine solution, is substituted that filled with water, or if an inverted sugar is taken, then ′ is filled. On now looking through the instrument, it is that uniformity of tint no longer exists, and that the two -discs are coloured by different shades. The uniformity is stablished by turning the large horizontal button H until two half-discs are again uniform.

s the saccharine solution is mostly coloured, the uniform re-established is not in general the sensible tint, to which, ever, it is necessary to return, and which the colour of the tion has caused to disappear. The milled head B is then ed to cause the *sensible* tint to reappear; this tint returned, equality of shade of the two half-discs, if not quite perfect, t be made so by turning again H. It now only remains to l the degree on the scale RR′, to which the index answers ; number corresponding to this degree gives immediately in ths the *titre*, or the richness of the solution.

he preparation of the saccharine solutions is as follows :—

1.) *Normal solutions of pure sugar.*—16·350 grms. of pure ar are dissolved in water, the volume made up to 100 cc., and erved in a tube 20 cms. in length ; marks 100 degrees on the harimeter.

.) *The raw sugar of commerce.*—16·350 grms. of the sugar powdered and dissolved in water, and the whole made up to cc. ; if the solution is too dark, it may be clarified by sugar ead. The tube BC is filled with the solution thus prepared adjusted.

3.) The next operation is to invert the sugar. 5 cc. of fuming HCl are added to 50 cc. of the sugar solution, and heated in the water bath up to 68°C.; when that temperature is reached, the solution is put in the tube B′C′, its rotating power (which is now inverse) observed, and at the same time the temperature at the moment of the observation.

We have now all the data necessary, and the amount of sugar may be readily found by tables, such as those of M. Clerget, or by the formula as below.

Supposing the number given by the first observation is 75, by the second (inverted) 21, at a temperature of 12°C., the sum of the two numbers (75 + 21) makes 96. Now, in referring to M. Clerget's table, under 12°, or in the third column corresponding to the temperature of 12°, the nearest number to 96° is in this instance 95·6; the horizontal line in which 95·6 is placed is followed, and there is found, first, in the column A the figures 70 per cent. of pure crystalline sugar; secondly, in the column B, the figures 114·45, placed by the side of 70, which indicates that the saccharine solution examined contains per litre 114·45 grms of pure sugar. If, however, as sometimes happens, the solution contains a polarising substance not modified by acids, in such a case the difference of the two numbers, and not the sum, is to be taken and dealt with as before. It is scarcely necessary to remark, that if the substance is known to contain only crystallisable sugar, and the tube BC be filled, one observation alone suffices.

If tables are not at hand, the following formula can be used:—Let T be the temperature, S the sum or difference of the two determinations, P the rotatory power, R the quantity of sugar contained in 1 litre of the solution—

$$P = \frac{200S}{288 - T} \qquad R = \frac{P \times 16{\cdot}350}{10} = P \times 1{\cdot}635 \text{ grms.}$$

Professor Jellett's instrument is a little more elaborate than Soleil's, and of great accuracy. The eye-piece or analyser of the apparatus consists of a suitably mounted prism, made from a rhombic prism of Iceland spar. The rhombic prism is cut by two planes perpendicular to the longitudinal edges, so as to form a right prism. The prism is next divided by a plane parallel to the edge just produced, and making a small angle with the longer diagonal of the base. One of the two parts into which the prism is thus divided is then reversed, so as to place the base uppermost, and the two parts are connected together.

Another distinctive feature of the instrument is, that the mechanical rotation of the analyser for the finding of any particular plane is dispensed with, this function being transferred to a fluid which has the power of turning the plane of polarisation opposite to that of the solution to be examined. The analysing tube slips into, and moves up and down in, the compensating fluid, so that different thicknesses of the latter fluid can be readily interposed and measured by a scale fixed to the instrument.

The Saccharimetre à Penombrés, of which the principle was enunciated by M. Jellet, as constructed by M. Duboscq, has some very great advantages. It requires the employment of a simple light, and the field does not present to the eye for comparison two different colours, but two intensities sensibly diverse of one and the same colour, so that the least variation can be appreciated. The simple light is best obtained by the insertion of a bead of some salt of soda on a platinum wire in the flame of a Bunsen burner.

III.—STARCH, $C_6H_{10}O_5$.

§ 3. It is convenient to consider the starches together, more especially as, however varied in form, the chemical composition of all starch is very similar, if not identical.

Every starch corpuscle is composed of at least two probably isomeric bodies, the one "*granulose,*" soluble in saliva, and coloured blue by iodine: the other coloured by iodine pale yellow, and only becoming blue after the addition of sulphuric acid; it is fully soluble in ammoniacal oxide of copper, and appears to agree very closely with the characters of *cellulose.*

These two substances may be most readily separated by diluted chromic acid, which dissolves granulose very easily, whilst cellulose remains unaltered. All starch is very hygroscopic; wheat starch, dried in a vacuum, still contains 11 per cent. of water, and air-dried from 16 to 28 per cent. of water. Starch is insoluble in cold water or spirit. Some chemists, indeed, assert that if finely powdered in agate mortars, or with quartz sand, a small portion dissolves; others contend that this is no true solution, but the starchy matter in a state of most minute division. If warmed with water, the starch granules swell, and when heated up to 100° most starches form a semi-solution in water. True compounds of starch with bases are scarcely established. Lime and baryta appear to form weak unions, and the intense colour produced by iodine, as well as bromine, seems to point to the formation of haloid combinations. Fritsche, indeed, states that he has isolated the iodide and the bromide of starch, the former containing ten equivalents of starch and one of iodine.

Starch heated in closed tubes up to 100°C. changes gradually into soluble starch. If the temperature is raised up to 160° or 200°C. it forms a transparent mass, consisting wholly of dextrine. At 220° to 280° still further change is produced, and the result is *pyrodextrin*, a substance easily soluble in water (but insoluble in absolute alcohol and ether), and with the composition of $C_{48}H_{36}O_{36}HO$. At still higher temperatures there is carbonisation, and the formation of products similar to those caused by the decomposition of sugar.

Starch is easily changed into sugar by the action of dilute mineral acids, as well as by oxalic acid, aqueous chloride of zinc, and by certain ferments—diastase, saliva, yeast, &c.

The estimation of starch in organic bodies generally is best carried out as follows:—The powdered and dried substance is heated in a 5 per cent. solution of caustic potash in absolute alcohol, in a closed tube in the water-bath for twenty-four hours, and filtered while hot. The residue is washed first with absolute alcohol, and then with ordinary alcohol, dried, and heated with a solution of 2 per cent. hydrochloric acid, in a flask fitted to a vertical condenser, until a blue colour is no longer produced by iodine. (See also p. 8.) The sugar is then estimated in the ordinary way.

Microscopical Identification of Starches.

The successful microscopical examination of starches requires practical study, and those who desire to identify them must use all drawings and descriptions as guides merely. It is not easy to preserve starches mounted as microscopical objects,* and the analyst is therefore recommended to fit up a little case, in small, wide specimen-tubes, so that he can have at hand a sample of every kind of starch possible to be obtained. These samples should be arranged in the five classes recently described by Dr. Muter,† a method which is strictly followed in this work.

A high magnifying power is not required, save for the very minute starches, such as rice and pepper. For ordinary work a magnifying power of 250 diameters is ample. Dr. Muter's classification of starches was founded on observations with a B. micrometer eye-piece and a $\frac{4}{10}$ inch power.

The value of the divisions of the eye-piece micrometer in use

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According to Muter, a mounting medium of 1 part of glycerine to 2 of water preserves the characters of starch longest.

† "Organic Materia Medica." London, 1878.

must of course be first obtained. This is easily done by comparing a stage micrometer, graduated in parts of an inch or a millimetre, with the micrometer. Thus, for example, supposing 25 main divisions equal ·01 of an inch, then each division equals $^{\cdot 01} = \cdot 0004$ inch for the particular power in use; for it is scarcely necessary to say that the values differ for each power, and the observer should fix a card in his microscope-table, with the exact values of his microscopic scale with different eye-pieces and object glasses. It is also by no means useless to observe the various samples of starch, and make tables of their dimensions. The proper way to do this is to put the smallest possible quantity of the well-mixed starch on a glass slide, add a droplet of distilled water, cover with a thin glass, take the exact size of all the starches in the field, enumerate them, and work them out into percentages for future reference.

The illumination of starches is to be particularly attended to. The light must strike obliquely through the granules, in order to observe the rings, which are by no means so easily seen as diagrams would indicate.

Polarised light is also useful, especially in the diagnosis of certain starches. Thus, the polarised starch of wheat, when examined in water, exhibits a dull cross; that of jalap, in shape and size like wheat, polarises brightly.

If adulteration in any case has been made out, approximative quantitative results may be obtained by making a standard mixture of the genuine starch with the adulterant found, and then counting the individual grains in the microscopic field. Thus, for example, supposing oatmeal to be found adulterated with barley-starch, and from a preliminary examination the mixture supposed to be 40 per cent., we proceed as follows:—

Pure barleymeal and oatmeal are carefully dried at 100°C. and mixed so that the mixture is exactly 40 per cent. A few grains of this powder are now rubbed up with glycerine and alcohol into a smooth paste, which is then further diluted to a certain bulk, a drop taken out with a glass rod, and covered with a glass, which is gently pressed down. The number of grains of barley and oat starch are now counted, and their relative proportion noted, and an exactly similar process is applied to the oatmeal in question.* If proper care be taken to repeat the experiments, the result is a near approximation to the truth.

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* *See* a paper by E. L. Cleaver, F.C.S., *Analyst*, January 31, 1877.

CLASS I.—*The hilum and concentric rings clearly visible, all the starches oval or ovate. The group includes tous les mois, potato, arrowroot, calumba, orrisroot, ginger, galangal, and turmeric.*

Tous les mois, or Canna arrowroot, is furnished by the *Canna edulis*, nat. order *Marantaceæ*. The granules vary in diameter from ·0939 to ·0469 mm. [·00370 to ·00185 inch]. They present themselves under several forms, the smaller being granular or ovoid, the larger pyriform, whilst the largest granules are flat, oval, and pointed at their extremities. The hilum is annular, eccentric, the rings are incomplete, extremely fine, narrow, and regular. The starch dissolves easily in boiling water; solution of potash causes the granules to swell rapidly, and gives to the hilum and lines remarkable clearness.

Tous les mois can only be confused with the potato; the size is the chief distinction. The granules burst in water at 72°C., and they give a more regular cross when examined by polarised light than those of the potato.

Curcuma arrowroot, which is also called East Indian (though the arrowroot ordinarily sold as East Indian is a Maranta), is furnished by the *Curcuma angustifolia*. The granules are elongated triangular, or irregularly oval, flattened, and almost transparent. The normal measurement varies from ·0304 to ·0609 mm. [·0012 to ·00238 inch]. The hilum is eccentric, not very distinct; the concentric rings are clearly visible, and form segments of a circle. The application of heat or a solution of potash deforms the grains in a very irregular manner; they begin to swell about 72°C.

Maranta arrowroot, syn. *Jamaica*, *St. Vincent*, is derived from *Maranta arundinaceæ*. The granules are somewhat ovoid, flattened, and tending to a triangular shape in the larger, but the smaller may be circular. The concentric layers are always visible and numerous, but not very marked. Nucleus is central, or about $\frac{1}{6}$ eccentric—in some circular, in others linear; from the nucleus a little slit, filled with air, often goes to the edge. Length of granule 0·010 to 0·070 mm., average 0·036 mm. [= ·00138 inch]. Tumefaction in water begins at 76°C. The specific gravity of the starch taken in petroleum or benzole is 1·504; if dried at 100°C., 1·565.

Natal arrowroot is probably the produce of *Maranta arundinaceæ*, the same plant from which Maranta itself is derived, but growing in a different climate. The majority of the granules are broadly ovate, but some are occasionally circular. The dimensions are from ·0375 to ·0327 mm. [·00148 to ·00129 inch].

The eccentricity of the hilum ranges between $\frac{1}{13}$ and $\frac{1}{3}$. The laminæ appear under water with special clearness, and on this account granules of Natal arrowroot have been frequently mistaken for those of the potato.

Potato starch, syn. *Potato arrowroot.*—The starch derived from the potato (*Solanum tuberosum*). The granules vary greatly in shape and size, some being small and circular, others large, ovate, and oyster-shaped. The hilum is annular, and the concentric rings incomplete. In the larger granules the rings are numerous and distinct. The normal dimensions are ·0376 to ·06858 mm. [·0027 to ·00148 inch]. The eccentricity averages $\frac{1}{6}$. The granules float on chloroform.

Potato starch is frequently used as an adulterant of the arrowroots. The most reliable method of examination is careful microscopic observation, but there is also a different behaviour with regard to reagents, viz. :—

(1.) Maranta arrowroot, mixed with twice its weight of hydrochloric acid, produces a white opaque paste, whereas potato starch treated similarly produces a paste transparent and jelly-like.

(2.) Potato starch evolves a disagreeable and peculiar odour when boiled with dilute sulphuric acid, which is not the case with arrowroot.

(3.) An acrid oil may be extracted from the starch of the potato, but not from that of the Maranta.

Ginger.—The granules are variable in shape, but characteristic. The usual form may be described as shortly conical with rounded angles; the hilum and rings are very faint. Measurement about ·0376 mm. [= ·00148 inch].

The remaining starches belonging to this group are distinguished as follows:—

Galangal granules, skittle-shaped, with faint incomplete rings, an elongated hilum, with a normal measurement of ·0342 mm. [·00135 inch].

Calumba.—The starch granules of Calumba are variable in form, most of them are pear-shaped. They have a semilunar hilum, and faint complete rings. The measurement is about ·0469 mm. [·00185 inch].

Orrisroot.—The starch granules are of a characteristic elongated, oblong shape, with a faint hilum. Measurement ·028 mm. [·00092 inch].

Turmeric has oval, oblong, conical granules, with the rings well marked and incomplete. Normal measurement ·0376 mm. [·00148 inch].

CLASS II.—*The concentric rings all but invisible; hilum stellate. To this group belong the starches of the bean, pea, maize, lentil, dari, and nutmeg.*

The nucleus of the Leguminosæ is seen usually as a long, more or less stellate, air-filled black hollow. The concentric layers are recognisable if the starch is treated with chromic acid.

The starch from the *bean, pea, and lentil* are in shape oval, oblong, and almost identical; but the bean and pea have both a stellate hilum, whilst that of the lentil is a long depression. The granules of the bean are fairly uniform in size, averaging ·0343 mm. [·00135 inch]; those of the pea, on the other hand, are very variable in size, ranging from ·0282 to ·0177 mm. [·00111 to ·0007 inch], the smaller size predominating. The lentil granules average ·0282 mm. [·00111 inch]. The granules of the *nutmeg* are of small size and of characteristic shape. Measurement about ·014 mm. [·00055 inch]. The starch from the *dari* is in small elongated hexagons; average size ·0188 mm. [·00074 inch]. The starch from *maize* varies in shape from round to polyhedral; the granules are the same size as those of the dari; the distinguishing mark is the rounded angles of the polygonal granules.

CLASS III.—*Starches having both the concentric rings and hilum invisible in the majority of granules. This important class includes wheat, barley, rye, chestnut, acorn, and a variety of starches derived from medicinal plants, such as jalap, rhubarb, senega, &c., &c.*

Wheat starch is extremely variable in size, being from ·216 to ·0022 mm. [·00185 to ·00009 inch]. The granules are circular, or nearly so, and flattened. Polarised light shows a cross, but in water the effect is not great.

Barley.—The granules of barley are of fairly uniform size, viz., ·0185 mm. [·00073 inch], but a few measure ·07 mm. The shape of the starch is that of slightly angular circles.

Rye.—Rye starch is similar in shape to barley starch. The measurements are from ·0375 to ·0022 mm. [·00148 to ·00009]. The small granules are perfectly round, and here and there cracked.

Chestnut.—The starch grains vary much in form; they are round or elliptical, or three- or four-angled, with the angles rounded. In the place of a nucleus there is almost always a central hollow filled with air. The size is small and regular, being from ·022 to ·0022 mm. [·0009 to ·00009 inch], and this regularity of size is the chief means of distinction.

Acorn.—The starch granules of the acorn are almost round, or round-oval. A nucleus may be made out after treatment with chromic acid; eccentricity $\frac{1}{4}$. Normal measurement ·0188 mm. [·00074 inch].

CLASS IV.—*All the granules truncated at one end. This class includes sago, tapioca, and arum, besides several drugs, viz., the starches from belladonna, colchicum, scammony, podophyllum, canella, aconite, cassia, and cinnamon.*

Sago.—A starch obtained from the pith of certain species of palms, especially *Sagus levis,* and *S. Rumphii.* It exists in commerce as *raw* and as *prepared* sago; both have oval-ovate granules, the normal measurements of which are from ·0660 to ·0282 mm. [·0026 to ·00111 inch]. There is a circular hilum at the convex end of the raw sago granules, and rings are faintly visible; but starch granules from prepared sago have a large oval or circular depression, covering nearly one-third of each granule.

Tapioca is a starch furnished by the *Manihot utilissima,* which is more or less altered by heat, having been dried on hot plates. This causes some of the granules to swell, and thus renders indistinct in some cases the original structure. The starch is in groups of 2 to 8, or in isolated granules. When resting on its flat surface, the granule shows a little circle, and round this is a broad flat zone; but if resting on its curved surface, the granule shows contours varying from a kettle-drum to a sugar-loaf shape, and it can then be recognised that the nucleus does not lie in the centre, but in the axis of the granule, and always nearer to the curved than to the flat surface. A conical hollow exists under the nucleus, filled with a substance slightly refracting light. The normal measurement is from ·01879 to ·0140 mm. [·00074 to ·00055 inch].

Arum starch, sometimes called *Arum arrowroot,* has somewhat smaller grains than tapioca; they are truncated by two facets, the hilum is eccentric. The normal measurement is about ·014 mm. [·00056 inch].

CLASS V.—*In this class all the granules are angular in form; it includes oats, tacca, rice, and pepper, as well as ipecacuanha starch.*

Oat starch or meal.—The starch of the oat is mostly polyhedral, being irregularly from three- to six-sided—·0094 mm. [·00037 inch]. The principal starch with which it has been found adulterated is barley; but great caution must be used, for oatmeal contains little round masses extremely similar to barley.

Tacca arrowroot, also called *Tahiti arrowroot*, is extracted from the *Tacca Oceanica* and *pinnatifida*. The granules, when viewed sideways, are muller-shaped, with truncate or dihedral bases; when seen endways they appear circular, occasionally angular or polyhedral; sometimes a sort of contraction gives them a subpyriform appearance. The hilum is well developed, often starred. The normal measurement is from ·0190 to ·0094 mm. [·00075 to ·00037 inch]. It may be confused with maize starch, but tacca has *sharp* angles; maize, *rounded*.

Rice starch.—Each individual grain is polygonal, mostly five- or six-sided, here and there three-sided. If a high magnifying power, such as $\frac{1}{8}$ or $\frac{1}{12}$, be used, a starred hilum may be seen. The normal measurement is from ·0076 to ·0050 mm. [·0003 to ·0002 inch].*

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* Since we have devoted no chapter to the consideration of rice, it may be well to state briefly its composition here:—

Composition of Rice (LETHEBY).

Nitrogenous matter—Gluten,	6·3
Carbo-hydrates,	79·5
Fatty matter,	0·7
Saline matter,	0·5
Water,	13·0
	100·0

Composition of Dried Rice (PAYEN).

Nitrogenous matter,	7·55
Starch,	88·65
Dextrine, &c.,	1·00
Fatty matter,	0·80
Cellulose,	1·10
Mineral matter,	0·90
	100·00

The following is the composition of the ash of rice:—

Potash,	18·48
Soda,	10·67
Lime,	1·27
Magnesia,	11·69
Oxide of iron,	0·45
Phosphoric acid,	53·36
Chlorine,	0·27
Silica,	3·35
	99·54

An oil may be obtained from the embryo of rice. It has a density of ·924 at 15°C., and at 5°C. acquires a butyraceous consistence. It contains a large quantity of oleic acid, and much albuminous matter.—(A. PAVESI and E. ROTONDI, *Gazzetta Chimica Italiana*, iv. 192–195.)

Pepper.—The starch of pepper is in small polygonal granules, each of which, with a high magnifying power, is seen to possess a hilum. The normal measurement is from ·0050 to ·0005 mm. [·0002 to ·00002 inch].

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PART II.

WHEATEN FLOUR AND BREAD.

I.—WHEATEN FLOUR.

§ 4. *Constituents of Flour.*—*Flour*, in the common acceptation of the term, is ground wheat freed from bran.

The *physical characters* which flour should possess are as follows:—It should be an almost perfectly white, fine powder, with only the slightest tinge of yellow; the odour should be sweet, and it should be free from acidity. It should exhibit no trace of bran when pressed smooth with a polished surface; and it should have a certain amount of cohesiveness sufficient to retain for some time any shape impressed upon it by squeezing. The microscopical characters of good flour are: the absence of foreign starches, of fungi, &c., and the presence alone of the elements of ground wheat. (See pp. 15-19, for measurements of the starches.)

The chemical composition of ground wheat is represented in the following table, giving the mean of fourteen analyses by Peligot:—

	Mean of 14 Analyses.	Extremes, Max.	Min.
Water,	14·0	15·2	13·2
Fat,	1·2	1·9	1·0
Nitrogenous matter insoluble in water,	12·8	19·8	8·1
Soluble nitrogenous matter—albumen,	1·8	2·4	1·4
Soluble non-nitrogenous matter—dextrine,	7·2	10·5	5·4
Starch,	59·7	66·7	55·1
Cellulose,	1·7	2·3	1·4
Ash,	1·6	1·9	1·4

The percentage of ash from the whole wheat is much higher than that of ordinary flour, the bran containing much ash. Thus, 100 parts of bran contain—

Water,	13·1	per cent.
Albumen, coagulated,	19·3	,,
Fat,	4·7	,,
Husk and a little starch,	55·6	,,
Ash,	7·3	,,

whilst 100 parts of flour, according to Wanklyn, contain—

Water,	16·5	per cent.
Fat,	1·2	,,
Gluten, &c.,	12·0	,,
Starch, &c.,	69·6	,,
Ash,	·7	,,

The nitrogenous matter of the cereals has been usually determined by a combustion and subsequent estimation of the nitrogen. Mr. Church has, however, shown that this method of estimation is not perfectly reliable as a measure of the flesh-formers or albuminous matters, properly so called. In a valuable recent series of researches on this point, with regard to wheat, barley, and oats, Mr. Wigner has shown that these nitrogenous flesh-forming constituents have been over-estimated, since nitrogen combined as nitric acid, nitrous acid, and alkaloids, is present in larger quantities than has been hitherto supposed. This is more especially true as regards the husk and bran, very little non-coagulable nitrogenous matter being contained in the flour, properly so called. These analyses were carried out as follows:—

50 grains of the sample were ground in a warm porcelain mortar with enough carbolic acid to form a paste. Two or three drops of dilute acid were added, and the paste then diluted with hot carbolic acid and allowed to cool, filtered, and the filter washed with carbolic acid of the same strength. By this treatment all the true albuminoids were coagulated and remained in the filter, while any nitrogenous matter, either as nitrates, nitrites, alkaloids, or gluten, passed through the filter. The residue in the filter was washed down into the point as far as possible, and the filter dried, the residue detached, and the filter itself finely shredded with scissors and ground to powder, and then burnt in a combustion-tube in the usual way.

The samples were collected so as to give examples of every class of wheat, barley, and oats, and ground by the operator. Treated in this manner, Mr. Wigner found that 17·7 per cent. of the total nitrogen in wheat, 17·6 per cent. of that in oats, and 14·7 per cent. in that of barley, as an average, deduced from the examination of fifteen samples of each, was present in such a form as not to be capable of coagulation by carbolic acid. The extremes in various samples differed widely, and it would appear as though we may have by this process a method of distinguishing the true nutritive value of one sample of grain from another.*

The nitrogenous constituents of flour comprised under the

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* See *Analyst*, July, August, 1878.

name of *gluten*, are composed of at least four bodies—*gluten-caseine, gluten-fibrin, mucedin, and gliadin.*

Gluten may be obtained by merely kneading the flour into a paste, and then washing all the starch out of the paste in a thin stream of water. As thus obtained it is in the moist state a yellowish-grey, very elastic, adhesive mass; and when dry, somewhat horny. It dissolves for the most part in alkaline liquids and in acetic acid. From the gluten the four bodies mentioned may be separated as follows :—

1. *Gluten-caseine.*—The well-washed gluten is digested a few days with potash solution (for every 100 grms. of gluten about 3 to 4 grms. KHO). The clear solution is decanted from the insoluble residue, and precipitated by acetic acid in the least excess. The precipitate is exhausted successively with 60 per cent. and with 80 per cent. alcohol, then with absolute alcohol, and lastly with ether. The insoluble portion now consists of *gluten-caseine*, which may be purified by solution in weak potash lye, precipitated by acetic acid, washed with water and alcohol, and dried in a vacuum. It forms a whitish-grey, voluminous, earthy mass, soluble in dilute alkaline solutions, but insoluble in water, whether hot or cold. At 100°C. it soon changes into a modification insoluble in alkaline fluids. Its solution in very dilute alkaline fluids becomes turbid on exposure to the air, and is precipitated in a flocculent condition by the heavy metals.

The gluten-caseine of rye seems to be similar to that of wheat [*Ritthausen.*]

2. *Gluten-fibrin.*—The substances remaining in solution from 1. are gluten-fibrin, mucedin, and gliadin. The first is separated by distilling the united alcoholic extracts to one-half, when it separates as a brownish-yellow mass. It may be purified by repeatedly dissolving in a little 60 to 70 per cent. alcohol, from which it separates on cooling. This property is, indeed, characteristic of gluten-fibrin. It forms a tenacious brownish-yellow mass, becoming horny on drying. It is insoluble in cold water; boiling water partly decomposes and changes it into a modification insoluble in alcohol, acetic acid, and potash.

3. *Mucedin.*—The alcoholic extracts from 2. contain mucedin and gliadin, and are united and evaporated to dryness. The varnish-like residue is treated with ether to remove fat, and dissolved in warm 60 to 70 per cent. alcohol, allowed to cool, and filtered from any gluten-fibrin still remaining. The *mucedin* is now precipitated in a flocculent state by strong alcohol, and by a repetition several times of this operation is obtained pure. When fresh, it is a whitish-yellow, slimy mass; when dry, a

horny, crumbling mass. It dissolves easily in 60 to 70 per cent. alcohol, but is precipitated by 90 per cent. alcohol. The acetic acid solution is coloured a beautiful violet on the addition of sulphate of copper and potash, and slightly warming.

The mucedin from rye is similar to that of wheat [*Ritthausen*].

4. *Gliadin.*—Gliadin is obtained by evaporating the alcoholic solution left from 3. It then remains behind as a clear yellow varnish, which is so tenacious that it may be drawn into threads. By treating it with absolute alcohol and ether, it is changed into a friable, lustreless mass. It is easily dissolved by 40 to 80 per cent. alcohol, and this solution is made milky by absolute alcohol and water, turbid by ether. By boiling it is changed into an insoluble modification. If digested with cold water it dissolves, and the solution is opalescent and frothy, giving a precipitate with tannic acid and soda. Gliadin dissolves in dilute alkaline and alcoholic solutions and in acetic acid; on neutralisation, or on addition of salts of the heavy metals, precipitates are formed.

The constituents of gluten, based upon the researches of Ritthausen, have been given at some length, because it is possible that more work done in this direction may be useful in the practical analysis of flour.

§ 5. *Analysis of Flour.*—A careful preliminary microscopical examination, combined with measurements by a micrometer, &c., ought to discover any foreign starches. There are, however, certain chemical tests which have been proposed for the detection of potato flour and of bean flour.

M. Chevallier has recommended equal weights of flour and sand to be triturated with water until a homogeneous paste is formed, which is then diluted and filtered; to the filtrate is added a freshly-prepared solution of iodine, made by digesting for about ten minutes 3 grms. of iodine in 60 cc. of water, and then decanting. If the flour is pure, this addition will give a pink colour, gradually disappearing; whilst if potato starch should be present, the colour is of a dark purple, only disappearing gradually; by comparing the reaction with flour known to be pure, this difference of behaviour is readily appreciated.

M. Robiné separates the gluten as much as possible from the starch, allows the latter to deposit in a conical glass, when, since the potato starch is much heavier than the wheat starch, the former occupies the apex of the cone. The water is removed by siphoning and pipettes, and lastly the upper layer of the cone, consisting of gluten, &c., is taken away by a teaspoon, or other suitable instrument; the cone is received on a lump of dry plaster, the apex cut off and triturated in an agate mortar (glass, porcelain, and Wedgewood mortars do not answer), and tested with iodine, which gives a blue colour with potato starch, but under these circumstances, not with wheaten starch, because the friction has not been sufficient to tear the envelopes of the latter.* This test of M. Robiné should, however, only be undertaken combined with microscopical examination, or else great errors might result.

M. Rodiguez has ascertained that when pure flour is submitted to dry distillation in a stone retort, and the distillate is collected in a vessel containing water, the latter will remain perfectly neutral. But if bean, pulse, or peameal has been added, the water will have an alkaline reaction. This test appears of doubtful value, for, provided the distillate is alkaline, the alkalinity may, it is evident, have arisen from a variety of causes besides the addition of the substances mentioned. It has also been shown by Bussy that certain cereals yield on distillation an acid product.

Lassaigne (taking advantage of the fact that haricot beans, as well as beans, contain a tannin in their envelopes) adds a salt of iron, which with pure flour gives a feeble straw colour, but mixed with either of the two mentioned, or, of course, with any substance containing tannin, gives various shades, from orange-yellow to very dark green.

The mineral adulterations are mainly to be sought for in the ash, with the exception of alum, which may with greater rapidity be detected in the cold extract.

Mr. Carter Bell directs 50 grms. of flour to be weighed out and mixed by the aid of a glass rod with 50 cc. of distilled water, to this is added 5 cc. of recently prepared logwood solution, alkalised by 5 cc. of solution of ammonium carbonate. If $\frac{1}{10000}$ part of alum is present, the flour will become of a lavender-blue colour instead of pink. An approximate estimate of the quantity may be obtained by having a standard solution of pure alum 1 grm. to the litre, and adding known quantities to exactly similar emulsions of pure flour, and testing as before with logwood, until an emulsion is obtained of very similar hue to the flour originally tested. If the cold extract gives a blue tint with the logwood test, or if the flour be submitted to dialysis, and the diffusate responds, alum is present as alum, and is not derived from dirt, clay, or from the millstones themselves.† It has

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* The process of subsidence itself is good, and, indeed, essential to ensure the detection of small percentages of potato flour in wheat flour, for it enables the microscopist to concentrate the substance sought for.

† The millstones are sometimes mended with an alum cement. This circumstance will of course from time to time be utilised for purposes of defence.

been proposed to trace the alum by estimation of the sulphates in the cold extract, but there are practical difficulties which cannot be fully surmounted.

Dr. Dupré has suggested shaking the flour up with chloroform, and then allowing it to stand: the flour floats, the mineral impurities subside to the bottom, and are removed. The author has recently made some experiments in this direction, and without hesitation recommends it as the best known process to obtain alum as alum. Directly water is added to alumed flour, it is impossible to isolate the alum again, for it not only is decomposed by the phosphate of potash, but also forms an insoluble combination with the gluten. Hence we are compelled to treat the flour with some liquid in which alum is insoluble, and of a specific gravity sufficient to allow of the separation of the alum from the lighter flour by subsidence. Chloroform answers this purpose admirably. A long cylinder, closed at the bottom with a tap of not too fine a bore, is taken, and a weighed quantity of the flour, from a quarter to half a pound, is placed in it, and sufficient methylated chloroform added to form a thin sort of paste; the cylinder is closed by a stopper, shaken up once or twice, and allowed to stand over night. The next morning the lower stratum of liquid is drawn off to the extent of from 10 to 30 cc. This will contain sand from the millstones, sulphate of lime, alum, or any other mineral powder of a greater specific gravity than chloroform, that happened to be in the flour; this fluid is placed in a burette, some more chloroform is added, and the matters allowed to again subside; lastly, the powder, with a little of the chloroform, is drawn off into a watch-glass, the chloroform evaporated, and the powder digested in warm water, filtered into a clean watch-glass, and allowed to evaporate spontaneously. If alum were present crystals will be obtained, easily identified by their form, and these if necessary can be produced in court as a "*corpus delicti.*"[*] The chloroform which has been used may be in a great measure recovered by simple filtration, then purified by distillation in the usual way.[†]

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[*] The estimation of the total alumina in flour is detailed at p. 33.

[†] The following case is one of great interest and importance as regards alum in flour:

THE SELBY FLOUR CASE.

The defendants were summoned on two separate informations under the Sale of Food and Drugs Act, 1875, for having sold flour mixed with alum, in one sample equal to 18 grains of alum to 4 pounds weight of flour, and in another sample to 10 grains of alum to 4 pounds weight of flour. A report was read from three of the analysts at Somerset House, giving the result of their analyses of the same samples, which was to the effect that

§ 6. *Proximate Analysis of Flour.*

§ 6. The constituents of flour to be determined are—

(1.) Water.
(2.) Fat.
(3.) Cold Water Extract. { Sugar, Gum, and Dextrine.
Vegetable Albumen.
Phosphate of Potash. }
(4.) Gluten.
(5.) Ash.

(1.) The *water* is taken in the ordinary way; that is, by

the sample marked 29 contained alumina equivalent to $9\frac{2}{10}$ grains of ammonia alum, and the sample marked 30 contained alumina equivalent to $21\frac{1}{10}$ grains of ammonia alum per 4 pounds of flour. Sample 29, according to their experience, contained no more alum than was found in genuine flour, and with regard to the excess of alumina in number 30, the results of their experiments did not enable them to confirm that it existed in the flour in the form of alum.

Superintendent Gill explained that he had sent to Somerset House particulars of Mr. Allen's analysis, in accordance with a request from the analysts there. Since the last hearing he had also sent a letter to Somerset House, to which he had received the following reply:—

"With reference to the preceding letter, we have to state:—First, We are of opinion that the samples did not contain alum, and we intended this to be understood by the terms of our certificate. Second, Both samples were very limited in quantity, that marked No. 30 barely weighing 5 ounces. Although we were enabled, with the quantity at our disposal, to prove by duplicate experiments the presence of an excess of alumina in No. 30, and to satisfy ourselves of the absence of alum in both samples, it would have been more satisfactory to us to have had a larger quantity, that we might have been able to determine and state in our certificate in what form the excess of alumina existed in No. 30 flour.—(Signed) J. Bell, R. Bannister, and H. J. Helm."

In the cross-examination of Mr. Allen, the analyst, he stated that he first tested the bread he had made from the sample of flour sent to him by the logwood test, which told him that there was something wrong with the flour. Having found this, he then ascertained the amount of alumina it contained by a process he had already described.

Mr. Cadman—To put it shortly, you found something wrong by one test; by another test you found what you call an excess of alumina, and then you put the two together and calculated alum. Is that so?—Yes.

Mr. Cadman—Did you by any process you used find one speck or tittle of alum as alum?—No, nor anybody else. Nobody ever found alum in bread as such.

Mr. Hemsworth—The analysts at Somerset House agree as to the alumina, but they don't say in what form it is. We want to know their opinion as to what that excess is. There is a property in the flour which ought not to be in it.

Mr. Cadman—That excess of alumina might arise from the process of veighing carefully about 1 to 3 grms. in a tared dish, and xposing it to the heat of the water-bath until it ceases to lose veight.

(2.) The *fat*, according to the researches of Peligot, must be letermined in the *perfectly dry* flour, error resulting in any other ase.

(3.) The *cold extract* is obtained by digesting 10 grms. of flour in 00 cc. of water, and filtering and evaporating down 250 cc. in platinum dish. According to Wanklyn, 100 grms. of flour ield to water—

	Grms.
Sugar, gum, and dextrine, ...	3·33
Vegetable albumen, ...	0·92
Phosphate of potash, ...	0·44
	4·69

On igniting the extract the ash should consist entirely of

nanufacture, and that being so, under the words of the section the defendnts cannot be convicted. They had heard that Egyptian wheat was very lirty. Well, the defendants had special machinery for scrubbing and vashing the wheat. They brushed it to take off every bit of clay, but if ny specks remained it might be sufficient to account for the presence of lumina.

Mr. Richard Bannister, one of the analysts at Somerset House, was then alled by Mr. Cadman, at the request of the Bench. His evidence was to he effect that the result of his and his colleagues' analyses of the flour was he same as Mr. Allen's, but they came to different conclusions as to the xcess of alumina. Mr. Allen said it existed in the form of alum, but they ound that it was not alum.

Mr. Hemsworth—Then what is it?—I am sorry I cannot tell you.

But there is something in the flour that ought not to be?—There is more lumina, but it may come from clay or dirt, or something else, we are unable o say what.

Mr. Allen, in answer to the Bench, said he still maintained his belief that here was alum present in the flour. At the same time Mr. Bannister was uite justified in what he had said, because he had failed to get the precise esult which he (Mr. Allen) got. He had the authority of Dr. Hassall hat the logwood tests sometimes failed.

Mr. Bannister said that at the time they tested the samples sent to hem, they also tested twenty other samples of what they knew to be pure lour, and the result in all the cases was the same. They then added lum to some samples, and the test showed when the alum was present; o that he thought they were justified in concluding that the test was a ood one.

After this evidence, the magistrates retired and consulted, and on their eturning into court, Mr. Hemsworth said that they had thought the matter ver, and found the evidence so conflicting that they had decided to dismiss he information.

Mr. Cadman said that had the Bench not thought it right to dismiss the harge at that point, he would have called witnesses to prove that it was npossible for a miller to put alum into the flour.

phosphate of potash. When the weight of the ash is known, it may be dissolved in water, and the quantity of phosphoric acid estimated by titration with uranium solution, and if from this there is any discrepancy between the calculated phosphate of potash and that found, the ash should be carefully examined.

The determination of the sugar and dextrine may be made by the processes described at p. 8; but it is usually sufficient to obtain merely the weight of the cold extract and the weight of its ash.

(4.) The *gluten* or *albuminoids* can only be approximately determined by the washing process, but more accurately estimated by a combustion with cupric oxide and careful measurement of the nitrogen. The percentage of nitrogen found, multiplied by 6·33,* equals the amount of albuminoids. The most rapid process of all, however, and one of very fair accuracy, is that proposed by Mr. Wanklyn,—viz., distillation with alkaline permanganate. 20 mgrms. of flour are distilled with a strongly alkaline solution of potassic permanganate, such as is used in water analysis, and the ammonia either titrated or estimated by the colorimetric process known as *Nesslerising*, 10 parts of ammonia equalling 100 of gluten.

(5.) The *ash* is burnt in the usual way, as described at p. 4. In the ash is detected any mineral adulteration such as chalk, magnesia, alum (see p. 33), &c.: it should be below 1 per cent., and if it even attains 1 per cent., mineral adulteration is probably present.†

II.—BREAD.

§ 7. *Adulterations of Bread.*—The adulterations of bread enumerated by writers are sufficiently numerous, but those actually proved to exist are but few. Among organic additions rice flour, potatoes, bean flour, and pea flour, are usually given; among mineral, alum, borax, sulphate of copper, sulphate of zinc, chalk, and carbonate of magnesia.

In 1843 and 1847, some bakers in Belgium were convicted of adding sulphate of copper to their bread, and this fraud has been repeated recently by a baker of Calais. There is,

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* As already explained, there is no great error in the case of flour in operating in this way.

† With regard to the adulteration of Ergot in flour, see the section on that subject in the second portion of this work.

however, but little evidence to show that English bakers, as a common practice, add anything in the way of adulteration save alum; at all events, no convictions for any other adulteration are known.

It is an extremely difficult thing to detect small percentages of rice flour, potato flour, bean flour, &c., when in the form of bread. The only feasible course appears to be, to make bread of flour adulterated with different quantities of these substances, and then to compare the microscopical appearances of sections of these with pure bread.

§ 8. *Alum in Bread.*—Alum is added to bad or slightly damaged flour by both the miller and the baker. Its action, according to Liebig, is to render insoluble gluten which has been made soluble by acetic or lactic acids developed in damp flour, and it hence stops the undue conversion of starch into dextrine or sugar.

The influence of alum on health, in the small quantities in which it is usually added to bread, is very problematical, and rests upon theory more than observation; as a fact, directly water is put to the dough, the alum (unless, indeed, it has been added in excessive quantities) is broken up and ceases to exist as alum. But notwithstanding the obscurity as to its action on the economy, there can be no difference of opinion that it is a serious adulteration, and not to be permitted.

In searching for alum, the crust and the crumb should be analysed separately, for many bakers use for the latter a flour technically called "cones," which is strongly alumed, and prepared from a fine species of wheat grown in the south of Europe, mixed with rice. This mixture is used for dusting the kneading trough and kneading boards; in point of fact, for "*facing*" the sponge previous to baking it. To search for alum in the crust, there is no other method save burning to an ash, as described at p. 4; but with regard to the crumb of bread, the *qualitative* test is the same as for flour, viz., an ammoniacal tincture of logwood (p. 28). The crumb of pure bread, when soaked in the tincture for a few minutes and then squeezed, exhibits a pink colour, the crumb of alumed bread a blue colour. This blue colour is not absolutely decisive of alum, for bread adulterated with magnesia carbonate exhibits the same reaction, but if such a colour is produced, the bread requires further examination. The *quantitative* method for estimation of the *total alumina* in bread, as originally proposed by Dupré, and slightly modified by Wanklyn, is as follows:—100 grms. of bread are incinerated in a platinum dish, until the ash does not exceed 2 grms. in weight. The ash is then moistened with 3 cc. of pure strong hydrochloric acid, and 20 to 30 cc. of distilled water added; the whole is boiled, filtered, and the precipitate (consisting of unburnt carbon and silica) well washed, dried, burnt, and weighed. To the filtrate containing the phosphates, 5 cc. of strong solution of ammonia are added. If the bread has been alumed, the phosphates now precipitated are those of lime, magnesia, iron, and alumina, of which the latter (viz., phosphate of iron and alumina) are insoluble in acetic acid, so that their separation is easy. The liquid is *strongly acidified* with acetic acid, boiled and filtered, and the phosphates of alumina and iron washed and weighed. Unless the liquid has been acidified sufficiently, phosphate of lime contaminates the precipitate and vitiates the results, so that this is an essential point. The last step is resolution of the precipitate in acid, and the estimation of the iron; this is usually best effected by a colorimetric process. A standard solution of metallic iron is made by dissolving a gramme of fine iron wire in nitro-hydrochloric acid, precipitating with ammonia, washing the peroxide of iron, and dissolving it in a little hydrochloric acid, and diluting accurately to one litre [1 cc. = 1 mgrm. of metallic iron]. On now adding to an unknown very dilute solution of iron a known quantity of strong ammon. sulphide, a certain colour is produced, and this colour is exactly imitated in the usual way by a similar quantity of ammon. sulphide and the standard solution, the whole operation being conducted on the well-known principles of colorimetric estimation. The amount of iron in the precipitate being known, it is calculated into phosphate, and the phosphate of iron subtracted from the total weight of the precipitate gives the weight of the phosphate of alumina. Unalumed bread appears to contain about ·005 per cent. of phosphate of alumina, $Al_2O_3PO_5$, or if expressed as the amount of alum in grains on the 4lb. loaf, equivalent to 6 grains. As a fact, however, most analysts allow a little more than this—viz., 8 grains on the 4lb. loaf, as possible from accidental impurities. From Mr. Wanklyn's experiments it would seem that in the case of bread ash, it is unnecessary to evaporate the hydrochloric solution to dryness, as is usually done, and that the separation of silica is complete by the method just detailed.

Another perfectly valid way of estimating alumina in bread or flour, consists in a modification of the old Normandy process. The bread is burnt up as before, the ash powdered and treated with hydric chloride, diluted with water, boiled, and filtered. The filtered solution is again boiled, and whilst boiling poured into a very strong solution of sodic hydrate, the whole boiled, filtered, and washed. To the filtrate is added a few drops of disodic phosphate, it is then slightly acidified with hydric chloride, and subsequently rendered just alkaline by ammonia. The precipitate is collected, washed, and weighed as alumina phosphate.

The following table will be of use in the conversion of phosphate of alumina into alum :—

Phosphate of Alumina, $Al_2 O_3 PO_5$		Ammonia Alum, $NH_4 Al2SO_4 12H_2 O$	Potash Alum, $KAl2SO_4 12H_2 O$
Parts.		Parts.	Parts.
1	=	3·733	4·481
2	=	7·466	8·962
3	=	11·199	14·443
4	=	14·932	17·924
5	=	18·665	22·405
6	=	22·398	26·886
7	=	26·131	31·367
8	=	29·864	35·848
9	=	33·597	40·329
10	=	37·336	44·813

Other mineral adulterants are not likely to be found in the ash of bread. The ash of bread varies from 1·3 to 2 per cent. If any weight beyond this be found in a properly burnt bread ash, it should be examined with great care, more especially for magnesia and soda salts.

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PART III.

MILK — BUTTER — CHEESE.

I.—MILK.

§ 9. *Constituents of Milk.*

§ 9. Any other milk than that derived from the cow can scarcely be said to exist in English commerce, so that cows' milk alone will be treated of in this work. The constituents of cows' milk are—

Water.	
Fat.	
Caseine,	Albuminoids.
Albumen,	
Nuclein,	
Lacto-protein,	
Milk Sugar.	
Potash,	Ash.
Soda,	
Lime,	
Magnesia,	
Phosphoric Acid and Chlorine, in combination with the above,	

The *fat* of milk is practically the same as butter fat, a description of which is given at p. 67.

The *albuminoids* comprise at least three, if not four, nitrogenous bodies, all of which are collectively in analysis termed *caseine.* As, however, only one of the four bodies is true caseine, this is a term of doubtful propriety; but it has been so long used, that it can hardly be changed without inconvenience. The other members are *albumen, nuclein,* and *lacto-protein.*

Caseine is almost peculiar to milk; its presence has, it is true, been asserted in the fluids of cysts, in serum, and in muscle, but it has probably been confused with globuline. There is, however, a substance in the nerve tissue which is without doubt allied to caseine. Precipitants of caseine are numerous—lead-acetate, cupric-sulphate, alum, mercuric-chloride, tannic acid, rennet, sulphate of magnesia, and mineral acids, if not too dilute.

The methods in use for the separation of caseine are—precipitation by sulphate of magnesia, a process not conveniently applicable to cows' milk, or precipitation by an acid.

To perform the latter with success, it is absolutely necessary to dilute the milk with a large volume of water, then hydrochloric acid is added drop by drop, until a good distinct flocculent precipitate is formed. The liquid is filtered, and the coagulum washed successively with cold water, alcohol, and ether. As thus obtained, moist caseine presents itself as a white, brittle, transparent substance, insoluble in water, easily soluble in very dilute hydrochloric acid, as well as in very dilute soda solution. It apparently is not otherwise acted on by such liquids; but in concentrated alkaline solutions it is changed—at common temperatures slowly, at higher quickly—with formation of sulphide of the alkali, but without any marked difference in the action of the caseine towards acids and alkalies. Whilst pure caseine is insoluble in solution of salt and in water; it is in the presence of phosphate of soda (as, for example, in the milk itself) not precipitated by simple neutralisation, but must first be strongly acidified. Cold alcohol precipitates caseine completely from a solution which is slightly alkalised, but also dissolves some of the precipitated caseine.

Caseine not being so easily soluble in dilute acetic as it is in dilute hydrochloric acid, a solution in the latter solvent (if not too acid) is precipitated by acetate of soda. Solutions in either of the acids mentioned give a precipitate with potassic platinic cyanide. When moist caseine is dissolved in hydrochloric acid, it gives a solution which becomes of a violet colour. Boiled with caustic potash, caseine evolves ammonia, and its putrefactive products are similar to those of fibrin.

Caseine in combination with sulphate of magnesia freed from fat, and in aqueous solution, turns a ray of polarised light $-80°$, in weak alkaline solution $-70°$, in very dilute alkaline solution $-87°$, in strong alkaline solution $-91°$. It has been supposed that caseine is held in solution by phosphate of lime, but this (according to A. Schmidt) is erroneous; for by rapidly removing by diffusion all soluble salts, a caseine precipitate can be obtained by the addition of an acid.

Serum albumen is found in milk, especially in the beginning of lactation. Its average amount in cows' milk, according to M. Nenzcki, is 3·14 per cent.; according to J. Kuls, it is from 3·40 to 3·43 per cent.

The albumen may be precipitated by neutralising with acetic acid, warming the mixture, and then adding alcohol to the extent of about 70 per cent. of the whole fluid. The more usual way of separating the albumen, however, is to dilute the milk wenty times its volume, and to drop from a burette very te acetic acid, until a slight precipitate begins to appear, then is passed through the liquid, and the diluted milk allowed tand for some hours. The caseine, mixed with fat, settles to bottom, and can be easily separated by filtration. The clear ate is now boiled, and the albumen precipitated.

ure precipitated serum albumen,* when carefully dried at w temperature or *in vacuo*, is a yellowish, brittle, glassy-sparent, and somewhat hygroscopic substance. If fully dry, ay be heated to 100°C. without decomposition. In water it s a clear, glutinous solution; it turns a ray of polarised yellow t to the left – 56°. If salts are present, it is precipitated by hol; but carbonic, acetic, tartaric, and phosphoric acids do not ipitate albumen. A small quantity of a dilute mineral acid s no opalescence; with a larger quantity of concentrated eral acid, the solution becomes troubled, and the deviation ray of polarised light increased; and through a still larger ntity of acid, it is precipitated as *acid albumen.* Pure con-rated hydrochloric acid, added in excess, gives first a floccu- precipitate, which again dissolves into a clear fluid, and in a solution the rotation of a ray of polarised light equals ·7°. By the addition of water to this solution, a flocculent ipitate is formed, which after filtration and pressing dissolves ater, and shows all the properties of *hydrochlorate of acid men;* in the acid solution a peptone-like body remains unpre-ated. Potash or soda-lye changes, in like manner, serum men into alkali albuminate.

n heating a solution of albumen in fluids containing salts to tle under 80°C., it coagulates or is precipitated. The exact perature at which this takes place is influenced by the salts ent. Common salt and other neutral salts of the alkalies r, carbonates of the alkalies raise, the coagulation tempera-. By most salts of the heavy metals albumen is precipitated, at the same time changed.

uclein, $C_{29}H_{49}N_9P_5O_{22}$, was first discovered by Miescher† in and in the yolk of eggs; but Lubavin‡ was the first who ined it from cows' milk. Besides these sources of nuclein, f§ has found it in beer-yeast;|| Plósz in the nuclei of the red d-corpuscles of birds and amphibia, and in the liver cells;

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t is almost unnecessary to say that the method given does not precipi-lbumen in a pure state; pure serum albumen can only be obtained by sing a solution of precipitated albumen.

Med. Chem. Untersuchungen herausgez. v. Hoppe Seyler. Heft 4, 1872, und s. 502.

b., s. 486.

§ *Ib.*, s. 461.

|| *Ib.*, s. 463.

and lastly, Miescher and Sertoli* in the spermatic fluid of various animals.

Freshly precipitated nuclein is colourless, amorphous, easily soluble in ammonia, soda solution, and phosphate of soda, and somewhat soluble in water. Strong nitric acid imparts no colour to nuclein when cold, but on warming it becomes a pale yellow, and if the solution be saturated by ammonia, a deep brown yellow. Iodine colours it slowly and weakly yellow, and the tint is tolerably permanent. When lead oxalate is added to a solution of nuclein in sodium acetate, the lead salt of nuclein is obtained as a granular precipitate.† The relation of lead to phosphorus in the precipitate is as Pb_3 to P_2.

The reaction which especially separates nuclein from other albuminoids is the production of no red colour, either by Millon's reagent, or by a copper salt added to a solution of nuclein alkalised by soda-lye. Sulphate of copper precipitates dilute solutions of nuclein, and the copper compound is insoluble in water. Nitrate of silver, as well as chloride of zinc, are also precipitants, but the solution must not be too dilute.

Nuclein is remarkable for its high percentage of phosphorus, the formula given above corresponds to 9·61 per cent. Miescher found 9·59 per cent.

Lacto-protein.—There is also present in milk a small quantity of an albuminoid called lacto-protein, which may be separated from albumen and caseine by adding a solution of carbolic acid, and then warming.

There are other methods of separating the albuminoids, *e.g.*, Selmi, fearing that acid or alkaline reagents alter the albuminoid constituents of milk, exposes the fluid to cold. This has the effect of precipitating a gelatinous caseine, which may be removed by simple filtration; the filtrate, on the addition of one-fifth of its volume of absolute alcohol, deposits a second albuminous body, and a third is thrown down on adding its own volume of absolute alcohol.

The estimation of the relative quantity of the different nitrogenous substances, though of minor importance in the general examination of milk, becomes of great interest in the question of whether a given milk is derived from a healthy cow, or not. This estimation is most conveniently carried out by Mr. Wanklyn's ammonia process:—5 cc. of milk are diluted with pure water, so as to measure half a litre, 5 cc. of this fluid (equalling ·01 cc. of milk) are placed in a flask and boiled with a strongly alkaline

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* *Verhandl. d. Naturforsch. Gesellschaft in Basel*, 1874, vi. 1, Heft. s., 138 *Gazetta Med. Veterinar.* Milano, 1872.

† Lubavin. *Bull. Soc. Chim.* [2], xxxi. 213.

solution of permanganate of potash, and the ammonia in the resulting distillate Nesslerised and estimated in the usual way. From another measured or weighed quantity the caseine is precipitated and filtered off, but in other respects dealt similarly with, the difference between the two estimations giving the albumen. No practical purpose is served in pursuing the research further, unless a complete scientific analysis is required, in which case the same principles may be applied.

§ 10. *Milk Sugar*, $C_{12}H_{22}O_{11}H_2O$, has been hitherto found only in human milk, in the milk of plant-eating animals, and in the milk of the bitch, and it is the only sugar that has been recognised in these secretions. It forms colourless, hard, glittering, and often tolerably large crystals belonging to the rhombic system. The specific gravity of milk sugar is 1·53, its solution turns a ray of polarised light to the right = + 58·2°. It is soluble in 6 parts of cold and 2½ parts of boiling water, but insoluble in absolute alcohol or ether. Its watery solution has a weak, sweet taste, and a neutral reaction. Heated to 100°C., it gives a brown-coloured solution; if heated carefully to 150°C., it loses an atom of water without further decomposition. Like grape sugar, milk sugar is more easily decomposed by alkaline than by acid solutions. The former, even at common temperatures, gradually becomes brown.

Milk sugar combines readily with bases. If hydrated copper oxide be dissolved in a solution of milk sugar to saturation, and the saturated liquid evaporated to dryness in vacuo, over sulphuric acid, deep blue crystals are obtained of the same form as those of milk sugar itself; they, however, quickly decompose with separation of copper oxide. The alcoholic fermentation with yeast of solutions of milk sugar is but imperfect; but on the other hand, lactic fermentation, either by adding to the solution a little cows' milk, or cheese and chalk, can be easily induced, at a temperature not beyond that of the blood; the lactic fermentation is always accompanied by the formation of a little alcohol and carbonic anhydride.

By acetate of lead and ammonia, milk, as well as grape sugar, is fully precipitated from its watery solution, whilst boiling with neutral acetate of lead neither precipitates nor changes it. Milk sugar reduces oxides of copper, bismuth, and silver, together with indigo, as easily as grape sugar. It, however, reduces an alkaline copper solution* in a different proportion

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* The standard solution is 34·64 grms. sulphate of copper dissolved in 200 cc. of water, and to this solution is added a solution of 173 grms. of double tartrate of potash and soda in 480 cc. of solution of soda; specific gravity 1·140; the whole made up to 1 litre. (See p. 7.)

from grape sugar. 100 parts of milk sugar = 147·76 CuO (*Muter*). (See p. 7.) If milk sugar be warmed with dilute nitric acid, mucic acid, tartaric acid, and acetic acid are among the products; if the decomposition be carried further, oxalic acid is also produced.

§ 11. *Ash of Milk.*—If a considerable quantity of cows' milk be taken, evaporated down, very gently charred, and then extracted with boiling water, the filtrate evaporated to dryness, and ignited with great care for the soluble salts, and the charred mass (now freed from volatile chlorides) ignited to a perfect ash, the following will be its average composition :—

	Per cent.
K_2O	18·82
Na_2O	11·58
CaO	22·97
Fe_2O_3	·06
P_2O_5	27·03
Cl	16·23
MgO	3·31

The ash from 100 grms. of genuine milk will approximate to the following composition :—

	Per cent.
K_2O	·1228
Na_2O	·0868
CaO	·1608
Fe_2O_3	·0005
P_2O_5	·1922
Cl	·1146
MgO	·0243
	·7020

About one-third of the chlorine, in the ordinary method of burning a milk residue, volatilises, so that the amount found by analysts is generally from ·06 to ·09 per cent. If the ash be treated in the way mentioned, higher figures for chlorine will always be obtained.

These different substances in milk—fat, caseine, salts, &c.—are partly in suspension, partly in solution. The fat is certainly emulsified, or in a fine state of division disseminated through the liquid, and some portion, if not all, of the caseine would also appear to be in suspension; for if milk be filtered through a porous earthenware cell, the filtrate contains albumen, but no caseine.—(*Baumhauer-Knapp.*) On allowing milk to rest, some portion of the fat rises to the surface in the shape of cream; but however long milk may stand, the lower stratum always retains some milk fat. The most complete removal of the fat in the shape of cream is obtained by adding a little water to the milk, and then llowing it to stand in large open pans in a warm place; in other vords, strictly following the practice of the Devonshire dairy nen in making "*Devonshire cream.*"

§ 12. *Average Composition of Milk.*—The cardinal point on vhich the analysis of milk depends is its fairly constant omposition. This was first rigidly demonstrated by Mr. Wanklyn in his treatise on "Milk Analysis," published in 1874; nd all subsequent researches, a few of great value, have lone little but confirm his conclusions. Mr. Wanklyn, in the reatise alluded to, divided milk into "*solids not fat,*" which ncludes the albuminoid principles, the ash, and the sugar, and '*fat,*" the main constituent of the cream. He showed that he "fat" varied within somewhat wide limits, whilst the "solids not fat" in healthy, fairly milked cows, never fell *below* 9·0 per ent., the average being somewhere between 9 and 10 per cent. This standard of the amount of solids was subsequently adopted by the Society of Analysts, who resolved to consider all milk sold s new milk, adulterated, which contained less than 9·0 per cent. of solids not fat, and 2·5 per cent. of milk fat. The following able gives the average composition of new milk :—

	Average Country Milk. (Wanklyn.)	Average Town-fed Milk. (Wanklyn)	Milk of Alderney Cow. (Wanklyn.)	Mean Results of Analysis of 181 Cows. (Carter Bell.)
	Per cent. by weight.	Per cent. by weight.	Per cent. by weight.	Per cent. by weight.
Water, ...	87·55	85·94	87·34	86·20
Fat, ...	3·07	4·01	3·22	3·70
Caseine, . . .	4·04	5·02	4·61 }	9·14
Milk Sugar, . .	4·62	4·30	4·13 }	
Ash, ...	·72	·73	·70	·76
	100·00	100·00	100·00	
Solids not fat, .	9·38	10·05	9·44	9·90
Total Solids, . .	12·45	14·06	12·66	13·80

Some hundreds of analyses might be collated, showing that, ractically, the standard adopted permits the milkman to water his milk at least 2 per cent. For instance, in the analysis made recently by Mr. Carter Bell * of the milk of 183 cows, milked in

Analyst, No. 21, 1877.

his presence, the lowest percentage of solids not fat is given as 9·2. Now, to such a milk, water could be added in the proportion of 2½ per cent. Six of Mr. Bell's cows averaged, solids not fat, 11·3 per cent., and such milk could be watered 20 per cent. Lastly (*vide* Table), Mr. Wanklyn's average country milk could be watered 4 per cent., his average town milk 10 per cent., the milk of the Alderney cow 4½ per cent., and Mr. Bell's mean of the milk of 181 cows 9 per cent., to bring it down to the Society of Analysts' standard. If, knowing these facts, any large firm should choose to send their milk out by analysis, carefully worked down to the lowest standard, the public would not be a loser; for, taking the commercial milk of the country as a whole, it is greatly to be feared that the average percentage of solids would be found *under* the lowest estimate of the Society.

§ 13. *Fore-milk.*—The average composition of milk has been stated, but it must be noted that milk *direct from the cow*, if only partially milked, may be very different in composition. There is a milk which may conveniently be called *fore-milk*, and this milk may be almost destitute of cream. Two cases, at least, are on record (one of them happening to the writer), in which milkmen endeavoured to throw discredit on certain analysts in particular, and chemical investigation generally, by having a cow only partially milked in the presence of such officials as policemen, &c., and sending this milk to be analysed;—*e.g.*, in a sample of fore-milk the author found—

Solids not fat, ...	9·70
Fat, ...	·20
Water, ...	90·10
	100·00
Ash, ...	·72
Specific gravity, ...	1035

This milk was sent to two other analysts with similar results. In view of the possibility of such cases, it is best to certify all milk deficient in cream as having had the cream "*abstracted*," discarding the word "*skimming*," for fat may be abstracted in other ways than those commonly known. With regard to a magisterial decision in "fore"-milk, see p. 64.

§ 14. *Skim Milk.*—Skim milk, as its name denotes, is milk which has been deprived of a portion of its cream. As existing in commerce, it varies in its content of fat from about 2 to 1 per cent., but if unwatered, the *solids not fat* are rather higher than in the milk from which it has been derived. Notwithstanding this fact, which admits of abundant proof, the Society of Analysts have iggested that skim milk should contain at least 9 per cent. of ilk solids, and it is the custom of analysts to pass skim milk hich comes up to this standard.

§ 15. *The Analysis of Milk* is very simple. A known quantity is ried up, the loss equals the water; the residue is exhausted by ther, the loss equals the fat; the remainder is now treated with eak alcohol, the loss equals the milk sugar; and lastly, the resiue is burnt and weighed as "ash."

Before all these operations, it is usual and advisable carefully to ke the specific gravity of the milk in the ordinary way by a pecific gravity bottle. Mr. Wanklyn very rightly throws discredit on the lactometer, but the specific gravity taken with reat care does not only confirm and verify the results of analysis, ut it enables the ordinary pipettes to be used, and then the esults to be stated by weight. Genuine milk, with no great xcess of cream, will be found to vary from 1029 to 1035; the ream lowering the specific gravity, the total solids raising it. Anything below 1029, according to the writer's experience, is vater, save in those exceptional cases of very rich milks.*

Specific gravity tables have been constructed, giving the perentage of water both in unskimmed and skimmed milk, but the ata are not as yet accurate and numerous enough to be relied pon, and therefore need not be reproduced here. After the pecific gravity is taken, the solids may certainly in the quickest vay be dried up, as proposed by Mr. Wanklyn, by putting 5 cc. n a little shallow platinum dish over a water bath; such a thin ilm dries up in from 2½ to 3 hours, without stirring or other nanipulation. A more convenient method, however, is that dvocated by Dr. Redwood—viz., evaporation in porcelain dishes. The latter are of a capacity of nearly 50 grms., and each carries glass stirrer, and bears a number, and its weight, including that f the stirrer, is carefully taken. This weight will often be ound not to vary materially for a considerable time. The dishes, n number according to the amount of work to be done, are supported on a suitable water bath, and 25 cc. are run from a pipette nto each dish; the water is made to boil strongly, and during he operation the film is frequently broken up by the glass rod. As the process proceeds, frequent manipulation in this way con-

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* A sample sold as new milk to an inspector, the writer found to have a pecific gravity 1·0192. It contained—

Solids not fat, ...	7·873
Fat, ...	8·310
Ash, ...	·59

It was probably a milk known in the trade as "fear milk;" that is, the inspector was known, and cream either added or served.

verts the solids into a granular powder, from which the fat is easily extracted by solvents. The total residue taken by this method will, according to the writer's experience, be a little in favour of the milkman; *e.g.*, a milk gave as a mean of two analyses—

5 cc. in a platinum dish, 13·35 (2½ hours),
25 cc. in a porcelain dish, 13·4464 (3½ hours).

Nevertheless, the larger quantity is to be preferred to the smaller; for if the latter be taken, it necessitates the determination of fat in another sample, whilst from 25 cc. the four chief constituents of the milk can be quantitatively separated. In either case, at the end of about two hours the dishes should be cooled, weighed, and replaced on the water bath, and reweighed every quarter of an hour until the weight is constant. This constant weight is seldom delayed beyond three hours.

Extraction of the Fat.—This is an important operation, and permits of a variety of manipulations.

Mr. Wanklyn recommends evaporating for about an hour 10 cc.; softening the caseine by the addition of a few drops of alcohol, then exhausting by successive quantities of ether, passing the ether through a filter, evaporating the filtrate, weighing it, and thus determining the fat directly.

The practice pursued by the author is usually to pour about 60 or 70 cc. of ether on the granulated milk solids, and if there be no necessity for the analysis to be concluded that day, it is allowed to stand over night. Next morning, a funnel connected with an inverted Liebig's condenser is placed over the dish, and the ether boiled for from five to ten minutes, or even longer. Some little concentration of the ether occurs, but if the funnel fit properly nearly all runs back into the dish. The ether is poured away through a filter into a waste ether-bottle,* and two successive portions of ether are used in a similar way; the solids are now freed from ether by evaporation at a very gentle heat, anything which has escaped on to the filter paper added, and the whole weighed, the loss being equivalent to the fat.

Some chemists prefer to mix the milk solids with sand or powdered glass, since the fine powder thus obtained is very easily exhausted from the fat by solvents. Others put the solids int a long tube, let it stand over night, then raise the boiling point o the ether by closing the aperture of the tube by the thumb, whils the lower portion is immersed in warm water.

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* When sufficient ether is collected in the bottle it is distilled, a littl caustic lime and chloride of calcium added to the distillate, and then redistilled.

Finally, the milk solids may be transferred to any apparatus milar to Fig. 11, and effectually and economically exhausted y a relatively small quantity of solvent. The solvent itself may lso be varied; pure benzole, for example, will give quite as good esults as ether.

The various modifications that have been enumerated will, in ustworthy and experienced hands, give practically the same esults. However, as the mixing with foreign substances, the ransference of the solids from the dish to tubes, &c., necessi- ate the use of a separate portion of the milk for the "ash," irect treatment of the solids in the original dish appears to have ome advantage; besides which, there is always danger of acci- ental loss in the removal of the solids—a risk varying with the kill and care of the operator. But on these objections no great tress need be laid.

Solids not fat.—The fat removed, the important factor "solids ot fat" is obtained. It is now open for the analyst (and in rdinary work the usual course) to burn up the solids in a latinum dish, and thus obtain the ash, making no estimation of he relative quantity of albuminoids and milk sugar, this estima- ion being in nine cases out of ten of no value whatever as espects adulteration.

The solids freed from fat may be scraped into a platinum dish (or 10 cc. of milk may be evaporated specially for this purpose), nd ignited at the lowest possible temperature, for the phos- phates fuse rather easily, and thus enclose particles of carbon, which, at a red heat, render complete combustion difficult. The volatilisation of the chlorides may be in a great degree controlled by covering the dish with platinum foil. When the ash ceases to diminish in weight, the final weighing is taken with great care, the ash further examined, and the following points noted:—

(1.) A milk ash should be white, or very nearly so.
(2.) It should contain no sulphates.
(3.) It should only contain a trace of alkaline carbonate.
(4.) It should contain no excess of chlorides.

If the weight of the ash agrees with the estimation of the milk solids, and responds to the above tests, mineral adulteration is not likely. Mere watering of the milk diminishes the ash; but if it be watered and adulterated as well with carbonate of soda or similar substances, the ash may either be of normal or excessive weight. In some rare cases a very hard gypsum-holding water may have been added to the milk, and reveal its presence by an ash containing sulphates. Such an inquiry, however, demands the evaporating down and burning up of inconveniently large quantities of milk (at least 100 cc.). To take the case of a water containing 10 grains per gallon of sulphate of lime (10 mgrms. in 70 cc.), a milk watered 10 per cent. would yield about 1·4 mgrm. of SO_3 from 100 cc.

The chlorides are taken in the ordinary way by titrating with a solution of silver nitrate, each cc. of which equals 1 mgrm. of chlorine, 4·79 grms. to litre, using as an indicator neutral chromate of potash. The presence of alkaline carbonate is denoted by effervescence, and the amount present is estimated by d. n. acid. Such an examination, only occupying a few minutes, is for practical purposes quite sufficient, unless some exceptional case arise demanding a more or less complete qualitative and quantitative estimation of the ash.

If the amount of caseine and milk sugar be required, they may both be determined, or one only estimated, and the other found by difference. The most convenient, and an extremely rapid, method of determining caseine is the one devised by Mr. Wanklyn—viz., to take 5 cc. of milk, dilute it with water in a half-litre flask to 500 cc., and then of this diluted fluid distil 5 cc. ($= \frac{1}{100}$ cc. milk) with a strongly alkaline solution of permanganate of potash, and estimate the ammonia in the distillate, either colorimetrically by "Nesslerising" or by titration. ·065 of ammonia equals 1 part by weight of caseine. The following table will save calculation:—

NH_3 Mgrm.		Albuminoids calculated as Caseine. Mgrm.
·01	=	·154
·02	=	·308
·03	=	·462
·04	=	·616
·05	=	·770
·06	=	·924
·07	=	1·028
·08	=	1·232
·09	=	1·386

A less expeditious, but very accurate, way of estimating caseine, is to make a combustion of about ·5 to ·7 of the dry solids with oxide of copper.* The amount of nitrogen found, multiplied by 6·33, equals the caseine.

The above are more or less direct methods, but the one in general use by analysts is simply to abstract the milk sugar from the caseine, and directly weigh the latter with its associated ash, the ash being subsequently determined by ignition, and subtracted from the total weight. This method has the advantage of esti-

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* Albuminoids do not give up all their nitrogen if ignited with soda lime. Pflüger's *Archiv. f. Physiologie*, vj., p. 284.

mating the milk sugar as well. It is performed as follows:—The milk solids freed from fat are treated first with alcohol of 80 per cent., and then finally extracted with boiling water, so as in point of fact to dissolve the sugar out with weak alcohol. The solution is filtered and evaporated to dryness, weighed, ignited, and then again weighed, when the loss equals the milk sugar, and the residue equals the small quantity of soluble ash which has been dissolved by the preceding operations. The caseine is then determined in precisely a similar way to that before described. The milk sugar may also be determined by taking a known volume of milk, precipitating the caseine by acetic acid, filtering, and then diluting with nine or ten times its volume of water, and titrating it with standard copper solution. (See p. 7.)

§ 16. *Adulterations of Milk.*

The only adulterations known to be practised in this country at the present time are—the addition of water, the addition of glycerine, the abstraction of cream [whether by fractional milking, skimming, or other means], the addition of salt, of borax, of sodic carbonate, and of salicylic acid, and lastly, the manufacture of "new milk" from condensed or concentrated milks. As for chalk and water, pulped-up brains, infusions of seeds, and the like, popularly believed to have been used as adulterants, they are in the present day unknown; and, indeed, the evidence of such adulteration at a former time is either untrustworthy or rests on some solitary case, which has been diligently copied from one book to another.*

The *addition of glycerine* to milk (of which one case is recorded by Dr. Muter) is detected as follows:—The dry and neutral milk solids are freed from fat by exhaustion with pure anhydrous ether; the glycerine is then dissolved out by a mixture of absolute alcohol and ether. The alcohol and ether are driven off by gentle evaporation, and the glycerine identified by its physical properties and the production of acroleine fumes, on mixing with a little sulphuric acid and heating.† The milk sugar in such

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* The writer was informed by an analyst last year, that he had found Thorley's Food for Cattle in some samples of milk. It was ultimately proved that a servant of the dairyman had regularly contaminated the milk from motives of revenge; but it is obvious that such a matter is wholly distinct from adulteration.

† A test for glycerine has been recently proposed and described by A. Senier and A. J. G. Lowe (*Chem. Soc. Journ.*, No. clxxxix., Sept., 1878). It depends upon the fact that glycerine sets free boracic acid from borax. A little powdered borax is placed in a watch-glass, and the solution to be

cases must be estimated by copper, and the albuminoids either by a nitrogen combustion or by the ammonia process.[*]

The addition of *common salt*, *carbonate of soda*, or other *mineral adulterant*, will be indicated by the relation of the ash to the caseine being abnormal, and also by the chemical characteristics of the ash itself. The chlorine will, of course, be raised if common salt has been added, and if sodic carbonate is present. Effervescence on the addition of d. n. acid and the unwonted alkalinity will at once betray it.

The detection of *borax* in large quantities is easy, in small difficult. At least 200 cc. of milk should be taken, alkalised by sodic carbonate, evaporated down in a large platinum dish, and gently ignited to an ash. This ash is decomposed with sulphuric acid, the excess of acid driven off by heat, and then the freed boric acid dissolved out by alcohol. The alcohol is concentrated at a very gentle heat until its bulk does not exceed that of half a cc.; this is then set on fire in a shallow watch-glass, and the flame (which will be green) examined by the spectroscope; the bands occupy the position shown in Fig. 2.

Salicylic acid is detected by the processes described in the article on *Beer*.[†]

§ 17. *Calculation of results.*—Mr Wanklyn has endeavoured to introduce the statement of results in grms. yielded by 100 cc. of milk,

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examined (first made *slightly* alkaline) is poured on to it. The mixture is stirred with a glass rod, and then a portion introduced on a looped platinum wire into the flame of a Bunsen burner, when, if glycerine be present, the green colour of boracic acid is immediately produced, and the flame will, of course, exhibit, on spectroscopic examination, the well-known bands (see Fig. 2). Ammoniacal salts, erythrite, and glycol, give with glycerine the same reaction; but none of these would be likely to be present in milk.

[*] *Analyst* [25], 1878.

[†] Whilst these sheets were passing through the press, two modifications of the ordinary process for milk analysis have been described:—

(1.) Mr. A. Adam, in a communication to the Académie des Sciences, recommends the employment of a glass tube of 40 cc. capacity, having a glass pipe above and stopcock below. Into this is introduced—first, 10 cc. of alcohol, containing $\frac{1}{200}$ of its volume of caustic soda; secondly, 10 cc. of milk; and thirdly, 12 cc. of pure ether; the tube is closed, well shaken, and allowed to rest for ten minutes, when it separates into two layers, the upper one containing all the fat. The remainder of the process essentially consists in separating the upper from the lower layer in the usual way by means of the stopcock, the recovery of the fat by evaporating the ether, the coagulation of the caseine by acetic acid, and the estimation of the sugar by Fehling's solution.

(2.) W. C. Heraeus (*Arch. Pharm.* [3], xii. 43), places 10 grms. of the sample, mixed with powdered glass, in a small silver boat, which is placed in an iron tube, and air at a temperature of about 35°C. is drawn over the milk for thirty minutes, at the end of which time it is completely dry. The remainder of the process is as usual.

which, since the average specific gravity of milk is 102·9, is equivalent to parts by weight in 102·9 parts. Such a method has one advantage, viz., that it involves but little calculation. It is, however, never likely to come into general use, from the difficulty which magistrates and others out of the scientific world find in understanding such calculations. The writer's own practice is always to state the parts per cent. by weight.

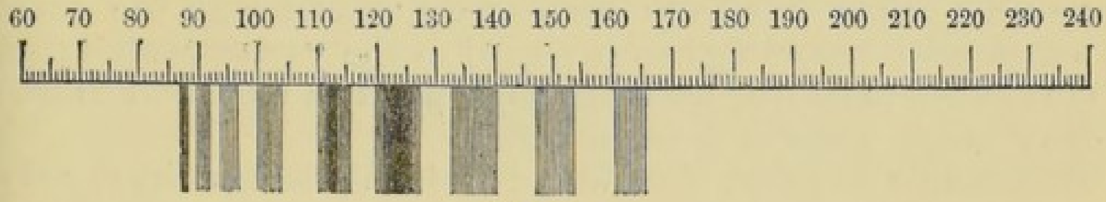

Fig. 2.

The specific gravity being known, the residues from 5, 10, or 25 cc. are multiplied to 100, and this number divided by the specific gravity, the result being parts by weight. Thus, 25 cc. of a milk, the specific gravity of which was 102·8, gave 2·5 grms. of solids :—

$$\frac{2·5 \times 4\ (100)}{102·8} = 9·75 \text{ per cent by weight.}$$

If the milk has been simply watered, the multiplication of solids not fat ($= s$) by 100 and dividing by 9, will give the number of parts by weight of genuine milk in 100 ($= x$) :—

$$\frac{100}{9}s = x.$$

If the milk has been simply skimmed, and the lowest standard be used, then if the solids not fat ($= s$) are subtracted from the percentage of fat ($= f$), the product multiplied by 2·5 and divided by 9, the result equals the percentage of fat removed $= x$:—

$$\frac{2·5}{9·0}x - y = x.$$

Finally, if a milk is both skimmed and watered, the following formula may be used, in which s and f mean respectively "solids not fat" and "fat," and x is extraneous water :—

$$100 - \frac{100 + 2·5}{9}s - f = x.$$

The above calculations, it will have been already observed, merely return a milk as watered or skimmed according to a certain standard. The farther the original milk deviates from the standard, the greater the error in the calculation. One thing is, however, certain, that the advantage is always on the side of the milkman. It would be possible to make the calculation approximate very nearly to the truth, if it were in the power of magistrates to order the analysis of half-a-dozen samples on consecutive days from the cow whence the original milk was derived; but such a course is wholly unnecessary, considering the extent of our present knowledge with regard to the variations of milk.

One of the most frequent questions put to analysts in court is —How much water is there in milk?

This simple inquiry, if answered suddenly and without reflection, may cause some embarrassment, for two milks may contain identical quantities of water, say 88·5 per cent., and the one an analyst might return as genuine, the other as adulterated; for in the one case the solids not fat might be 9, the fat 2·5, in the other the solids not fat 8, and the fat 3·5. So that the proper reply is, that genuine milk has never been known to contain more than 88·5 per cent. of water; but the judgment with respect to watering depends on the percentage of solids not fat, and a milk with even a less percentage than 88·5 may have been watered.

Decomposed Milk.—The putrescible matters of milk are albumen, caseine, and milk sugar. The fat will remain for a long time good, and the ash or mineral constituents are practically permanent. The most common change is the "lactic fermentation," in which some small quantity of ethylic and other alcohols are formed, and a considerable portion of the milk sugar passes into lactic acid. On drying such a milk up, the lactic acid may char the residue, and thus there will be loss; besides this, since lactic acid is soluble in ether, if the milk is analysed in the ordinary way, the ether will not extract fat alone, but lactic acid. On igniting the ash, chlorides will volatilise more completely than usual, so that the ash will be lower. If milk is kept still longer, the albumen and caseine become putrid, the glycerides break up, and there is an evolution of CO_2 and ammonia.

If milk is kept cool and in the dark, there often occurs slow fermentation, entirely analagous to the fermentation of cheese (p. 81), in which some portion of the caseine changes into fat. This change is of great importance to the analyst, especially with regard to the reference of samples to Somerset House — the same milk analysed at different dates often giving from 1 to 2·5 per cent. more fat than it held originally.* This fatty change of the albuminoids should not be ignored by any laboratory of

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* *See* the author's paper on the Fatty Metamorphosis of the Albuminoids in Milk and Cheese, *Analyst*, 1878, pp. 230–235.

appeal, or a false charge of inaccuracy may be brought against an analyst.

The complete analysis of a decomposed milk involves the determination of the total residue—alcohol, volatile acids, fat, sugar, lactic acid, ammonia, albuminoids, ash.

(1.) *The total solids.*—It is always well, if the milk be acid, to take a weighed quantity, and to neutralise it carefully with a known quantity of sodic carbonate, correcting for loss of hydrogen and carbonic dioxide, thus $2C_3H_6O_3 + Na_2CO_3 = 2C_3H_5NaO_3 + H_2O + CO_2$, and also for the weight of the sodic carbonate produced.

(2.) The *alcohol* is obtained by exactly neutralising the milk with sodic carbonate, and distilling at least one-third. The flask is best connected by a proper cork to a small Liebig's condenser, and the receiver should be a flask with a mercury valve, the whole forming a closed system, rendering loss impossible. The liquid is again distilled so as to concentrate the alcohol in a small bulk, and lastly oxidised into acetic acid, in the way described at p. 131.

(3.) The *free volatile acids* are estimated by distillation on the principles fully described in the article on *Wine.*

(4.) The *fat* is obtained by exhausting the solids by petroleum ether, or ether. If the latter is used, it will be necessary first to neutralise the milk carefully with sodic carbonate.

(5.) The *sugar*, as described p. 7.

(6.) The *lactic acid* may be very approximately found by taking first the total acidity of the milk, evaporating nearly to dryness, dissolving in water, again titrating, and expressing the results as lactic acid.

(7.) The *ammonia* and the *albuminoids* are determined by the usual methods.

(8.) *The ash.*—In all decomposed milks the amount of ash gives a fair indication whether any watering has taken place, or not. At least 50 cc. of neutralised milk should be taken, and an estimation of the phosphoric acid and chlorine is advisable. In completely putrid milks, the only possible data upon which to base an opinion must be derived from the ash; questions of skimming under such circumstances should not be dealt with. Some chemists appear to imagine that all milks decompose according to a fixed ratio. This certainly is very erroneous, and a supposition entirely unsupported by facts. The decomposition of milk depends upon such a variety of circumstances, that it follows no regular course or law.

§ 18. *Unhealthy and Abnormal Milks.*

One of the chief symptoms of "lacteal albuminuria," an affection from which cattle suffer, is a viscid, stringy condition of the milk a little while after it has been drawn. Such milk is highly albuminous, containing from 8 to 12 per cent. of albumen. Samples of milk causing flatulence and diarrhœa in young children are occasionally brought to the writer, and doubtless to others; they all agree in entering rapidly into lactic fermentation; but so far as is known, there is no absolute impurity or poison. The cause may be referred either to dirty cans, foul dairies, or in a few cases to some local affection of the cow's udder. Blue milks* are on record, probably due to some fungoid growth; according to Moslem, they have caused intestinal disturbance in children.

Milk is influenced by diet. In this way, bitter and purgative principles taken by the mother are liable to be excreted by the mammary glands; thus the bitter of the turnips is tasted in the butter, and a successful method of giving a suckling infant a purgative is to indirectly administer it through the system of the mother. This being so, it is in no way surprising, if occasionally milk should be poisoned through an animal eating poisonous herbs. In June, 1875, the inhabitants of the Rione Borge in Rome suffered from an epidemic of gastro-intestinal irritation; the cause was traced to the use of goats' milk, the goats having browsed on the meadow saffron. Professor Ralti succeeded in isolating colchicine from the milk.† Of recent years much attention has been given to the spread of the contagion of such diseases as scarlet- and typhoid-fever by milk. The cases are too numerous now to deny that sometimes these fevers are propagated through the medium of the milk. Some of the instances cited are, however, to the writer's mind untrustworthy, and narrated by observers who appear, before they commenced their investigation, to have resolved to accuse and convict the milk. It must, of course, be borne in mind, that the milk in cases where it has really been the agent is not itself in fault, but has been contaminated with infected water, epithelial scales, and other substances, and plays pretty well the same part as an infected garment, or as any liquid polluted with specific excreta.

A very serious question has of late years been discussed, on the possible transmission of tubercular disease by milk. In 1866,

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* This blue fungus (*Oidium lactis*) at times prevails over large tracts of country on the Continent, and causes great individual loss to dairy-keepers. In England it is of extreme rarity.

† Similar illness has been caused in the Western States of America and in Australia, by the milk of cattle which had fed on poisonous shrubs or herbs.

Gerlach fed two calves, two pigs, one sheep, and two rabbits with the raw milk from a phthisical cow for from twenty-one to fifty days; the whole of the animals, with the exception of one which died from foot and mouth disease, suffered from severe illness, and the post-mortem examination showed the pathological signs of tubercle. Klebs subsequently made a similar experiment, and fed nine guinea-pigs with milk from a phthisical cow, and the animals also became tuberculous. Still more striking was the accidental infection of a large St. Bernard dog, from drinking milk of a phthisical cow, detailed at length in Klebs' memoir. Several other observers have since endeavoured to propagate tubercular disease by feeding various animals with the milk of diseased cows, with the following results as summarised by Bollinger:—

Three pigs—one successful, two doubtful cases.
Three calves—two successful, one died accidentally during the course of the experiment.
One lamb—successful.
Two dogs—both unsuccessful.
Two cats—both unsuccessful.
Fourteen rabbits—two successful, six unsuccessful; the remainder were fed with the boiled milk, and the experiment was negative.

On the other hand, Harms and Gunther (although successful in inducing tuberculosis in rabbits) state, that the young rabbits sucking their mothers thus artificially phthisical, remained free from disease. Dr. Schreiber has failed to induce tuberculosis in rabbits; and lastly, according to E. Perroncito of Turin, a whole family, consisting of a man and wife and two children, drank for eight days the milk of a cow most decidedly tuberculous, as proved by an autopsy, yet two and a half months after, at the date of his memoir, they remained well. It may then be legitimately concluded that,—

(1.) A disease similar, if not identical, with tuberculosis may be propagated from animal to animal by the means of a milk derived from a diseased cow.

(2.) That, therefore, such milk is unfit for human food.

(3.) That nothing definite is known with regard to the propagation of tubercle from the lower animals to man.

In any case, phthisis in cows, although it may be a rare and occasional danger, is not one of any magnitude. The milk of an animal thus diseased so rapidly decreases in quantity, that the cost of maintenance exceeds the returns of produce, and therefore the animal is soon slaughtered. The disease also appears not to be so common as some writers believe.

M. Vallin, aided by some of the most eminent veterinarians of Paris, searched for four months in vain for a phthisical cow, and in his memoir* he states that out of 28,000 beasts slaughtered annually at the abbatoirs, the carefully inspected viscera of only twenty to twenty-eight bear any trace of tubercle, while those rejected as unfit for slaughter are an insignificant number.

There are occasional instances of apparently healthy cows giving an abnormal milk. Mr. Pattinson found a roan cow give a milk characterised by a remarkably low percentage of albuminoids, and so much common salt that the milk tasted saline. The following is his analysis :—†

Water,	90·15
Fat,	3·00
Caseine,	2·00
Milk sugar,	3·90
Ash,	0·95
	100·00
Chlorine in ash,	0·27
Equal to sodium chloride,	0·44

The milk in *anthrax and anthracoid* diseases is said to be of a dirty-bluish colour, streaked with blood, and soon becoming putrid. Diarrhœa has been produced from its use. The milk of cattle suffering from pleuro-pneumonia has been drunk with impunity, and the same may be said of that from cattle suffering from cattle plague. In such diseases, however, there is nearly always early suppression of the secretion, and but little is known of the chemical qualities of the fluid. Milk derived from rabid cows also does not appear to be hurtful,‡ but here again little is known of the matter.

§ 19. *Milk from Cattle affected by Foot and Mouth Disease* (*Eczæma epizootica*).

Microscopical Characters.—If milk be taken on the first day of the disease and microscopically examined, no abnormal elements whatever may be discovered in it; but, on the other hand, instead of the globules remaining free and separate, as is usually the case, they show a tendency to aggregate into groups—in other words, the first stage is *aggregation of the milk corpuscles.* About the third day some new bodies (first observed and

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* M. Vallin—Lait des Vaches Phthisiques. *Annales d'Hygiène publique*, July, 1878.

† *Analyst*, May, 1876.

‡ *Nova Cupa. Nat. cur.*, vol. i., obs. 55. Bandot in *Mém. de la Société Royale de Méd.*, an. 1782-83, t. xi., p. 911.

described by the author[*]) make their appearance.] These consist of elongated, flattened, highly refractive bodies, ranging in length from $\frac{1}{800}$ to $\frac{1}{1000}$ of an inch.[†] In some there are divisions at intervals, which appear to be rather the contraction of a sarcode substance than an indication of cells. These bodies are not perceptibly altered by dilute acetic acid or iodine, nor are they stained by magenta. By the fourth day they are fewer in number and rather larger. In the later stages they are absent.

If, as frequently happens, there are ulcers on the teats themselves, pus-cells, epithelium, and blood will be found in the milk. These are, of course, accidental products, and not secreted by the gland; frequently there is a circular ulcer, not very evident unless looked for, just within the teat, and this ulcer contaminates the milk.

§ 20. *Chemical Composition of the Milk.*—This interesting subject requires further investigation. The writer made some partial analyses during the epizootic of 1876, the results of which are detailed in the following table. The analyses are termed "partial," because the relative quantity and the nature of the albuminoid constituents have not been determined, and this in diseased milk is all-important. There are also a few analyses by Mr. Thomas of Cardiff,[‡] the results differing greatly, and it is to be suspected that in these cases the milk was contaminated by pus and blood; so that, though Mr. Thomas' analyses represent what is far more likely to be found in commerce, viz., high fatty residues, they probably do not represent entirely the secretion of the mammary gland in aphthous fever.

It will be necessary now to inquire, whether the milk of an animal ill of aphthous fever should be certified as injurious to health, or not. The answer to this question *sans phrases*, is, that it should be absolutely condemned as unfit either for man or animals. In one stage of the disease, indeed, it is directly poisonous, and no one can be well acquainted with the literature of aphthous fever without knowing that a number of calves have suddenly died after sucking their aphthous mothers. Such cases have, indeed, fallen under the author's observation in the epizootic of 1876. Moreover, the milk which possessed the characters before described has been injected by the writer under the skin of kittens, and also been given by the mouth; in both instances

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[*] *Chem. News*, vol. xxxii., p. 245.

[†] This observation has been recently confirmed by Mr. Wigner and by Mr. Heisch. See On Diseased Milk, C. Heisch, F.C.S., and Some Recent Cases of Diseased Milk, G. W. Wigner, F.C.S. *Analyst* [26], May, 1878.

[‡] *Chem. News*, xxxii., 836.

TABLE.—GIVING ANALYSES OF MILKS OF VARIOUS COWS AFFECTED WITH FOOT AND MOUTH DISEASE.

	1st Day.	2nd Day.		3rd Day.			4th Day.		5th Day.			6th Day.	7th Day.	14th Day
					J. W. Thomas.			J. W. Thomas.		J. W. Thomas.		J. W. Thomas.		
		(1.)	(2.)	(1.)	(2.)	(3.)	(1.)	(2.)	(1.)	(2.)	(3.)			
Water, . . .	91·239	79·903	86·320	87·676	76·40	84·04	83·852	81·80	87·900	78·38	82·39	86·87	86·067	83·882
Fat, ...	0·390	5·010	3·838	0·891	9·91	3·86	7·798	7·01	1·062	8·26	4·60	4·01	1·587	3·961
Caseine, . .	2·899	14·380	9·135	3·948	8·07	5·43	3·469	5·92	10·376	8·22	6·00	4·03	10·849	11·478
Milk Sugar, .	4·809			7·152	4·69	5·94	4·669	4·47		4·25	6·20	4·39		
Ash, . . .	0·663	0·707	0·707	0·333	0·99	0·73	0·212	0·80	0·662	0·89	0·81	0.70	0·507	0·679
Solids not fat,	8·371	15·087	9·842	11·433	13·69	12·10	8·350	11·19	11·038	13·36	13·01	9·12	11·356	12·157

the animals appeared perfectly well for a short time, and then died in convulsions. The post-mortem appearances of the calves, as well as the kittens, revealed intense pulmonary congestion. Professor Simonds has also given the infected milk to pigs with a fatal result; Professor Brown to cats, and in the latter it has induced evident indisposition. In addition to this proof of absolutely poisonous properties, there are numerous cases on record in which it has propagated the disease itself.

The first definite notice of the propagation of aphthous fever by milk is in a small Latin work by Michel Sagar, 1765,* in which he treats of the aphthous fever prevailing in Moravia (1763-64), and declares that the milk of the sick cows communicated the disease to dogs, cats, and people who made use of it. Moreover, there exists the important evidence of actual experiments upon man.

In the year 1834, MM. Wenberburg, Tilgner, and Lebnard observed several cases in Germany of the transmission of the disease by milk; and three German veterinarians, MM. Hertwig, Mann, and Villain, in order to set the question at rest, made themselves the subject of experiment. The cow chosen was one which had been seriously affected for five or six days. Each took a pint of the warm milk for four consecutive days. On the third day from the commencement of the experiment, M. Hertwig shivered, became feverish, and had uneasy sensations in the skin of the hand and between the fingers; by the sixth day, counting from the commencement of the symptoms, the mucous membrane of the mouth was swollen; by the seventh, vesicles had formed on the edge of the tongue, the lips, and the internal surface of the cheeks—the largest were about the size of a lentil, they were of a light yellow colour, and contained a whitish liquid. At the same time vesicles formed on the hands and fingers. On the eighth and ninth days, the vesicles grew larger, and on the tenth and following days burst; the fever disappeared, the ulcers dried up, and there was desquamation of the parts affected about the twenty-fourth day. MM. Mann and Villain were similarly attacked, but in a less degree.† But these direct experiments are not the only facts on record showing the facility with which the milk may propagate the disease to man.

In a locality in which there was an aphthous epizootic, an infant four months old was suddenly seized with diarrhœa, followed by an eruption of vesicles in the inside of the upper lip. It subsisted

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* *Libellus de Aphthis Pecoris.* Vienna, 1765.

† *Nouveau Dictionnaire de Médecine Veterinaire.*

on milk entirely, and just previous to the attack had taken some milk of a cow in the incubation of the disease.* In the practice of Dr. Crawford, Beccles, Suffolk, over one hundred cases of patients suffering from vesicular eruption of the mouth and diarrhœa, occurred synchronously with the prevalence of foot and mouth disease in cattle; several of the patients were proved to have taken milk derived from diseased cows.† Mr. Fred. Wallis, F.R.C.S., communicated to Dr. Thorne the remarkable instance of thirteen persons simultaneously affected with ulcers on the mucous membrane, over the lips and gums, and underneath the tongue, with enlargement of tonsils and submaxillary glands. All these patients were visitors in the country from London, and had drunk largely of milk which was derived from a dairy where foot and mouth disease was prevailing.‡

Dr. T. Briscoe has recorded a most severe case of foot and mouth disease occurring in the person of a farmer's daughter. There was great salivation, a peculiar odour about the breath, and the tongue swelled so that it protruded from the mouth, and suffocation at one time was dreaded. On the twenty-seventh day, there was hœmorrhage from the tongue, and the duration of the disease altogether was thirty-six days, during which milk alone was taken. Dr. Briscoe also alludes to milder cases which he observed about the same time in children who drank the milk of diseased cows.§ Mr. Charles Lingen, Hereford, has published a well-marked case of aphthous fever which occurred in the person of a farmer's child who habitually drank a large quantity of milk; the farmer's cows at the time were suffering from foot and mouth disease.||

It is probable that since milk, in the making of butter or cheese, is not submitted to the temperature of boiling water, the contagion survives the process of churning or of cheesemaking. J. Schneider, indeed, affirms that he has seen whole families made ill by the consumption of butter and cheese from the milk of infected cows,¶ and five cases of injury from similar milk and butter are related by Boulay.**

The general opinion that the infected milk after being boiled is harmless, is supported by the following incident :—"Foot and mouth disease having been brought into the commune of Morchier by a pig dealer, it extended in a few days to a hundred adult

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* Dr. Thorne's Report on Foot and Mouth Disease. *Appendix to Twelfth Report of Medical Officer to the Privy Council.*

† *Op. cit.* ‡ *Op. cit.*

§ *Brit. Med. Journal*, Vol. ii., 1872, p. 464.

|| *Brit. Med. Journal*, Vol. ii., 1876, p. 26.

¶ *Hensinger. Pathol. Comparée*, ii.

** *Receuil*, t. ix., ser. 5, p. 651.

animals on one side of the village, and by a striking contrast spared the calves, the reason being that the proprietors had followed the advice given them, to feed the latter with boiled milk and water."*

§ 21. *Analysis of Abnormal Milks.*—The analysis of abnormal milks should be preceded by a microscopical investigation. Pus cells, epithelium, and blood may be readily recognised by any person who has made himself acquainted with the characteristics of those bodies. The chemical investigation should be specially directed to the determination of the relative quantity of albumen to caseine proper, to the amount of chlorine in the ash, and to the presence and amount of urea. Dr. Beale was the first to observe that in pneumonic patients practically the whole of the chlorine was withdrawn from the urine. It is, therefore, probable that in some internal inflammatory diseases of the cow attended with exudation, the chlorides in the milk would disappear. This hypothetical observation, however, the writer has hitherto lacked opportunity to verify. Certain diseases of the kidney cause in milk an increase of urea, and though the presence of the latter may be found in minute traces in normal milk, any quantity capable of determination would be evidence of ill health.

The analysis of the albuminous principles having been already detailed, there only remains to describe the best method for separating and estimating urea.

The process is carried out as follows:—The milk is precipitated by three times its bulk of strong alcohol, filtered, the coagulum washed with alcohol, the filtrate evaporated at a moderate heat over the water-bath, and the residue extracted with absolute alcohol. This alcoholic extract is evaporated at a gentle heat, the dry residue dissolved in water, and the solution precipitated drop by drop by basic acetate of lead, so long as a precipitate appears. The filtered fluid is then titrated with nitrate of mercury solution, as in the process devised by Liebig, but must be prevented from getting too acid by the cautious addition from time to time of a little soda solution. The precipitate containing the urea may now be filtered off, washed with water, transferred to a small retort or a flask with a lateral tube, and distilled two or three times to dryness with strong potash solution, free from ammonia, the ammonia in the distillate being estimated either by titration or by "Nesslerising." Or, instead of decomposing with potash, the precipitate may be freed from mercury by SH_2, the filtrate evaporated nearly to dryness, and then transferred to a tube with hydrate of baryta and a little chloride of barium.

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* *Op. cit.*, p. 604.

The tube, hermetically sealed, is heated in an oil-bath to 200°C., from three to four hours, and after cooling it is opened, the resulting carbonate of baryta filtered off, well washed, and ultimately decomposed by sulphuric acid, and weighed as sulphate of baryta (1· $BaSO_4$ = 0·2574 urea).

§ 22. *Legal Cases relative to Milk.*

The following convictions are of interest :—

Appeal case in which the defence was, that the milk had been deprived of cream from being unintentionally skimmed by serving the customers.

This case occurred at the Liverpool Sessions, and is fully reported in the "*Analyst*," 1877, p. 214.

Dr. Campbell Brown proved that the milk was deprived of its cream, the appellant affirming that the milk had been put into an eighteen-gallon can, without the slightest sophistication, and that the cream had been abstracted by serving the customers.

The Recorder said, nobody would convince him that a milk dealer could not, if he liked, take care that each of his customers should get a fair proportion of cream. . . . He was perfectly certain that the milk had not been skimmed, but that it had been weakened by the process of selling to the earlier customers. He was certain that when the appellant sold the milk to the earlier customers, he knew he was abstracting the cream from it—not skimming the milk, but abstracting the cream, although with no fraudulent intention. He was equally certain, too, that the appellant sold the residuum of the milk, knowing that it had been reduced to the condition in which it was when he sold it. He was quite satisfied, therefore, that an offence had been committed against the Act of Parliament. . . . The conviction was confirmed.

The officials at Somerset House have, in an appeal case also declared their belief in the fact that milk on being served from a can, in the usual way, may have the top layer of cream entirely abstracted. The writer has always had doubts about this, for the difference of specific gravity between the cream and the solution of the other milk solids is not great, and the mere use of a dipper in serving the milk stirs it up sufficiently to render this removal improbable. We have, however, at least *one* definite experiment on this subject.

Mr. Carter Bell states,* "One day in July I bought two gallons of milk, and analysed it, and found 100 cc. to have the composition of—

Total solids, ...	12·30
Fat, ...	2·70
Solids not fat, ...	9·60

The milk was put in the cellar, and at every hour from nine in the morning till twelve o'clock at night, one pint of milk was taken out at the commencement of each hour, and a portion of each pint was analysed. In taking out the pint, great care was taken not to stir the milk, the measure was simply dipped into the milk and taken out. The whole experiment was conducted throughout in the favour of the milkman, and according to these experiments it is more advantageous for customers to be late than early."

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* *Analyst*, No. 21, December, 1877, p. 162.

	Total Solids.	Fat.
8 o'clock in the morning,	12·30	2·70
9 ,, ,,	12·68	3·08
10 ,, ,,	12·68	3·08
11 ,, ,,	12·70	3·10
12 ,, ,,	12·70	3·10
1 p.m.,	12·24	2·64
2 ,,	12·30	2·70
3 ,,	12·28	2·68
4 ,,	12·88	3·28
5 ,,	12·80	3·28
6 ,,	12·40	2·80
7 ,,	12·54	2·94
8 ,,	12·30	2·70
9 ,,	12·48	2·88
10 ,,	12·88	3·28
11 ,,	12·60	3·00
12 ,,	12·90	3·30

Manufacture of New Milk from Condensed.

The only interest of the following case lies in the revelation it affords of the tricks of the trade. A man was summoned by his employer, a dairyman, for adding dirty water to milk. The prisoner did not deny the accusation, but cross-examined the prosecutor, to show that the latter had been in the habit of making his men, when the milk ran short, mix with water a quantity of white stuff that was kept in the cellar, and take out to the customers to make good the deficiency in the supply of good milk. The process he called "*the fake*" of the trade. The prosecutor admitted that he kept condensed milk to make up the supply when the demand was too great, the "white stuff" referred to by the prisoner.*

Novel Defence.

A defence was set up, in a Swansea case, that the poverty of the milk was owing to its having been taken from a cow a few hours only after she had been milked dry. Mr. Morgan instituted experiments on this point. In eighteen experiments on the same cow:—†

Total solids—	
Highest,	17·60
Lowest,	12·59
Average,	13·93
Fat—	
Highest,	8·60
Lowest,	2·96
Average,	4·41
Solids not fat—	
Highest,	9·95
Lowest,	9·00
Average,	9·52

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* *Analyst*, ii., 1878, 184.

† *Proceedings of Society of Public Analysts*, i., 1876, p. 191.

Conviction for selling "Fore" Milk.

In August, 1877, a dairy proprietor of Dublin was prosecuted for selling milk deprived of its cream. The defendant stated that it was "fore" milk, and that he had sold the "strippings" as cream. The magistrate expressed his opinion that the milk should be sold whole, *i.e.*, with both "fore" milk and "strippings," and fined the defendant £10.[*]

Diseased Milk.

At the Woolwich Police Court, in December, 1875, a dairyman was convicted and fined £20 for selling diseased milk. Mr. Wigner, the analyst, proved that the sample had a peculiar colour, and that it contained no less than 13 per cent. of fat, 8·2 solids not fat, and 20 per cent. of blood. Other witnesses proved that the defendant had a number of cows, and at least one of them was suffering from foot and mouth disease. There was practically no defence.[†]

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[*] *Analyst*, i., 1877, p. 82.

[†] *Conviction for Selling Milk yielded by a Cow suffering from Disease.* London, 1876.

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II.—BUTTER.

§ 23. *Constituents of Butter.*—In the manufacture of butter, the cream is violently agitated in a churn or other suitable apparatus, and in this manner the thin membrane enclosing the fat globules is ruptured. The free fat then coalesces, entangling with it some caseine and serum; the butter is well pressed together to free it as much as possible from moisture, and salt added to assist its preservation. Butter, therefore, consists principally of milk fat, with a small and variable quantity of water, caseine, and ash, the latter consisting chiefly, but not entirely, of the salt added.

The "*fat*" of butter consists of a mixture of the glycerides of the fatty acids—palmitic, stearic, and oleic—not soluble in water; and also of the glycerides of certain soluble and volatile fatty acids, principally butyric, with small quantities of caproic, caprylic, and capric acids. It is the association of about 7·8 per cent. of the triglycerides of these volatile acids with the glycerides of the insoluble acids, which gives to butter fat its peculiar and distinctive characters.

Palmitin or Tripalmitin, $C_3H_5(C_{16}H_{31}O)_3O_3$, is a white solid, but little soluble in cold, easily soluble in hot, alcohol or ether. On cooling of the hot saturated solution, fine needles of palmitin readily separate out. The melting-point of palmitin, as of all fats, varies according to the process by which it has been separated, and affords at present but little guide to its identification—melting-points, 36°, 46°, 62°, and 63°C., having all been given by different observers. On decomposition it yields 95·28 per cent. of palmitic acid ($C_{16}H_{32}O_2$). Palmitin occurs in most fats, and especially those of low fusing points. A mixture of stearin and palmitin, which crystallises in little tufts of needles, is the *margarin* of the older writers.

Stearin or Tristearin, $C_3H_5(C_{18}H_{35}O)_3O_3$, in appearance resembles palmitin; it melts at a higher temperature than other fats, and therefore is an especial constituent of the fats with high melting-points. It is also not so easily soluble in hot alcohol or ether as other fats. On the cooling of such solutions it separates ordinarily in rectangular tables, sometimes in rhombic prisms. The melting-point usually given is 63°C., but stearin, according to the processes used, may melt at 66°C. Tristearin on decomposition yields 95·73 per cent. of stearic acid, $C_{18}H_{36}O_2$.

Olein or Triolein, $C_3H_5(C_{18}H_{33}O)_3O_3$, is at ordinary temperatures a colourless fluid oil, solidifying about 5°C. It easily oxidises in moist air, and becomes yellow in colour; it is readily soluble in absolute alcohol or ether. Olein dissolves copiously stearin and palmitin. On decomposition it yields 95·70 per cent. of oleic acid.

Butyrin, an oily liquid, yielding on decomposition butyric acid, has not yet been separated in a pure state, and the same remark applies to *caproin* and *caprylin,* so that their respective acids will alone be described here.

Butyric Acid, $C_4H_8O_2$, specific gravity 0·97, boiling point 157°C. This acid, besides occurring with glycerine in butter, is found in the locust bean (*Siliqua dulcis*), in the fruits of the *Sapindus saponaria* and the *Tamarindus Indica,* in the *Anthemis mobilis,* the *Tanacentum vulgare, Arnica montana,* the fruit of the *Gingko. biloba,* and probably several other plants. So far as is known, it occurs in no other fat than butter. Butyric acid is volatile, distilling unchanged; it is soluble in all proportions in water, alcohol, and ether. Most of the salts of butyric acid are soluble. Baric butyrate crystallises in long prisms with $4H_2O$; zincic butyrate in anhydrous, very soluble, pearly tables; cupric butyrate is bluish-green, and sparingly soluble. The most characteristic salt is calcic butyrate, which is more soluble in cold than in boiling water; consequently, when a solution is boiled, some of the salt is precipitated.

Caproic Acid, $C_6H_{12}O_2$, specific gravity of liquid 0·922, boiling point about 202°C. This acid occurs not only in butter, but in cocoa-nut oil, in the fruit of the *Gingko. biloba,* in the flowers of the *Sutyriam hircinum,* and in *Arnica montana,* and is probably widely distributed through the vegetable kingdom. It also occurs in human sweat and in cheese. It is slightly soluble in water, is volatile, and may be distilled unchanged. The odour is peculiar, and similar to that of acid sweat. The caproate of baryta is soluble in water; the caproate of silver is sparingly soluble in water.

Caprylic Acid, $C_8H_{16}O_2$, fusing point 58°C., boiling point 236°C. This acid becomes solid at about 12°C.; it is usually accompanied by rutic acid. The caprylate of barium is more soluble than the rutate, and the two may be more or less completely separated by fractional precipitation. It may be dissolved in boiling water, but its solubility is not great.

Rutic or Capric Acid, $C_{10}H_{20}O_2$, is a white crystalline body, fusing at 29·5 to 30°C.; it is slightly soluble in water, and easily soluble in alcohol and ether. It occurs in butter, cocoa-nut oil, cod-liver oil, and the fousel oils obtained by fermentation.

The exact proportion of all these different principles in butter fat, it is at present impossible to determine with accuracy. The *general composition* of butter fat, however, appears to be—

Glycerides Equal to Fatty Acids.

Olein,	42·21	=	Oleic Acid,	40·40	
Stearin and Palmitin,	50·00	=	Stearic and Palmitic Acids,	47·50	
				87·90	Total insoluble solids.
Butyrin,	7·69	=	Butyric Acid,	6·72	
Caproin, Caprylin, and Rutin,	·10	=	Caproic, Caprylic and Rutic Acids,	?	
	100·00	=		94·62	Total acids, calculating soluble as butyric.

Pure, dry butter fat, melted at a heat not exceeding 100°F., has at that temperature a specific gravity ranging from ·91200 to ·91400; its fusing point, taken in the manner to be described, ranges from 33·9° to 36·5°C.

The relative proportions of fat, caseine, and salt, in genuine butters, may be gathered from the following table, in which it is seen that the butter fat ranges from about 82 to nearly 87·5, the average given by Angell and Hehner being 85·45 per cent.

	Normandy Butter. Angell and Hehner.	A Sample of Fresh Butter. Angell and Hehner.	Butter from Isle of Wight. Angell and Hehner.	Butter from Guildford. Angell and Hehner.	Butter from Winchester. Angell and Hehner.
Fat, ...	82·643	83·871	84·740	85·480	87·223
Curd, . . .	5·137	2·721	3·462	2·789	2·054
Salt (Ash), .	2·915	0·424	2·089	3·151	2·108
Water, . . .	9·305	12·984	9·709	8·580	8·615

§ 24. *Analysis of Butter.*

The analysis of butter naturally divides itself into—(1.) The general examination and analysis, and, (2.) The investigation of the fat.

1. *The General Examination and Analysis of Butter.*—The colour, taste, and odour of the sample should, of course, be noted. It will also be found useful to examine it in thin layers microscopically. If it has been mixed by fusion with any fat, and cooled slowly, crystals may be discovered. The best way to seek these crystals is to place a minute portion of the fat on a slide, add a drop of castor or olive oil, press the thin disc of covering glass so as to get a very thin layer, and examine by polarised light. Under such circumstances, if crystals should be

present, there will be seen dark crosses similar to those in potato starch. Such crystals are suspicious, because they show that the butter has been melted; and it certainly must be a most unusual process to melt butter save for the purpose of mixing with other fats. The rare adulteration of any other substance, such as starches, &c., by mechanical admixture, cannot fail to be detected by the microscope.

The general analysis is performed best by weighing 10 to 20 grms. of the butter into a counterpoised porcelain dish, melting it over a low gas flame, and keeping it at any temperature between 105°C. and 110°C., with constant stirring, until all effervescence has ceased. (By using a thermometer as a stirrer, this is easily effected.) The weighing of the dish and its contents when cool, subtracted from the first weight, gives the loss equalling the water, and it may be worked into percentage.

The above method has the merit of expedition, and it is tolerably accurate; but the water may also be estimated by placing about 1 grm. of the butter fat in a large platinum dish, so that the fat forms a thin layer, and then exposing to the heat of the water-bath until it ceases to lose weight. The fat is next melted from the curd and salt (both of which settle to the bottom), and is poured off as far as possible, the residue being thoroughly exhausted by boiling benzine, ether, or petroleum, which can be effected, if care is taken, in the same dish without transference to a filter. On now weighing, the loss equals the fat. Lastly, the curd is burnt away at a low red heat, and the ash weighed.

The general analysis finished, it remains to consider the results :—

(1.) *Fat.*—The fat should not be below 80 per cent.; any figure under this should justly be considered evidence of adulteration.

(2.) *Water.*—There is no standard followed or fixed with regard to the percentage of water. In those cases in which the fat is below 80 per cent., the deficiency of fat is usually from excess of water; and seeing the variable quantity of water found in butter, it is wisest not to certify on the ground of water alone, unless there is sufficient to lower the percentage of fat below 80 per cent.

(3.) *Caseine.*—The average quantity of caseine is 2·5 per cent., but it may reach 6 to 7 per cent., and the higher the percentage of caseine the less likely is a butter to keep, although this usually is evidence of error in the manufacture rather than of adulteration.

(4.) *The Ash.*—This should consist of common salt and phosphate of lime. Butter is said to be adulterated occasionally with sodium silicate, and therefore the ash should be fused with sodic carbonate, dissolved in hydrochloric acid, evaporated to dryness, and dissolved in water. Any residue will consist of silica. If other mineral adulteration is suspected, a complete analysis of the ash may be necessary (see p. 5). There is no definite standard fixed with regard to the weight of the ash. Angell and Hehner consider that it should not exceed 8 per cent., with which most analysts agree.

The following are a few examples of adulterated butters, the adulteration being detected simply from the proximate analysis:—

	Devon Butter.	Devon Butter.	A Sample of Butter. Angell and Hehner.	A Sample of Butter. Angell and Hehner.
Fat, ...	78·50	76·34	67·580	47·019
Caseine, . . .	1·72	6·60	6·880	7·854
Water, ...	17·10	13·36	23·981	42·358
Salt, ...	2·68	3·70	1·559	2·689

2. *Examination and Analysis of the Fat.*—By far the most important process in butter analysis is the examination of the fat. The data by which the analyst judges whether a butter consists of foreign fats entirely or partly, are derived from—(*a.*) The melting-point; (*b.*) the specific gravity; (*c.*) the relative proportion of the soluble and insoluble fatty acids. To take any or all of these, the first requisite is a pure dry fat. This is easily accomplished by melting a sufficient quantity of the butter over the water-bath. In a short time the water, curd, and salt, sink to the bottom, and the nearly pure fat can be poured off. Should it not be clear, it must be filtered through filtering paper or glass-wool. This operation will necessitate the filter being kept warm in a suitable steam-jacket.

(*a.*) *The Melting-Point.*—Various methods have been proposed for the determination of the melting-points of fats. The one used by most analysts is to take the melting-point in a fine tube. A piece of quill-tubing is drawn out, so as to make a tube about the diameter of a knitting needle, and from two to three inches in length. The fat is now drawn up to the extent of about an inch, and permitted to solidify. The tube thus charged is placed in some cold water in a small beaker, which is "nested" in a second beaker, a little water being between the two, the inner beaker carrying also a thermometer. Heat is now applied, and the moment the fat runs up the tube the temperature is noted.

It is unnecessary to add that the more slowly the temperature is raised, the more accurate will be the observation. This simple method is easy of execution, and can hardly be improved upon.

Another method is the employment of a little bulb weighted with mercury, so as to weigh from 3 to 4 grms.; the bulb rests on the surface of the fat in a test tube, which is immersed in a beaker of water provided with a thermometer, and the moment the bulb sinks is noted. A modification of this is the employment of a light float sunk to the bottom of the fat, and retained there until it is solid; on now applying heat, the float rises at a certain temperature, which is taken as the melting-point. The melting-point of various fats is as follows:—

Butterine,	31·3°C.
Cocoa Butter,	34·9°C.
Butter (average),	35·8°C.
Beef-Dripping,	43·8°C.
Veal-Dripping,	47·7°C.
Mixed,	42·6°C.
Lard, from	42°C. to 45°C.
Ox-Fat, from about	48°C. to 53·0°C.
Mutton-Fat, from about	50°C. to 51·6°C.
Tallow,	53·3°C.

It hence follows that a low melting-point indicates the probable presence of butterine, which is partly manufactured from a concrete oil, obtained from the seeds of *Garcinia Indica*, and is known under the name of Mangosteen oil, or kokum butter. A higher melting-point indicates as a probable adulterant, dripping, lard, or other animal fat.

(*b.*) *Specific Gravity.*—The method of obtaining the specific gravity of butter fat is to fill a counterpoised specific gravity bottle, provided with a thermometer stopper, of 50 to 100 grms. capacity, with water of 35°C. (95°F.), and immerse it in a beaker of water of about 43°C. (109·4°F.) By thus heating the specific gravity bottle by a liquid which is falling in temperature, the water in it can be brought exactly to 37·7°C. (100°F.), at which temperature the bottle is taken out, slightly cooled and weighed; and in this manner the weight of that particular bulk of water at 37·7°C. (100°F.) is obtained, and this value used for the subsequent operations. To take the specific gravity of the fat, the pure filtered fat, at 35°C. (95°F.), is poured into the clean dry bottle, and the exact process just detailed followed.

The specific gravity, as first pointed out by Mr. Bell, of Somerset House, has a direct relation or correspondence to the percentage of insoluble acids, a fact, it must be remembered, only applicable to pure unadulterated butter fat. Thus—

Specific Gravity at 100°F. (37·7°C.)	Actual Insoluble Acids Found. Per Cent.
·91382	87·47
·91346	87·89
·91337	87·98
·91290	88·48
·91286	88·52
·91276	88·62
·91258	88·80
·91246	89·00*

The fats used for the adulteration of butter are of low density. Vegetable butterine has a specific gravity ·90294; dripping, ·90659; so that a low specific gravity—that is, anything below ·91101—is strongly indicative of foreign fat.

Instead of the above method, which requires a considerable quantity of material, the density may be approximately taken by the well-known specific gravity bubbles, a process which we owe to Mr. Wigner. If the butter fat be placed in a wide test-tube, and a bubble of the specific gravity, say of ·896, be kept just beneath the surface by a thermometer passing through a cork in the mouth of the tube, at a certain temperature the bubble will slowly sink to the bottom. In butters of ·911 density, above which a sample may be passed, beads will sink as follows:—

Specific gravity of beads,	·8890	·8896
Temperature, . .	145°F. (62·7°C.)	132°F. (55·5°C.)

If the bead sinks at any temperature lower than these, the butter will need further examination by actual determination of the fatty acids. As a guide to the gravity, it may be assumed that a difference of one degree in the sinking temperature indicates ·30 actual density, equal to about ·35 per cent. fatty acids, and nearly 5 per cent. of foreign fats.†

(*c.*) *The Decomposition of the Fat into Fatty Acids and Glycerine.*—This is effected by saponifying with an alcoholic solution of potash, decomposing the soap with sulphuric acid, washing the subsequent fatty acids with water, titrating the soluble, and weighing the insoluble acids. The details of the process have been so simplified by successive improvements, that what was

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* Muter, *Analyst*, i., p. 7, 1877.

† A method of taking the specific gravity of fats recommended by Mr. Estcourt (*Chem. News*, Vol. xxxiv., p. 254) deserves notice. The bulb of a Westphal's balance is suspended in a test-tube containing the fat, the test-tube itself is immersed in a metal tube containing paraffin, and itself secured in a water-bath; when the paraffin-bath shows a temperature of 92·2°C. (206°F.), the weights are adjusted.

formerly a tedious and even difficult operation, is now moderately speedy and simple. The solutions requisite are as follows:—*

(1.) Approximately semi-normal alcoholic potash solution, 28 grms., roughly weighed, of KHO, dissolved to a litre with alcohol; specific gravity ·840.

(2.) Approximately semi-normal sulphuric acid, *i.e.*, 25 grms. of the strong acid to the litre.

(3.) Deci-normal soda solution of exact strength, most conveniently made by dissolving metallic sodium in water, in the exact proportion of 2·3 grms. to the litre. [1 cc. equals ·0088 of butyric acid.]

It is necessary to know with the greatest exactitude the relationship between the potash and the sulphuric acid solution; the exact quantity of alcoholic potash that is to be used in the analysis is delivered from a 25 cc. or 50 cc. pipette, as the case may be, litmus or cochineal solution added, and then titrated by the acid. It is also necessary to know the relationship between the d. n. soda and the sulphuric acid, which must also be found in the usual way. 4 to 5 grms. of the pure dry fat are weighed by difference into a flask, and 50 cc. of potash solution added; the flask, closed by a glass marble, is now heated on the top of the water oven, and by occasionally giving it a rotatory motion, saponification is complete under the hour at the low temperature of 50°C.

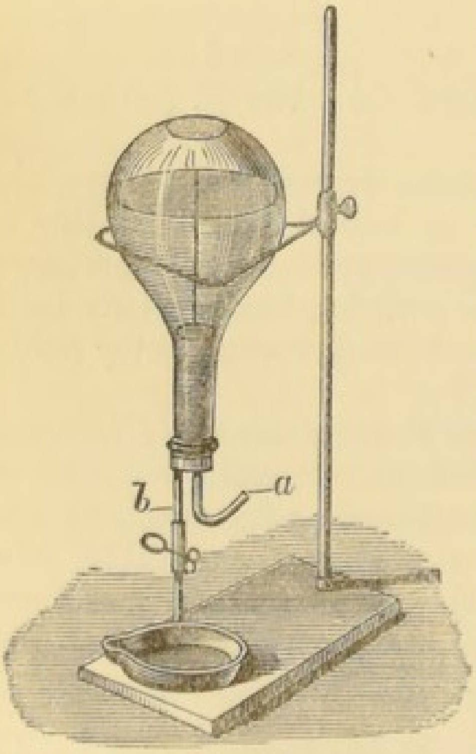

Fig. 3.

The author does not himself follow the above process, but uses the strong small assay flasks recommended by Dr. Dupré. These flasks are of about 70 cc. capacity, and with rather long narrow necks, the whole capable of bearing considerable pressure. 4 to 5 grms. of the fat are poured into such a flask, 25 cc. of potash solution added, well corked with a caoutchouc stopper, which must be secured by string and strong linen or canvas, and then the flask suspended in the boiling water of a water-bath. At the end of an hour or less it may be taken out completely saponified.† When cool the flask is opened, the soap gently melted and poured into

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* "Butter Fat," by E. W. Jones, F.C.S. *Analyst*, May, 1877.

† The reason for preferring this method is, that less potash is required.

a flask of about 500 cc. capacity, having a long, rather narrow neck (see Fig. 3). which can carry the tubes *a* and *b*—the tube *a* for the admission of air, the tube *b* furnished with a stopcock. In this flask the soap is decomposed by adding about 1 cc. more sulphuric acid than is necessary to neutralise the potash; if, for example, the latter is neutralised by 25 cc. soap, the fatty acids melt and form a layer on the surface of the acid water. At this point the whole may be diluted with warm water up to 200 cc. or 300 cc., the cork carrying the tubes inverted and the flask turned upside down, as represented in the figure. After standing a few hours the cake is more or less solid, and the lower stratum of liquid may be run off almost clear. It will, however, always be safest to pass it through a filter. By adapting an india-rubber tube to *a*, warm water may be sucked up through *b*, and the fat washed in the flask (perfectly closed by pinching the india-rubber), and then the cake allowed to form as before. The fluid is now again run off from the solid, and this time cold water may be sucked up through *a*, and the whole process of alternations of hot and cold water repeated. Lastly, the cork with its tubes is removed, any adherent fat washed off with warm water into the flask, the latter adapted either to an upright Liebig's condenser and boiled, or connected in the usual way with a Liebig, the latter having as a receiver a flask, adjusted by a cork tightly to the bent tube of the condenser, and furnished with a mercury valve, the whole forming a closed system. In the latter case also, the heat is applied to boiling for five or ten minutes, and the distillate added to the filtrates; lastly, the cork with tubes is again connected, the flask inverted, the liquid when cool run off, and the fat finally washed with a little cold water and allowed to drain.

The watery liquid contains sulphuric acid, sulphate of potash, alcohol, butyric, and the other soluble fatty acids; it will be in bulk from 600 to 700 cc., and may be made up to any definite quantity. In any case, a portion of it—a quarter, a fifth, or even a tenth—must be taken and titrated with d. n. soda, which, when the quantity required to neutralise the 1 cc. of sulphuric acid in excess is subtracted, indicates the amount of soluble acid, and is always returned as butyric, which is near enough to the truth.

Instead of this method it may be useful to titrate the acid liquid, distil until all the volatile acid which can be obtained has gone over, and then titrate the distillate. It is also possible to separate in great measure the volatile fatty acids from such a solution by shaking up with ether, the latter dissolving the acids freely.

The *insoluble fatty acids* remaining partly in the flask, with a trace on the filter, are now united in a flat porcelain dish. This is done by melting the acids in the flask, pouring off, and extracting by alcohol and ether—the same solvent also dissolving the acids from the filter. On evaporation of the alcohol and ether, one or two large bubbles of water may be formed in the acids, and it is best to add a few drops of absolute alcohol. The dish is now placed on the top of the water-bath (the water in which should only boil gently), and weighed at short intervals; if after twenty minutes only 1 or 2 mgrms. are lost, the weight is considered constant.

The insoluble fatty acids are, as already stated, oleic, palmitic, and stearic—it is their total weight which is alone valuable, and to separate the three with accuracy is not easily effected. The first can, however, be very readily isolated by the following process, the details of which have been worked out by Dr. Muter. The process depends upon the well-known fact that the oleate of lead, $Pb2C_{18}H_{33}O_2$, can be separated from plumbic palmitate, $Pb2C_{16}H_{31}O_2$, and plumbic stearate, $Pb2C_{18}H_{35}O_2$, by taking advantage of the solubility of the former in ether.

About 1 grm. of the fatty acids is combined with potash, and the solution well diluted with boiling water, and carefully treated with acetic acid added to the boiling solution until a permanent turbidity is produced; solution of potash is now dropped in with constant stirring, until the liquid just clears again. The solution is now precipitated by plumbic acetate in slight excess, and is stirred until the precipitated soap settles thoroughly. The supernatant liquid is poured off, and the soap once washed by boiling with a large volume of water and decanting; plumbic oleate, palmitate, and stearate are thus obtained as perfectly neutral salts, the first being soluble in ether, the last two quite insoluble. The lead soap is now transferred to a flask of 100 cc. capacity, and the plumbic oleate dissolved out by ether, the ethereal solution being passed through a filter. The end of the process is known by the washings ceasing to blacken ammonium hydrosulphide. The filtrate and the washings should not exceed 200 cc., a fractional portion of which may be evaporated to dryness in a platinum dish, and weighed as plumbic oleate. To ensure perfect accuracy, the remainder should be ignited and weighed as $Pb + PbO$; the residue treated with acetic acid to take up the PbO, and the residual Pb calculated to PbO. By deducting the weight of plumbic oxide thus obtained from the total plumbic oleate, and allowing for the hydrogen displaced, the oleic acid is obtained.

Dr. Muter recommends, however, an easier method. This requires a long graduated tube of 250 cc., having a well-ground stopper and a stopcock, which is placed at 50 cc. from the bottom. The ethereal solution is placed in this, the soap decomposed by hydrochloric acid [1 : 2]; and (when the chloride of lead is fully settled) a known quantity of the supernatant ethereal solution drawn off, evaporated, and weighed as oleic acid.

In the majority of adulterated butters, the specific gravity, the melting-point, and the fatty acids are all widely different from that of genuine butter, so that there is no room for doubt. Occasionally, however, a butter may be met with in which a small proportion only of foreign fat has been used, and in such a case the analysis must be repeated several times lest a mistake be made. Of all the above determinations, the percentage of insoluble and soluble fatty acids is of the greatest importance. A marked deficiency or complete absence of soluble, and an increase of insoluble, are the characteristic features of fats other than butter.

The following are a few examples of percentages of fatty acids found in genuine butters:—

	(1.)	(2.)	(3.)	(4.)
Soluble,	5·92	5·76	5·37	4·77
Insoluble,	87·86	88·10	87·68	88·44
	93·78	93·86	93·05	93·21

It is generally accepted that 88 per cent. of insoluble acids, if associated with 6·3 of soluble acids, is a fair standard of butter calculation, and that if a butter shows anything less than 89·5 insoluble, with 5 soluble, it may be passed as genuine.*

A few examples of adulterated butter fat are as follows:—

	(1.) A Commercial Butter.	(2.) A Commercial Butter.	(3.) Butterine.
Soluble,	1·98	2·34	·58
Insoluble,	93·30	93·82	95·51
	95·28	96·16	96·9

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* Muter, *Op. cit.*

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III.—CHEESE.

§ 25. *Constituents of Cheese.*—Cheese consists essentially of the coagulated albuminous matters of milk, and especially of caseine, with a variable quantity of fat, common salt, alkaline, and earthy phosphates. It may be made from the milk of any mammal, but the great majority of cheeses in commerce are made from cows' milk.

The different varieties of cheese depend upon the processes employed, and also upon the proportion of cream left in, or added to, the milk—the poorest horny skim-cheeses, with regard to percentage of fat, being at one end of the scale, and cream-cheese, made entirely of cream, at the other. The chief commercial cheeses are as follows :—

American Cheeses, made from unskimmed milk, and of extremely uniform quality. The general composition of two fine-flavoured Americans, sold at 9d. per lb., the author found to be—

		(1.)		(2.)
Water,		22·59		31·80
Fat,		35·41		28·70
Caseine,		37·20		36·00
Ash, Soluble in water,	1·19		1·13	
Ash, Insoluble,	3·61	4·80	2·37	3·50
NaCl in Soluble Ash,		1·08		1·01
Phosphate of Lime in Insoluble Ash,		2·21		2·37

Cheddar Cheese is made with entire milk ; the cheeses are usually thick, and weigh up to 200 lbs. each. Two sound, good-flavoured Cheddars, sold at 11d. per lb., had the following composition :—

		(1.)		(2.)
Water,		27·83		28·34
Fat,		24·04		21·01
Caseine,		44·47		47·03
Ash. Soluble in water,	1·14		1·14	
Ash. Insoluble,	2·52	3·66	2·48	3·62
NaCl in Soluble Ash,		1·04		1·14
Phosphate of Lime in Insoluble Ash,		1·52		1·69

Cream Cheese is made entirely of cream.

Dunlop Cheese is made with entire milk, and is not dissimilar in general composition to American cheeses. A sample examined by Johnstone had the following composition :—

	Per cent.
Water,	38·46
Fat,	31·86
Caseine,	25·87
Ash,	3·81

Gloucester Cheese.—Two varieties of Gloucester cheese exist in commerce, single Gloucester and double Gloucester—the only difference between the two being that the latter is richer than the former, single Gloucester being made from a mixture of skimmed and entire milk, double Gloucester from entire milk. A single Gloucester, sold at 9d. per lb., of good flavour, and free from mould, had the following composition :—

	Per cent.
Water,	21·41
Fat,	25·38
Caseine,	49·12
Ash,	4·09

An analysis by Johnstone of a double Gloucester is as follows :—

	Per cent.
Water,	35·82
Fat,	21·97
Caseine,	37·96
Ash,	4·25

Notwithstanding that in the single the fat was 25 per cent., in the double but 21 per cent., the latter is really richer than the former, if the water be subtracted, and the percentage be taken on the dry substance; or if the proportion of the fat to the caseine be considered—in the double the fat being to the caseine as 10 : 17, in the single as 10 : 19.

Parmesan Cheese.—This is a peculiar cheese, never made in this country, but imported from Parma and elsewhere. The essential points in the manufacture are, that the rennet is heated to about 120°F., and an hour afterwards the milk set over a slow fire until heated to about 150°F. These operations cause the curd to separate in hard lumps. It is usually coloured with saffron. The outer crust of the cheese at the end of fourteen days is cut off, the new surface varnished with linseed oil, and one side coloured red. It is a very dry cheese, with a large amount of caseine, and only a moderate percentage of fat. A Parmesan analysed by Payen gave—

	Per cent.
Caseine,	44·08
Fat,	15·95
Salts,	5·72
Water,	27·56
Non-nitrogenous matter, &c.,	6·69

The Roquefort Cheese is a very celebrated French cheese, largely eaten on the Continent. It is not made from cows' milk, but from that of the ewe. A fresh Roquefort, analysed by Blondeau,* had the following composition :—

	Per cent.
Caseine,	85·43
Fat,	1·85
Lactic acid,	0·88
Water,	11·84

The same cheese, in the condition most highly prized (after it had been kept two months in a cold cellar), had the following composition :—

		Per cent.
Caseine,		43·28
Fat, Margarin,	18·30	32·30
Fat, Olein,	14·00	
Butyric Acid,		0·67
Chloride of Sodium,		4·45
Water,		19·30

Roquefort cheese is usually coloured with reddle or arnatto. The manufacturers of these cheeses attach great importance to their being kept at a rather low and uniform temperature during the ripening process. The most famous cellars are subterraneous mountain-caves, kept constantly cool (at about 41° to 42°F.) by currents of air coming through clefts and grottoes. The commercial value of these cellars is directly proportionate to their uniformity of temperature.

Skim Cheese.—The quality of skim cheese depends upon the amount of fat it contains. A cheese which shows under 5 per cent. of fat may with propriety be called skim, the majority of skim cheeses containing from ·5 up to 5 per cent. of fat. The writer found a sample of skim cheese, at 6d. per pound, to have the following composition :—

		Per cent.
Water,		43·14
Fat,		·86
Caseine,		49·79
Ash, Soluble in water,	2·16	6·21
Ash, Phosphate of Lime,	3·98	
Ash, NaCl in Soluble Ash,	2·00	

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* *Annales de Chimie et de Physique* [4], t. i., 1864.

Stilton Cheese is made from entire cows' milk, to which some cream has been added. When fully mature, these cheeses are similar in composition to ripe Roqueforts.

There are various other cheeses, such as *Dutch,* which are usually highly salted; *Gruyère,* a peculiarly flavoured cheese made in Switzerland; *Neufchatel,* a Swiss cream cheese; *Schabzieger,* or green cheese, also of Swiss origin, and flavoured with melilot; besides various English cheeses taking their names from the county in which they are made.

The Ripening of Cheese.—The transformation that cheese undergoes, and by which it usually acquires a more agreeable taste and flavour, is without doubt a fermentation of a slow character, induced by the agency of minute mycoderms; possibly, as F. Cohn suggests, the very active thread-bacteria, which rennet always contains, have something to do with the process. The chemical changes appear to consist essentially in a fatty metamorphosis of the albuminoids, a subsequent decomposition of the fat, or rather of the glycerine, and the liberation of butyric, capric, caproic, and other fatty acids. Ammonia and carbonic dioxide are also produced, *e.g.*, the Roquefort cheese (two analyses of which are given above) was analysed at the end of a year, and its composition found to be as follows:—

	Per cent.
Caseine,	40·28
Margarin,	16·85
Olein,	1·48
Butyrate of Ammonia,	5·62
Caproate of Ammonia,	7·31
Caprylate of Ammonia,	4·18
Caprate of Ammonia,	4·21
Chloride of Sodium,	4·45
Water,	15·62

Valerianic acid has also been detected in Roquefort cheese by M. Bolard, and by Messrs Jljenko and Laskowski in a Limbourg cheese.

Besides the transformation of caseine into fatty products, the margaric acid decomposes the phosphate of lime, the result being margarate of lime and phosphate of caseine (the latter soluble in water); so that if only a sufficient time is given, a cheese which originally gave up, after removal of the fat, very little to water, becomes almost wholly soluble. Occasionally, instead of the process described, a true putrefaction of the cheese ensues, and fœtid products containing sulphur are given off.

§ 26. *Analysis of Cheese.*—The mode of procedure differs little from that used with milk. Small quantities only of the cheese must be taken for the water, and prolonged drying is necessary. Ether is not suitable for extraction of fat, owing to the solubility of the lactic acid which many cheeses contain, but petroleum answers every purpose. The ash is taken in the usual way, and the difference may be returned as caseine, or the latter may be found by a combustion with cupric oxide, or by the ammonia method (p. 48).

The *adulterations* of cheese which have actually been found are not numerous. All mineral adulterations, save those of volatile metals, must be looked for in the ash, which consists normally of common salt, alkaline, and earthy phosphates. Cheese has from the earliest to the present time been coloured by vegetable matters, and so long as the latter are not injurious, such addition cannot be considered as adulteration.

Thin slices of cheese should be examined microscopically after dissolving out the fat, &c., by ether; in this way starches and vegetable substances may be detected. Arsenical washes and lead pastes have often been applied to the rind to prevent the attacks of the fly. As this part is habitually eaten by a few people, it is necessary to examine it, especially for these metals, and, in a complete investigation, to make two separate analyses, one of the rind, and the other of the substance of the cheese.

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PART IV.

TEA — COFFEE — COCOA.

I.—TEA.

§ 27. *Varieties of Tea.*—Tea is the dried leaf of different species of *Thea*, a section of the genus *Camellia.* The botanical varieties do not appear to be numerous. *Thea Bohea*, *T. viridis*, and *T. sinensis*, all Chinese plants, *Thea Assamica*, indigenous to Assam, and one or two hybrids, are the principal plants from which the numerous teas of commerce are derived. The difference depends on the selection of young or old leaves, and special treatments in drying and otherwise preparing the leaf, rather than on essential botanical variation.

The varieties of tea imported into this country are extremely numerous; but seldom does any one of them reach the consumer unmixed, for the wholesale tea merchants carefully improve their teas by "blending." The most common sorts are — Gunpowder, Hyson, Congou, Capers, and Indian tea. Of these, the Gunpowder and Hyson are dried at a higher temperature than the others, and contain less hygroscopic moisture. The Capers may be generally told by the leaves being rolled up into little lumps with starch or gum; as a class, they are much adulterated, and, in fact, can hardly be called genuine tea.

Besides these, there are a number of special teas, some of a very high price, and imported in a state of great purity, but such teas are used almost entirely for mixing or blending. They are known under the names of Moyone, Moyone gunpowder, Oolong, Mannuna Kaisow, scented Pekoes, Indian Souchong, Assam, Java, &c. The names by which the teas of commerce are most familiar to the public are simply "green" and "black," which differ merely in accordance with the method of preparation followed. Green tea is prepared from young leaves, which are roasted over a wood fire within an hour or two after being gathered. The black tea leaves, on the other hand, are allowed to lie in heaps for ten or twelve hours after they have been plucked, during which time they undergo a sort of fermentation; the leaves then pass through certain processes, and are slowly dried over charcoal fires.

§ 28. *Structure of the Tea Leaf.*—The border is serrated nearly, though not quite, up to the stalk. (See Fig. 4.) The primary veins run out from the midrib almost to the border, and then turn in, so that a distinct space is left between them and the border. The diagnostic mark of a tea leaf is, however, the microscopic appearance of its epidermis, which, especially that of the lower side (see Fig. 5), exhibits numerous small stomata formed of two reniform cells of an average length of from ·0001328 to ·001662 inch, and average breadth ·001162 to ·000996 inch. Around the stomata are seen elongated and curved epidermic cells. This appearance, so far as is known, is met with only in the tea plant. Stomata are infrequent on the upper surface, the epidermal hairs are simple.

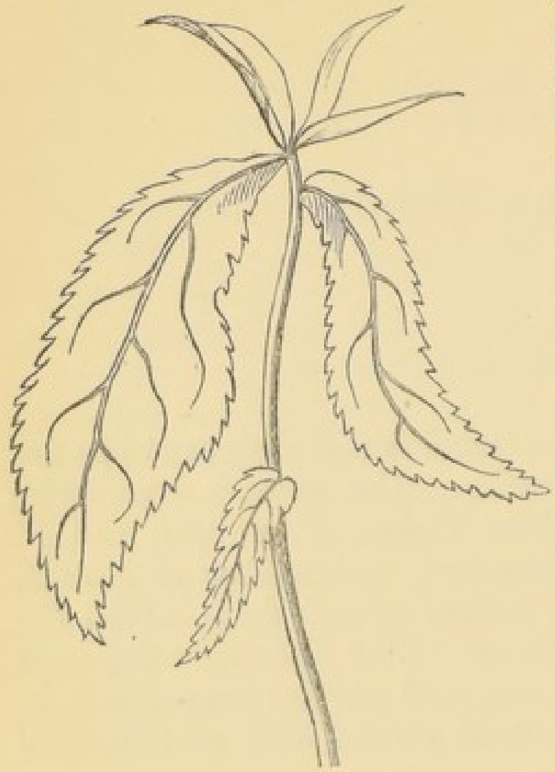

Fig. 4. TEA PLANT

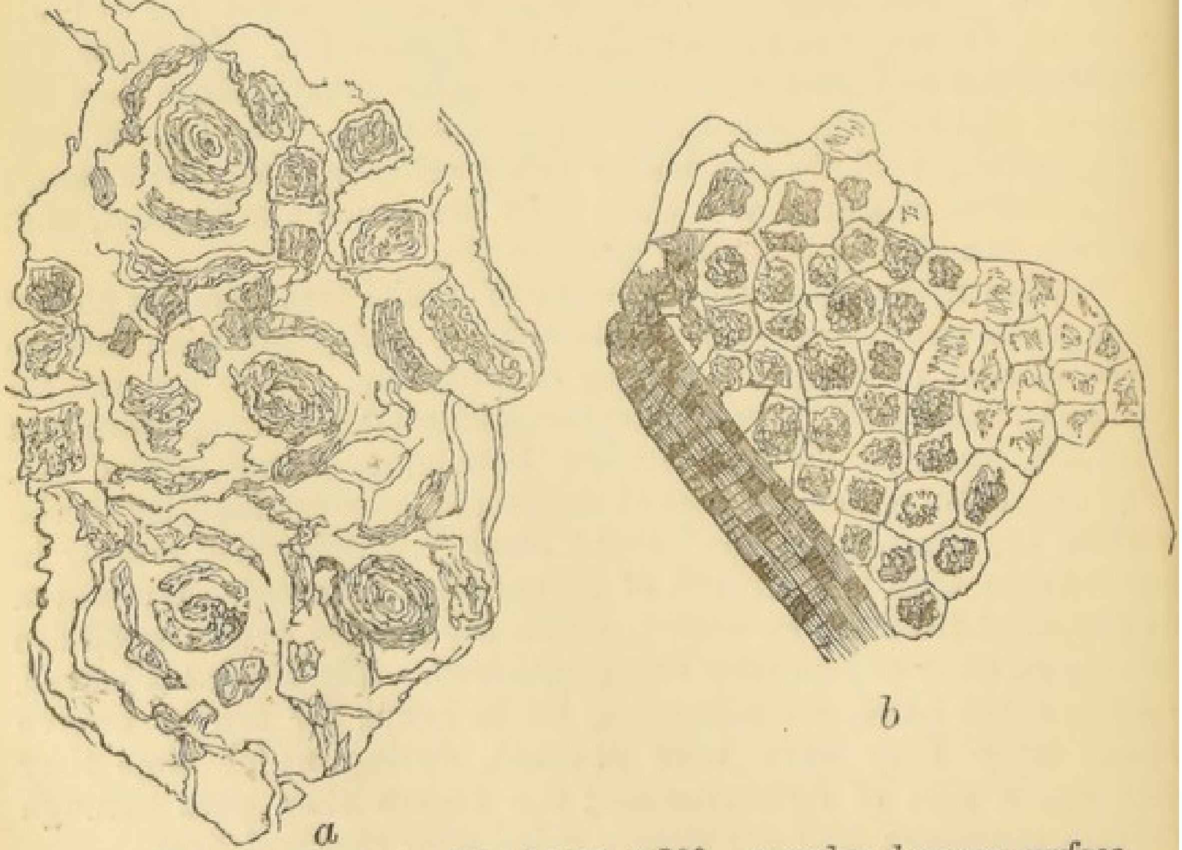

Fig. 5.—Epidermis of Tea Leaf, × 300. *a* under, *b* upper surface.

§ 29. *Chemical Composition of Tea.*—The constituents of tea are—*Essential oil, theine, boheic acid, quercetin, tannin, quercitrinic acid, gallic acid, oxalic acid, gum, chlorophyl, resin, wax, albuminous, woody, and colouring matters, and ash.* The essential oil of tea varies from 0·6 to 1 per cent. It is citron-yellow, lighter than water, has a strong odour of the tea plant, solidifies easily by cold, and resinifies on exposure to air.*

§ 30. *Theine, Caffeine,* $C_8H_{10}N_4O_2$.—This alkaloid was first separated in an impure condition by Runge, from coffee berries, in the year 1820. It was found by Corput and Stenhouse also to be a constituent of the leaves of the coffee tree. Oudry, in 1827, finding it in various species of tea, named it "Theine," and Oudry's "Theine," Mulder and Jobst showed in 1838 to be identical with caffeine. The alkaloid has also been discovered in guarana, maté, and the kola nut, by Martius, Stenhouse, and Attfield respectively.

Theine crystallises from an aqueous solution with 1 atom of water; from ether, in an anhydrous state. It sublimes in minute dots at 78·8°C., in crystals at 79·4°C. (175°F.), and above.† The sublimate consists of microscopic needles: that which is first produced is of extremely fine, light elements; after a little time, at such temperatures as 120°C., the crystals become longer and larger. The melting point of theine is somewhere between 177°C and 228°C. Theine possesses a slightly bitter taste, but is without odour. According to a recent research, the solubility of theine in different solvents is as shown in table on next page.

Theine forms numerous salts of definite composition—the hydrochlorates, $C_8H_{10}N_4O_2$, HCl and $C_8H_{10}N_4O_2$, 2HCl; a platinum compound, $C_8H_{10}N_4O_2$, HCl, $PtCl_2$; a chloride of gold compound, $C_8H_{10}N_4O_2$, HCl, $AuCl_3$; a chloride of mercury and theine, $C_8H_{10}N_4O_2$, 2HgCl; an argentic nitrate with theine, $C_8H_{10}N_4O_2$, $AgNO_3$, and many others. Some of these, such as the silver compound, separating from a concentrated watery solution, and the mercury compound, almost insoluble in ether, and capable of being dried at 100°C., might possibly be of use in the estimation of theine.

Theine is, in large doses, a poison. Frerichs, C. J. Lehmann,

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* A fixed oil, serving many purposes in China, is extracted from the seeds of the tea plant. It is citron-yellow, specific gravity 0·927, and is composed of one part of stearin and one of olein.

† The subliming point given by Pelouse, 178°C., and by Mulder, 184·7°C., must have been obtained by extremely faulty methods. If a little theine is placed between two watch-glasses on the water-bath, the almost instantaneous rise of crystals to the upper glass will at all events show that the subliming point is below 100°. See the author's paper, "Temperature at which the Alkaloids sublime," *Journal of Chemical Society*, 1878.

SOLUBILITY OF THEINE.

	100 grms. of Solvent at 15° to 17°C. dissolved of Theine.		Co-efficient of Solubility at 15° to 17°C.		100 grms. of Solvent at the boiling point dissolved of Theine.		Co-efficient of Solubility at the boiling point.	
	Hydrated.	Anhydrous.	Hydrated.	Anhydrous.	Hydrated.	Anhydrous.	Hydrated.	Anhydrous.
Chloroform, . .	...	12·97	...	1/7·72	...	19·02	...	1/5·25
Alcohol of 85 per cent., . . .	2·51	2·30	1-40	1/44·4	...	...	...	...
Water, ...	1·47	1·35	1-68	1/74·2	49·73	45·55	1/2·01	1/2·19
Absolute Alcohol,	...	0·61	...	1/164·7	...	3·12	...	1/32
Commercial Ether,	0·21	0·19	1/476	1/526	...	0·454	...	1/220
Carbon Bisulphide,	...	0·0585	...	1/1709	...	...	...	...
Purified Anhydrous Ether, .	...	0·0437	...	1/2288	...	0·36	...	1/277
Essence of Petroleum, . . .	...	0·025	...	1/4000	...	...	...	...

Husemann, and others, have made themselves the subject of experiment. Lehmann, after taking ·5 grm. suffered from frequency of the pulse, irritation of the bladder, cerebral excitement, slight hallucinations, and lastly desire to sleep. Husemann took ·25 grm. with somewhat similar symptoms. Pratt, with subcutaneous injections, of from ·12 to ·8 grm., suffered from symptoms rather different from the foregoing; ·3 grm. lessened the pulse and caused sleeplessness; ·4 to ·5 grm. quickened the pulse, and caused a desire for frequent micturition, but no dilation of the pupil; ·8 grm. caused great uneasiness and anxiety, trembling of the hands and arms, so that he was unable to write, and later a restless sleep, with continual dreaming. In opposition again to all these statements, is that of the late Mr Cooley,* who is said to have taken 20 grains (1·29 grm.) of pure theine every day for a month without experiencing any other symptom than some slight elevation of spirits. According to Strauch, the least fatal dose for cats is ·25 grm., a quantity which killed a cat in 35 minutes. In all experiments on animals there has been increased frequency of the heart's action, and repeated emptying of the bladder and intestine. No case of poisoning in the human subject appears to be on record. When given to animals it has been chemically separated from the blood, urine, and bile.

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* *Vide* Cooley's "Dictionary of Practical Receipts," Art. Caffeine.

Tests for Theine.—Concentrated sulphuric and nitric acids dissolve theine in the cold without the production of colour. If the alkaloid is treated with fuming nitric acid, and evaporated to dryness, the reddish-yellow residue becomes, when moistened with ammonia, of a splendid purple-red colour. If a solution of theine be evaporated with chlorine water in a watch-glass, a red-brown residue is obtained, which on cooling, and exposure to the vapour of strong ammonia, becomes purple-violet. The chief precipitants of theine are—phosphomolybdic acid, yellow precipitate; iodine with potassic iodide, dirty brown precipitate; chloride of platinum, yellow hair-like crystals, insoluble in cold hydrochloric acid, slowly separating; chlorides of gold, mercury, and nitrate of silver also give precipitates.

§ 31. *Boheic Acid*, $C_7H_{10}O_6$, was first separated by Rochleder in 1847,* from the leaves of *Thea sinensis.* The hot watery decoction of tea is precipitated whilst boiling by sugar of lead, filtered, the filtrate neutralised by ammonia, the resulting precipitate collected, suspended in absolute alcohol, and freed from lead by SH_2; the filtrate from the lead precipitate is evaporated to dryness in a vacuum, and purified by re-solution in water, &c. It is a pale yellow amorphous powder, melting at 100°C. into a tenacious mass, and decomposing at common temperatures if exposed to the air. It is soluble in all proportions in water and alcohol, is coloured brown (but not precipitated) by chloride of iron, and forms for the most part amorphous salts insoluble in water.

§ 32. *Quercitrinic Acid*, $C_{33}H_{30}O_{17}$, first discovered by Chevreul and Brandt in the *Quercus tinctoria*, and stated by Hlasiwetz to be in tea leaves, can be crystallised from an aqueous solution. It forms sulphur or chrome-yellow microscopic tables, containing 3 atoms of water, part of which is expelled at 100°C., the rest at from 165° to 200°C. Its reaction is neutral, and it is without odour, but has a marked bitter taste when in solution. It melts at from 160° to 200°C. to a resinous, amorphous mass. Its solubility is as follows:—Cold water 2485, boiling 143; cold absolute alcohol 23·3, boiling 3·9; ether dissolves it slightly, warm acetic acid copiously. Sugar of lead precipitates almost completely; the precipitate is soluble in acetic acid.

§ 33. *Quercetin*, first obtained by Rigaud, 1854, from the splitting up of quercitrinic acid, is, according to Filhol, to be found in the green leaves and flowers of all plants. Its formula is given as $C_{27}H_{18}O_{22}$; it forms fine yellow needles, or a citron-yellow powder, which gives up at a temperature of 120°, 7 to 10 per cent. of water of crystallisation. It melts, according to Zwenger and

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* Rochleder, *Ann. Chem. Pharm.*, lxiii. 202.

Dronke, above 250°C. without decomposition, solidifying again in a crystalline mass, and it may be also sublimed with only partial carbonisation. It is very little soluble in water. Warm acetic acid dissolves it copiously, but it separates on cooling. Alcohol dissolves it: 229·2 parts of cold, 18·2 parts of hot and absolute, are required. A solution of quercetin colours linen bright yellow, sugar of lead precipitates the alcoholic solution cherry red, and chloride of iron dark red. A combination with sodium or potassium can be obtained, $Na_2O, C_{27}H_{18}O_{22}$.

The other constituents of tea, such as gallic and tannic acids, gum, &c., are too well known to need description.

§ 34. *Analysis of Tea.*

We possess no complete analysis of tea; partial analyses are numerous. An often quoted one by Mulder is as follows:—

	Black Tea.	Green Tea.
Essential Oil,	0·60	0·79
Chlorophyl,	1·84	2·22
Wax,	0·00	0·28
Resin,	3·64	2·22
Gum,	7·28	8·56
Tannin,	12·88	17·80
Theine,	0·46	0·43
Extractive Matter,	21·36	22·80
Colouring Substances,	19·19	23·60
Albumen,	2·80	3·00
Fibre,	28·33	17·80
Ash (Mineral Substances),	5·24	5·56

The theine here is certainly too low, but the amounts of the other constituents are a tolerably just representation of what may be usually found. Some partial analyses recently published by Dragendorff may be reproduced here, as probably the only extended and trustworthy researches on the amount of theine, the alkaloid having been extracted by a fairly reliable method. (*See annexed table.*)

The time is probably not far distant when the tea trade will buy entirely by analysis, supplemented in a few cases by a "taster's" report. An experienced palate will detect particular flavours which analysis may fail to show; but a fairly complete chemical examination of tea is of the highest value, whether as a guide to the purchaser, or merely to show its freedom from adulteration.

(1.) *Preliminary Examination of Tea.*—The tea leaves should be soaked in hot water, carefully unrolled, and their shape and structure examined. Sections can be made of leaves by placing them between two pieces of cork, and cutting fine slices

AN COMM

from luble tuents. ent.	Potash. Per cent. [On the Tea.]	P [On
16	2·53	
99	...	
12	...	
79	2·10	
74	2·27	
50	...	
04	2·48	4
39	2·23	3
58	...	
75	...	
04	...	
9	...	
	...	
79	1·97	3
59	2·28	3
5	...	
2	...	
7	...	
7	...	
5	...	
8	...	
4	...	
9	2·23	38

of both the cork and the enclosed leaf; on floating the sections in water, the film of cork may be readily separated from the leaf. The epidermis of the lower or upper surface can, with a little practice, be detached in small portions by the aid of a sharp razor, and examined in water, glycerine, or dammar balsam, under the microscope.* The structure of the tea leaf has been already noted. The following is a brief description of the principal leaves supposed to be used as adulterants:—

§ 35. *Beech* (*Fagus sylvatica*). (See Fig. 6.)—The leaves of the beech are ovate, glabrous, obscurely dentate, ciliate at the edges, the veins running parallel to one another right to the edge. The leaf, slightly magnified, is seen to be divided into quadrilateral spaces by a network of transparent cells. On section, the parenchyma of the leaf is found to consist of an upper layer of longitudinal cells, and a lower of loose cellular tissue, enclosed between the epidermis of the upper and under surface. The whole section is thus divided into oblong spaces by trans-

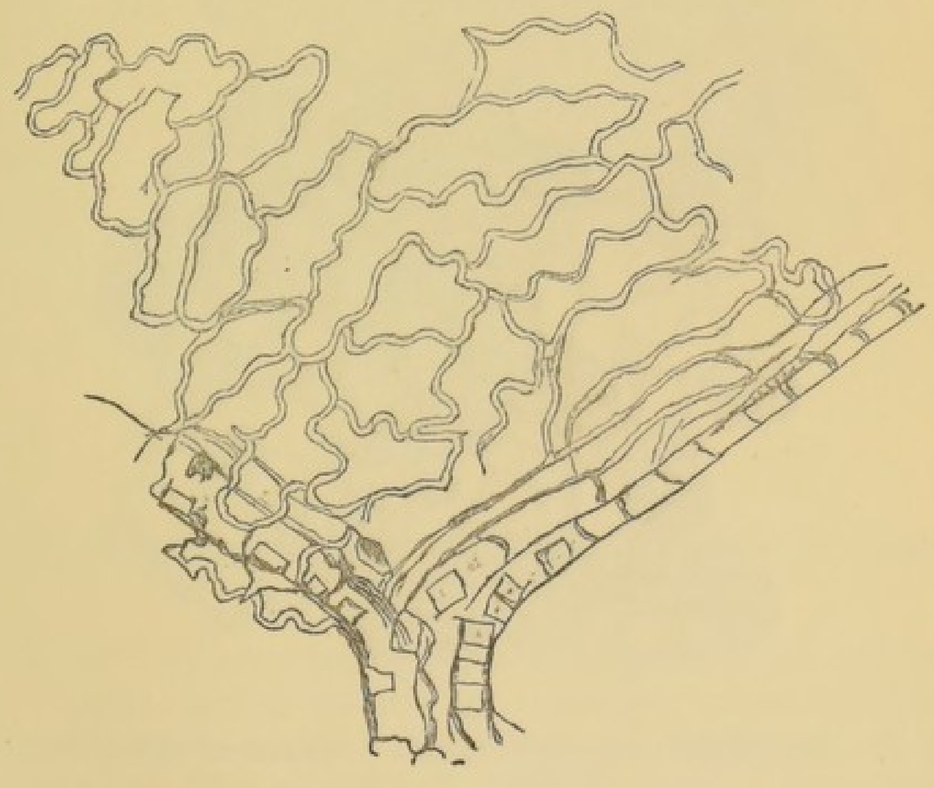

Fig. 6.—Epidermis of Beech Leaf, × 300.

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* There are various section-machines in use, but after trying several I have forsaken all, save in cases of soft, pulpy tissues, &c., where it is convenient to freeze the substance. With a very little practice, sufficient manual dexterity to obtain a fine section is acquired with the fingers alone. The whole of the beautiful preparations whence Schleiden obtained the illustrations for his botanical works were taken by the aid simply of a sharp razor.

parent cells connecting the cuticle of the upper and lower surfaces. The epidermis of both the upper and lower surfaces is composed of cells with an extremely sinuous outline (see Fig. 6). The stomata are small, not numerous, and almost round; average length, ·000996 inch, average breadth, ·00083 inch. Beech leaves contain manganese.

§ 36. *Hawthorn* (*Cratægus oxyacantha*).—At least two varieties, the more common of which is the *C. monogyna*, with obovate three- to four-deeply lobed leaves, with the lobes acute. The leaf is divided into quadrilateral spaces, like the beech and many other leaves, by a transparent network. The epidermis of the upper surface is composed of a layer of thin-walled cells, generally quadrilateral, outline seldom sinuous. The epidermis of the lower surface has a layer of thin-walled cells, with a very sinuous outline. Stomata large, distinct, and numerous, in many instances nearly round, but the shape mostly oval. The average length of the stomata is ·00166 inch, the average breadth ·00149 to ·0015 inch. (See Fig. 7.)

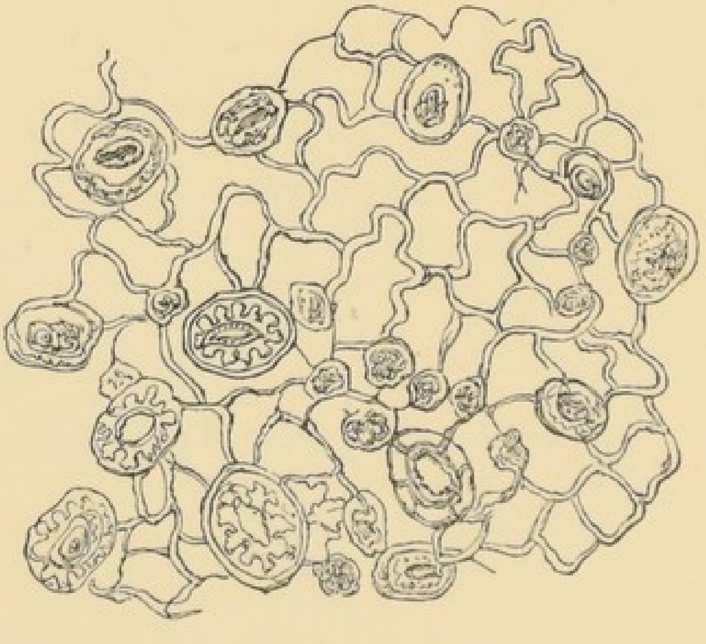

Fig. 7.—Epidermis from the Under Surface of the Hawthorn Leaf, × 300.

§ 37. *Camellia Sassanqua.*—The leaves of *Camellia sassanqua* are oval, obscurely serrate (the younger leaves entire), dark green, glabrous, of somewhat leathery consistence; the lateral veins of the leaf are inconspicuous.

Micro-structure.—The parenchyma of the leaf is placed between two thickened epidermal layers; the epidermis of the upper surface, as seen upon a section, forms a wrinkled, continuous, thick membrane, in which a cellular structure is not very evident. Below this there are two or three layers of large cells, more or less oblong, with their long diameter at right angles to the surface of the leaf; and underneath this again is a loose network of cells, resting upon an epidermis in every respect similar to that of the upper surface, but only half as thick. A thin layer of either the upper or lower epidermis shows a peculiar dotted or reticulated appearance, not unlike the rugae of a stomach. The lower epidermis is studded with frequent stomata, which are of an oblong shape, length ·001328 inch, breadth ·00083 inch. (See Fig. 8.)

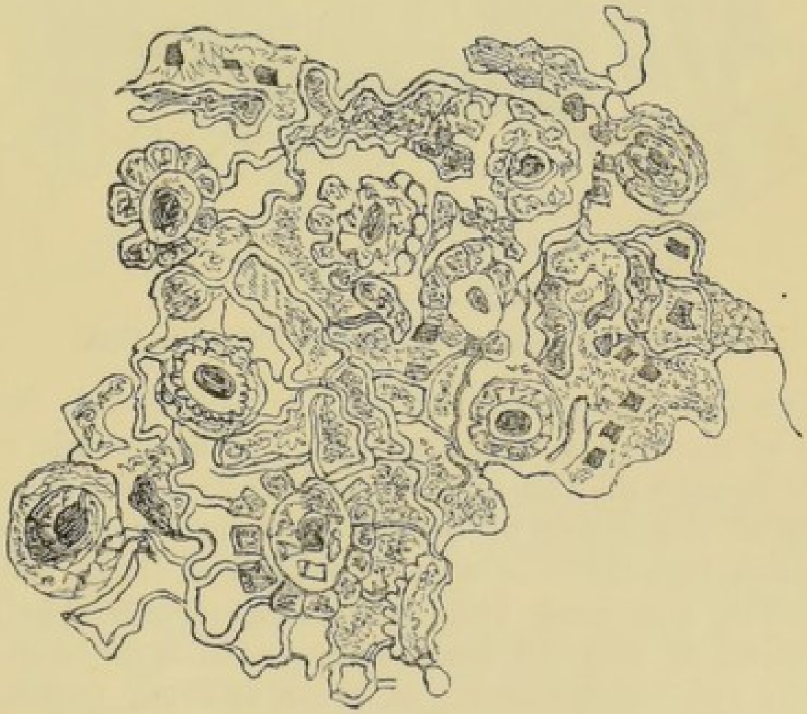

Fig. 8.—Epidermis of Under Surface of the Leaf of Camellia Sassanqua, × 300.

§ 38. *Sloe* (*Prunus communis*).—The leaves of the common sloe are rather small, elliptic or ovate-lanceolate in shape, and slightly downy beneath. The sectional thickness of the leaf is the same as that of tea, viz., ·00664 inch. The stomata on the lower surface are scanty, in length about ·00166 inch; in breadth, ·00083 inch. The microscopical appearances are wholly different from those of tea leaves, more especially as seen in section. (See Fig. 9.)

§ 39. *Chloranthus Inconspicuus.*—The leaves of the *Chloranthus inconspicuus* are long, oval, serrate, wrinkled, the veins running nearly to the edge, and there forming a network in such a manner, that at the point of intersection little knots are formed,

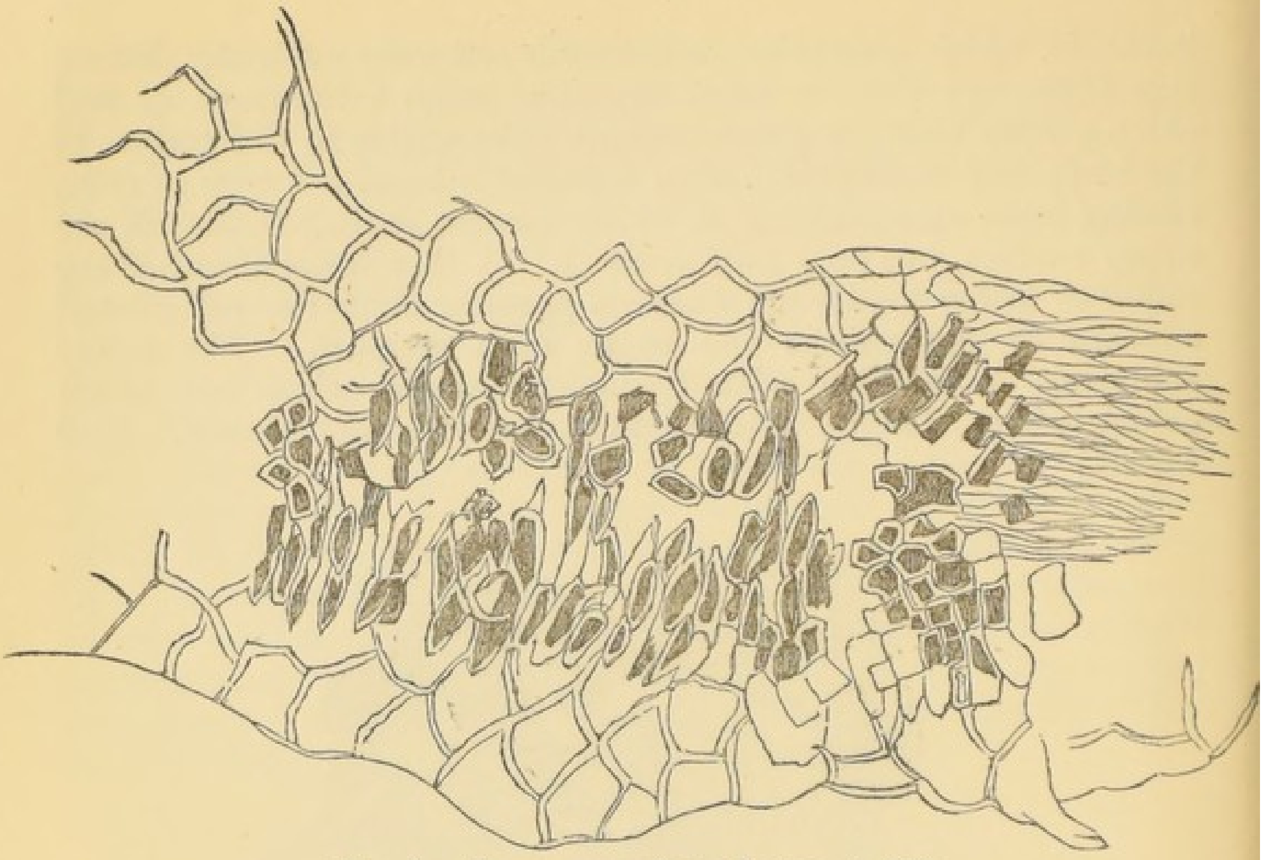

Fig. 9.—Section of Sloe Leaf, × 300.

which give the margin of the leaf a very rough feeling. The structure of the leaf is very simple. The epidermis of the upper surface is formed of one or two layers of thin-walled cells, the epidermis of the lower of one or two layers also of cells, and between the two there is a parenchyma of loose cellular tissue. The stomata are oval and rather numerous; their length is from ·001992 to ·002188 inch, their breadth ·001338 inch. The cells of the epidermis are large, some of them ·005 inch or more in their long diameter.* (See Fig 10.)

The dimensions of the stomata of the various leaves just described may be conveniently arranged in a tabular form, thus—

	Length of Stomata. Inch.	Breadth of Stomata. Inch.
Beech,	·000996	·00083
Camellia sassanqua,	·001328	·00083
Tea,	from ·001162 to ·001328	from ·000996 to ·001162
Sloe,	·00166	·00083
Hawthorn,	·00166	·00149
Chloranthus inconspicuus,	·001992	·001328

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[*] The leaves of *Epilobium angustifolium* (*common willow herb*) are said to be extensively used in Russia for the adulteration of tea. The dried leaves are sold for from four to six roubles a pound, and are used by the poorer classes in the place of tea. Alcohol produces in infusions of epilobium a precipitate of mucilage.—*Pharm. Zeitsch. für Russland*, and *Year-Book of Pharmacy*, 1876.

A chemical method for the detection of foreign leaves (adulterants) was first described by the writer in June, 1877.* It is based upon two facts, firstly, that every part of a *theine*-producing plant—wood, stem, leaf, flowers, and even hairs—contains the alkaloid; and secondly, that this can be readily sublimed. The leaf, or fragment of a leaf, is boiled for a minute in a watch-glass

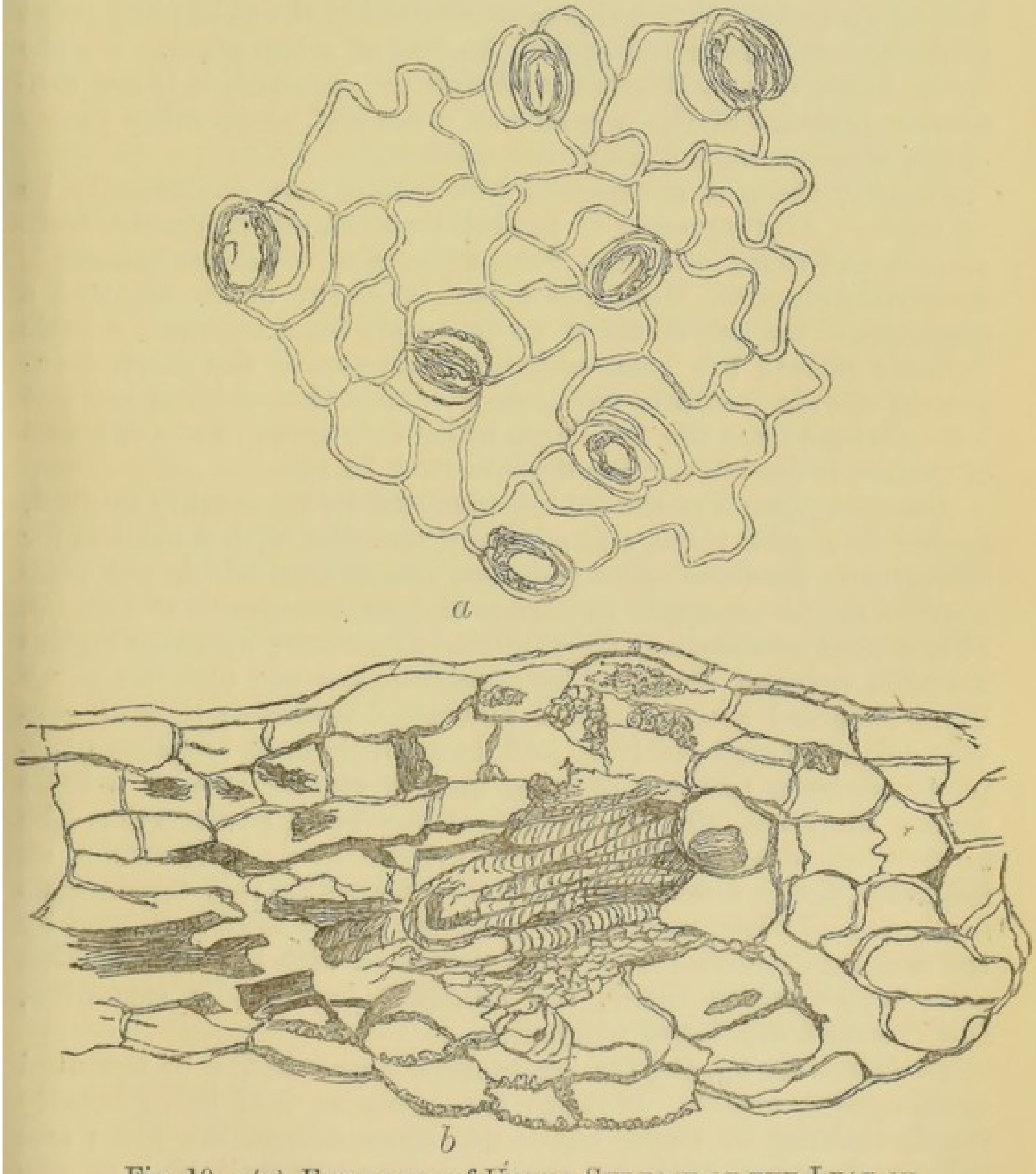

Fig. 10.—(*a*) Epidermis of Under Surface of the Leaf of Chloranthus Inconspicuus, × 300.
(*b*) Section near Edge.

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* "Micro-Chemistry, as applied to the Identification of Tea Leaves." By A. Wynter Blyth. *Analyst*, June, 1871.

with a very little water, a portion of burnt magnesia equal in bulk is added, and the whole heated to boiling, and rapidly evaporated down to a large-sized drop. This drop is transferred to the "subliming cell," described in another portion of this work, (see *Index*,) and if no crystalline sublimate be obtained, when heated up to 110°C. (a temperature far above the subliming point of theine), the fragment cannot be that of a tea plant. On the other hand, if a sublimate of theine be obtained, it is not conclusive evidence of the presence of a tea leaf, since other plants of the camellia tribe contain the alkaloid.

Finally, there is a negative test which may occasionally be valuable. All fragments of tea hitherto examined contain manganese, and there are a few foreign leaves in which manganese is constantly absent. Hence, if a leaf be burnt to an ash, and a fragment of the ash be taken up on a soda-bead, to which a little potassic nitrate has been added, the absence of the green manganate of soda would be sufficient evidence that the leaf had not been derived from the tea-plant, while conversely, as in the case of theine, it does not in itself prove it to be tea.

Another portion of the tea leaves should be thoroughly bruised, spread on a glass plate, and carefully searched with a magnet for ferruginous particles—the so-called iron-filings, which are occasionally found, especially in Capers and certain species of Congou. It is almost unnecessary to state that the black, irregular masses found in tea, and attracted by a magnet, are not metallic iron.* Their chemical composition is somewhat variable; they all contain magnetic oxide of iron, and many of them in addition phosphate of iron, titanate of iron, quartz, and mica with a little sand. They are, without doubt, sometimes an adulteration (the author has himself found over 1 per cent.), and sometimes an impurity, for in a few teas mere traces only of this ferruginous sand may be discovered. Any particles of the kind extracted by the magnet should be collected and treated with hot water, which soon disintegrates them; the adherent tea-dust is separated, and the sand dried and weighed.

To detect facing, the tea in its dried state should be mounted as an opaque object. If it has the appearance of being heavily faced, soaking in warm water will soon detach the film; and indigo, Prussian blue, or similar substances will sink to the bottom, and may be collected and examined. Indigo may be identified by the microscope. Prussian blue may be tested for

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* Mr. Allen appears to have found metallic iron in tea. The test for metallic iron is, that nitric acid, 1·2 specific gravity, dissolves it with the production of red fumes; it also precipitates metallic copper, if added to an acidulated solution of cupric sulphate.

by warming the deposit with caustic alkali, filtering, acidifying the filtrate with hydrochloric acid, filtering again if necessary, and testing the filtrate with ferric chloride. The residue left after treatment with caustic alkali may be tested for magnesium silicate, by first extracting with HCl, and then collecting the insoluble residue, and fusing it with an alkaline carbonate. The silica is now separated in the usual way by evaporation with HCl to dryness, subsequent solution in weak acid, and filtration; any lime is removed by ammonia and ammonic oxalate; and lastly, magnesia is precipitated as ammon. mag. phosphate. Magnesia found under these circumstances must have been present as steatite or other magnesian silicate.

(2.) *Chemical Analysis.*—The preliminary examination of the tea having been concluded, the sample is next submitted to chemical analysis. If the question to be decided is simply that of adulteration, the taste of the infusion, the percentage of extract, and a determination of the chief constituents of the ash is in most cases all that is necessary; but a more or less complete examination embraces a quantitative estimation of hygroscopic moisture, theine, total nitrogen, tannin, extract, gum, and ash.

§ 40. *Hygroscopic Moisture.*—The ordinary method of taking the hygroscopic moisture of tea is to powder as finely as possible an indeterminate quantity of from 1 to 2 grms., and to heat it in a watch-glass over the water-bath until it ceases to lose weight. It should be finally weighed between two watch-glasses, since it rapidly absorbs moisture from the air.

The method given is in its results incorrect, since some volatile oil and a small proportion of theine are always volatilised. That theine is actually lost is capable of rigid demonstration; it is only necessary to heat a few leaves of tea between two watch-glasses over the water-bath, and theine crystals can be readily discovered by the microscope. To devise a process of drying tea which will represent water only is easy; but since the loss both of volatile principles and theine does not materially affect the results, it is scarcely worth while to complicate the analysis by the use either of a lower temperature or of processes of absorption. The highest amounts of moisture in a genuine tea which are on record are two specimens from Cachar, analysed by Professor Hodges—the one (indigenous) gave 16·06 per cent., the other, a hybrid, 16·2 per cent. These were, however, not commercial teas, and appear to have been simply dried in heated rooms. The average hygroscopic moisture found by Mr. Wigner in thirty-five teas, consisting of Hysons, Capers, Souchongs, Gunpowders, and others, was 7·67 per cent., the driest teas being the Hysons and Gunpowders, the moistest the Congous:—

				Per cent.
The maximum	amount of moisture	found in	Hyson,	5·68
The minimum	,,	,,	,,	4·84
The maximum	,,	,,	Gunpowder,	6·55
The minimum	,,	,,	,,	4·94
The maximum	,,	,,	Congou,	10·33
The minimum	,,	,,	,,	6·36

§ 41. *The Estimation of Theine or Caffeine.*—The modern processes for extracting theine fall chiefly under three heads :—

(1.) *Extraction by treating a decoction of the theine-containing substances with lime or burnt magnesia, evaporation to dryness, and subsequent solution of the alkaloid by chloroform, ether, or benzine.*—The fundamental idea of this process perhaps belongs to Müller; it has also, with various modifications, been recommended by Clous, Commaille, Dragendorff, and many other chemists.

Commaille adopts the following method :—5 grms. of finely powdered and carefully sifted substance are made into a hard paste with 1 grm. of calcined magnesia. This, after standing for twenty-four hours, is dried upon a water-bath and powdered. The resulting green powder is exhausted three successive times in a flask with boiling chloroform, the flask being connected with an inverted Liebig's condenser, so that the action may be continued for a long time. The cool solution is filtered, the chloroform recovered by distillation, and the residue in the flask dried. This residue consists of resinous fatty matters and theine; the former are removed by treating the contents of the flask with hot water and 10 grains of powdered glass, which have been previously washed with dilute hydrochloric acid. The water is boiled and the contents shaken up with the glass, the resinous matters attach themselves to the latter in the form of little globules. The solution is poured on a wet filter, and the residue completely exhausted by repeated boiling with fresh quantities of water. On evaporating the united filtrates in a tared capsule, pure caffeine is left in the form of white crystals.

Dragendorff takes 5 grms of the substance, exhausts it with boiling water, evaporates to dryness, adding 2 grms. of burnt magnesia and 5 of ground glass; the finely powdered residue is soaked in 60 cc. of ether for twenty-four hours, and finally thoroughly exhausted by ether. The latter, when separated and evaporated, leaves the theine in a tolerably pure state. He also states that ether may be replaced by chloroform. Cazeneuve and Caillot recommend a very similar process, but magnesia is replaced by recently slaked lime,* ether by chloroform. Markownikoff uses benzine instead of the solvents mentioned.

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* The present writer does not believe that magnesia can be replaced with lime without loss of theine from decomposition.

In all the above processes there is one source of error which does not appear sufficiently guarded against—viz., loss of theine during the evaporation to dryness, since it is absolutely impossible to evaporate a decoction of tea and magnesia to dryness at 100°C. without loss of the alkaloid—a loss which, so far as the author's experiments go, does not take place until the mixture is quite dry. The following modification may therefore be proposed:—4 to 5 grms. of the tea are boiled in a flask with an inverted Liebig's condenser for a couple of hours, the liquid and leaves are transferred to an evaporating dish, some magnesia added, and the whole concentrated to a pasty condition. This paste is treated and thoroughly exhausted by chloroform; the latter is separated and evaporated, and the chloroformic extract redissolved in a little boiling water, the solution filtered, evaporated to dryness at a very gentle heat, and weighed.

(2.) *Simple treatment of the powdered leaves by solvents.*—Legrif and Petit soften the leaves first with boiling water, and then extract the moist mass by the aid of chloroform. Other chemists simply exhaust the powdered substance by chloroform or ether; subsequent purification may of course be necessary.

(3.) *Sublimation.*—A method of utilising tea dust by making it a source of theine, was recommended by Heijnsius (*Journ. Prac. Chem.*, xlix. 317). The tea dust was simply treated in a Mohr's benzoic acid subliming apparatus. Stenhouse improved this process by precipitating either a spirituous extract, or a decoction, of tea by acetate of lead, evaporating the filtrate to dryness, mixing the residue with sand, and subliming. These processes of sublimation, however, were proposed simply for the extraction, not the estimation, of theine.

The writer, in 1877,* proposed the following quantitative method of sublimation:—A convenient quantity of the tea was boiled in the way mentioned, magnesia added, and the whole evaporated to a paste, which was spread on a thin iron plate, and covered with a tared glass funnel. The heat at first was very gentle, but was ultimately raised at the later stages of the process to 200°C. The theine sublimes perfectly pure and anhydrous, and forms a coherent white coating on the sides of the funnel; the increase of weight is simply anhydrous theine. To ensure success it is absolutely necessary—

(1.) That the layer be as thin as possible.

(2.) That the heat be only gradually increased.

(3.) That the mixture be occasionally cooled, and then thoroughly stirred.

(4.) That the sublimation be prolonged for a sufficient time.

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* *Op. cit.*

The sublimation is finished when a funnel, inverted over the substance, heated to about 150°C., and left for half an hour, shows no crystals.

§ 42. *Determination of Total Nitrogen.*—Peligot, and Wanklyn as well, have laid particular stress on the large amount of nitrogen contained in tea leaves. This nitrogen is, of course, largely dependent on the theine, and it is questionable whether, with the improved methods for the extraction of the latter, it is worth while to make a combustion, more especially as the exhausted leaves are highly nitrogenous, from the presence of an albuminous body. The process is conducted in the usual way in a combustion tube, and best with copper oxide. The following are a few determinations of total nitrogen:—

	Per cent.	Analysed by
A sample of genuine tea from Cachar,	4·74	*Hodges.*
A hybrid variety, do., .	2·81	,,
Another sample from Cachar, . .	4·42	,,
Sample taken from 60 green teas slightly faced, ...	3·76	,,
60 Black teas, ...	3·26	*Wigner.*
6 Assam teas, ...	3·64	,,
6 Caper teas, ...	3·32	,,
Assam tea, from Dr. M'Namara's garden,	3·88	,,
Sample of exhausted leaves, . .	3·80	,,

Mr. Wanklyn has applied his ammonia process to the examination of tea. The soluble matter from 100 mgrms. of tea is heated with a 10 per cent. solution of potash in a flask fitted to a proper condenser, until all the ammonia is distilled over. It may be necessary to add water once or twice, and redistill; then 50 cc. of a strongly alkaline solution of permanganate of potash are added and distilled; the ammonia in the distillates is estimated by "Nesslerising." Mr. Wanklyn gives the following figures as yielded by a genuine tea—

	Mgrms.
Free Ammonia, ...	0·28
Albuminoid Ammonia, ...	0·43
	0·71

100 mgrms. of genuine tea, sent to the writer by Dr. Shortt, of Madras, yielded total ammonia ·81. We only require a few hundred determinations of ammonia in this way, to have some guide to the variations met with in all kinds of tea: this would afford far more information than an ordinary combustion.

§ 43. *Determination of Tannin.*—The methods proposed for the determination of tannin are very numerous. Three only, however, require any notice here—viz., the gelatine process, Mr. Allen's acetate of lead process, and Löwenthal's process.

(1.) *By Gelatine.*—The best process by gelatine is decidedly that which dispenses with the drying and weighing of the precipitate. A solution of gelatine is carefully made by first soaking the gelatine in cold water for twelve hours, then raising the heat to 100°C., by placing the bottle on the water-bath (the strength should be about 3 per cent.), and finally about ·8 per cent. of alum should be added. A portion of the solution thus prepared is put into an alkalimeter flask (*e.g.*, Schuster's), and carefully weighed. A solution containing a known quantity of tannin is now titrated with the gelatine until a precipitate no longer occurs; the flask is reweighed, and the loss shows approximately the strength of the solution. One or two more exact determinations will be required to get the correct value. It is necessary to allow the precipitate now and then to settle, and a few drops of the supernatant fluid should be placed on a watch-glass, to which a drop of gelatine may be added, and thus the point of saturation ascertained. The tannin in a decoction of tea is, of course, estimated on precisely similar principles.

(2.) *Mr. Allen's Lead Process.*—A filtered solution of lead acetate ·5 per cent., a solution of 5 mgrms. of pot. ferridcyanide, 5 cc. of strong ammonia water, and 5 cc. of pure water, and lastly, solution of pure tannin (·1 per cent.) are required. The process essentially depends upon the precipitation of tannin by lead acetate, and using ammoniacal pot. ferridcyanide as an indicator. The latter agent strikes a pink colour with tannin. The solution is standardised by taking a known volume of the lead solution, and dropping in the tannin liquid until a small portion filtered gives a pink colour with the indicator.

Tea is tested in a precisely similar manner. Mr. Allen's method is tolerably speedy and accurate; the writer has, however, found the final reaction somewhat difficult to observe.

(3.) *Löwenthal's process.*—Up to the present time this method (originally worked out for barks) is the best we possess; it depends on the oxidation by permanganate, and indigo is used as an indicator. It not alone gives us the tannin, but the amount of other astringent matters as well. The following solutions are required:—

(1.) A solution of potass. permanganate, 1·333 grms. per litre.
(2.) Precipitated indigo, 5 grms. per litre.
(3.) Dilute sulphuric acid (1 : 3).
(4.) A solution of gelatine, 25 grms. to litre, saturated with table-salt.*

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* Löwenthal prepares the solution by steeping 25 grms. of the finest Cologne glue in cold water over night; it is then melted on the water-bath, saturated with NaCl, and made up to 1 litre with saturated NaCl solution, filtered, and kept well corked.

(5.) A saturated solution of pure salt, containing 25 cc. of sulphuric, or 50 cc. of hydrochloric acid per litre.

The analysis as applied to the determination of tannin in barks, is performed thus :—10 grms., say, of sumach are taken and exhausted by boiling with water, and the solution made up to 1 litre; of this infusion, 10 cc. are mixed with 75 cc. of water, 25 cc. of the indigo solution added, and 10 cc. of the dilute sulphuric acid. The permanganate solution is run drop by drop from the burette with constant stirring, till the blue colour changes to yellow, when the amount of permanganate used is noted (x). The same process is repeated with indigo and sulphuric acid, and the amount read off (y); subtracting y from x = total astringent matters. The permanganate oxidises both tannin and indigo, but the tannin being the easier to oxidise, is consumed first. In order to obtain accurate results, the proportion of indigo should be such as to require about twice the quantity of permanganate which would be consumed by the tannin alone. Thus, if indigo alone requires 10 cc. of permanganate to decolorise it, the indigo and tannin together must not take more than about 15 cc.; if it does so, the tannin must be diluted accordingly. The total astringent matters being known, the next step is to throw the tannin out, and estimate the gallic acid and impurities. 100 cc. of the infusion are mixed with 50 cc. of the salted gelatine infusion; after stirring, 100 cc. of the salt acid solution are added, and the mixture allowed to stand for twelve hours. It is then filtered, and an aliquot part of the filtrate is oxidised by permanganate and indigo, as before.

Löwenthal gives the following example: 10 grms. of sumach were boiled in 750 cc., and after cooling made up to one litre :—

		Permanganate.
(1.) 10 cc. of sumach infusion, 25 cc. of indigo solution,	consumed, . .	16·6
Do.,	repeated, . .	16·5
		33·1
50 cc. of indigo solution alone, ...		13·2
Total permanganate for 20 cc. of sumach, .		19·9
(2.) 50 cc. filtrate from the gelatine, 25 cc. indigo solution,	consumed, . .	11·2
Do.,	repeated, .	11·1
		22·3
50 cc. indigo alone, ...		13·2
Gallic acid and impurities, ...		9·1

Deducting 9·1 cc. from 19·9 cc. equals 10·8 cc. as permanganate, equivalent to the tannin of 20 cc. of sumach infusion, or 0·2 grms.

of dry sumach. It is well to ascertain the value of the permanganate solution by oxalic acid, adopting the numbers given by Neubauer and Oser—viz., that 0·063 oxalic acid is equal to 0·04157 gallo-tannic, and ·062355 quercitannic acids. Should it be preferred to use tannin, the purest commercial tannin must be precipitated by lead, the precipitate freed from lead in the usual way, and the solution of pure tannin then evaporated to complete dryness, and a solution of convenient strength made. The process requires but little modification to be applicable to tea.

The amount of tannin in genuine teas seems to be variable, the lowest number being apparently about 8 per cent., whilst Mr. Wigner, as example of very astringent teas, gives the following:—

	Per cent.
Moyone young Hyson,	39·0
Very choice Assam,	33·0
Indian young Hyson,	39·0
Assam tea from Dr. M'Namara's garden,	27·7
Caper, mixed,	42·3

Exhausted tea leaves yield from 2 to 4 per cent of tannin. A tea giving only 6 or 7 per cent. of tannin is to be regarded as suspicious, but care must be taken not to rely upon any single indication.

§ 44. *The Extract.*—The extract is a measure of the soluble matter in tea. Peligot exhausted the leaves and then redried them, and thus estimated the soluble matter by difference. Wanklyn, however, has proposed a more rapid and convenient method. It consists in taking 10 grms. of tea, and boiling with 500 cc. of water, the flask being adapted to a Liebig's condenser. When 50 cc. are distilled over, the process is stopped, and the 50 cc. returned to the flask; 50·3 grms. of the hot strained liquid are then weighed out and evaporated to dryness. Wigner boils with a vertical condenser for an hour, and finds that 1 per cent. strength yields the most constant results. Perhaps, on the whole, the best process is the following:—Place one part of tea in 100 of water, boil for one hour with a vertical condenser, and then take an aliquot part of the filtered liquid for evaporation. In every case the time occupied in boiling, and the strength, should be mentioned in reporting, for two analysts operating by different methods may differ as much as 6 or 8 per cent.—the soluble matter not being entirely removed for a very long time. Since the substances that are at once dissolved are really those upon which its commercial value depends, it is a question whether it would not be better simply to pour boiling water on the leaves, let the infusion stand for one hour, and then estimate the extract, calling it *extract of infusion.*

Any addition of exhausted leaves lowers the percentage of extract. The following are some determinations of extract :—

	Per cent.	Analysed by
Java tea, dried,	35·2	Peligot.
,, not dried,	32·7	,,
Pekoe, ordinary, dry,	41·5	,,
,, undried,	38·0	,,
Gunpowder, dry,	51·9	,,
,, undried,	48·5	,,
,, dry,	46·9	,,
,, undried,	50·2	,,
Moyone Gunpowder,	40·7	Wigner.
,,	39·3	,,
,,	38·5	,,
,,	37·9	,,
,,	33·3	,,
Imperial, dry,	43·1	Peligot.
,, not dried,	39·6	,,
,, dry,	47·9	,,
,, not dried,	44·0	,,
Hyson, dry,	47·7	,,
,, not dried,	43·8	,,
Hyson skin, dry,	43·5	,,
,, not dried,	39·8	,,
Congou,	36·8	,,
,, dried,	40·9	,,
,, bon,	40·7	,,
,, ,, dried,	45·0	,,
,,	33·0	Wigner.
,,	29·8	,,
,,	29·8	,,
,,	26·2	,,
,,	26·1	,,
Caper, dried,	39·3	Peligot.
,, not dried,	35·8	,,
,,	37·9	Wigner.
,,	37·7	,,
,,	32·4	,,
,,	30·0	,,
Assam, dried,	45·4	Peligot.
,, not dried,	41·7	,,
,,	33·3	Wigner.
Hyson,	36·8	,,
Moyone Young Hyson,	44·8	,,
Tea direct from China, dry,	41·7	Wanklyn.
,, ,,	40·2	,,
,, ,,	41·2	,,
Indian Tea, dry,	33·9	A. Wynter Blyth.
,,	43·8	Wigner.
Broken Indian,	43·4	,,
Indian Souchong,	32·5	,,
Scented Orange Pekoe,	34·2	,,
Manuna, fine,	37·0	,,
Himalayan Tea,	38·6	Wanklyn.
,,	35·4	,,

Since the extract of genuine tea appears to vary from 26 per cent. up to more than 40 per cent., it is unfortunately of no very great value for purposes of estimation. The extract, after being weighed, is burnt up to an ash, which will always be found to be heavy, rich in alkaline salts, and varying usually from 4 to 7 per cent.

§ 45. *The Ash.*—The percentage of total ash is taken by burning up 1 to 5 grms. of the tea in a platinum dish. The leaves readily ignite, and the operation may take place at a very low temperature, so that there is, with care, very little volatilisation of chlorides. The comparative composition of the ash of fresh and of exhausted tea leaves is shown in the following table:—

	ZOLLER.	HODGES.		ZOLLER.	WIGNER.	
	Ash of fine young Himalaya Tea.	Tea from Cachar (indigenous).	Tea from Cachar (hybrid).	Exhausted Tea Leaves.	Ash of a number of Mixed Black Teas	Ash of a number of Mixed GreenTeas
Potash, . .	39·22	35·200	37·010	7·34	30·92	28·42
Soda, . .	0·65	4·328	14·435	0·59	1·88	2·08
Magnesia, . .	6·47	4·396	5·910	11·45	...	...
Lime, . .	4·24	8·986	5·533	10·76	...	...
Oxide of Iron, .	4·38	2·493	2·463	9·63	...	...
Manganous Oxide	1·03	1·024	0·800	1·97	...	...
Phosphoric Acid,	14·55	18·030	9·180	25·41	...	...
Sulphuric Acid,	trace.	5·040	6·322	trace.	4·88	5·66
Chlorine, . .	0·81	3·513	2·620	trace.	...	...
Silica and Sand,	4·35	0·500	1·300	7·57	1·70	7·50
Charcoal, . .	...	2·900	1·830	...	...	...
Carbonic Acid, .	24·30	13·590	12·600	25·28	11·60	6·43
	100·00	100·00	100·00	100·00		
Percentage of total Ash soluble in water,	...	...	...	...	57·00	52·85

The ash, on being cooled and weighed, is next boiled up with a little water, the soluble portion filtered from the insoluble, and washed in the ordinary way. The filtrate is evaporated to dryness, very gently ignited, and returned in percentage as soluble ash. The insoluble portion is next treated with acid, and the remaining sand dried, ignited, and weighed. The alkalinity of the soluble portion should also be taken, and may be returned as potash. This simple examination of the ash, consuming very little time, gives tolerably well all the information afforded by a complete and exhaustive analysis. The following table shows a few percentages of ash, and may be compared with the percentages of beech, bramble, &c.:—

	Total Ash. Per cent.	Ash soluble in Water. Per cent.	Ash soluble in Acid. Per cent.	Silica.	Potash.	Authority.
Average of 17 ordinary Teas from original chest, consisting of 2 Indian, 12 Congous, 2 Gunpowders, and 1 Hyson,	5·75	3·07	2·25	0·43	1·38	G. W. Wigner.
Maximum,	6·03	3·35	2·87	0·76	1·88	,,
Minimum,	5·53	2·75	1·99	0·15	1·17	,,
Average of 25 special Teas,	5·95	3·33	2·09	0·53	1·38	,,
Maximum,	7·02	3·88	2·68	1·67	1·96	,,
Minimum,	5·17	2·64	1·33	0·04	1·08	,,
Genuine Indian Tea,	5·61	2·90	...	...	...	A. Wynter Blyth.
Common Tea,	5·92	3·55	...	...	...	Wanklyn.
Paraguay Tea,	6·28	4·22	...	...	...	,,
Average of 7 Teas,	5·75	...	...	...	...	A. S. Wilson.
,, 9 Teas,	5·66	3·00	...	...	...	A. H. Allen.
Horneman's p. black,	5·30	3·50	...	...	...	,,
,, green,	5·60	3·80	...	...	...	,,
Ambrosial black,	5·60	3·40	...	...	...	,,
Genuine blk., 2s. 6d. lb.,	5·60	3·09	...	...	...	,,
,, ,,	5·70	3·28	...	...	...	,,
,, ,,	6·02	3·26	...	...	...	,,
,, ,,	6·34	3·20	...	...	...	,,
,, ,,	6·10	3·96	...	...	...	,,
,, ,,	5·75	3·06	...	...	...	,,
,, 3s. lb.,	5·50	3·55	...	...	...	,,
Broken leaf with stalks,	5·40	2·80	...	...	...	,,
Caper (4·8 silica),	11·40	1·50	...	...	...	,,
Mixed, dry exhausted leaves from various teas,	4·30	0·52	...	...	...	,,
Coffee leaves,	10·32	3·77	...	...	...	,,
Beech,	4·52	2·00	...	...	...	Wanklyn.
Bramble,	4·53	1·84	...	...	...	,,
Raspberry,	7·84	1·72	...	...	...	,,
Hawthorn,	8·05	3·78	...	...	...	,,
Willow,	9·34	4·16	...	...	...	,,
Plum,	9·90	5·66	...	...	...	,,
Elder,	10·67	3·19	...	...	...	,,
Gooseberry,	13·50	7·83	...	...	...	,,

All the analyses hitherto published show that the percentage of ash in genuine tea never reaches 8 per cent. An ash beyond 8 per cent., calculated on the dried tea, is certainly adulterated. In the same manner, all genuine tea possesses soluble ash not less than 3 per cent. For examples of obviously impure ashes, Mr. Wigner's paper may be quoted from again :—

	Total Ash.	Ash Soluble in Water.	Soluble in Acid.	Silica.	Alkali, calculated as Potash.	Extract.
Gunpowder, . .	19·73	1·00	6·15	12·58	0·14	37·78
Caper, ...	14·44	1·95	2·47	10·02	1·03	35·45
,, ...	15·20	1·69	5·35	8·16	0·61	31·60
,, ...	15·08	1·96	5·65	7·47	0·73	35·60
,, ...	12·74	2·68	5·44	6·62	1·04	...
,, ...	14·60	2·67	5·67	6·06	1·04	...

All these teas, although imported in this state, are evidently mixed with sand to a considerable extent.

§ 46. *Determination of Gum.*—If it is necessary to determine the gum in tea, as sometimes happens, the aqueous decoction should be evaporated nearly to an extract, and the residue treated with methylated spirit, filtered, and washed with the spirit. The gum is dissolved off the filter by the aid of hot water, and the solution evaporated to dryness, and weighed; it is then ignited to an ash, and the mineral deducted from the total weight.

§ 47. *General Review of the Adulterations of Tea.*—The most frequent are certainly the addition of sand, generally strongly impregnated with iron, the addition of foreign and exhausted leaves, and the addition of astringent principles, such as catechu, &c. All these adulterations must take place abroad, there being no evidence that a single hundredweight of tea has been tampered with in England,—the blame *may* lie with the home-traders, but proof is wanting. On the other hand, it not unfrequently happens that cargoes of tea recovered from sunk vessels, or teas damaged in some other way, are sold and blended by wholesale manufacturers with those that are genuine. Such samples contain usually an excess of salt, and show more or less evidence of the addition of exhausted leaves.

The facing of tea is rapidly decreasing. There has been much dispute as to whether this is to be considered an adulteration or not; a thin film of graphite, or any other harmless substance, in such quantity as to add no appreciable weight, can hardly be called adulteration. Each case, however, must be judged of by its merits. A small addition of such a substance as catechu, to impart astringency, is probably frequent, and difficult of detection. Any amount present, to the extent of 3 per cent. or over, is shown by precipitating an infusion of the tea with a slight excess of neutral lead acetate, filtering, and adding a little dilute ferric chloride solution. If catechu be present there is a bright-green colour, and ultimately a precipitate of a greyish-green colour. The same infusion filtered from the lead precipitate gives a copious precipitate with argentic nitrate. Mr. Allen has pointed out the advantage of his lead process in cases of adulteration with catechu, and it is self-evident; for catechuic acids possess a precipitating power so widely different from that of tannin, that, if reckoned as tannin, there are always anomalous results, indicating a much higher astringency than could possibly exist, —*e.g.*, a sample of brown catechu examined in this way, and reckoned as tannin, gives the paradoxical number of 11 per cent.

Soluble iron salts, alkaline carbonates, and other substances, are stated to be occasionally added, but no conviction relative to these appears to be on record. The soluble iron salts may, of course, be dissolved from the tea leaves by a little cold dilute acetic acid, and the liquid tested in the usual way; there is then no confusion between the iron naturally present and that added.

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II.—COFFEE.

§ 48. Coffee is the produce of the *Caffea arabica*, nat. order *Cinchonacea*. Before use, the berries are roasted to a chocolate brown, and then ground in a mill. The effect of the roasting is to drive off a large quantity of water, to volatilise a small portion of caffeine or theine, to destroy a portion of the sugar by changing it into caramel,* and to swell the berry by the extrication of gases, consisting principally of carbonic acid.

§ 49. *Chemical composition.*—The chemical composition of coffee is somewhat complex; its main properties are apparently due to four distinctive substances—(1.) An essential oil, but little studied; (2.) Caffeo-tannic acid; (3.) Caffein or theine; (4.) A fatty substance.

Caffeine is described at p. 85.

§ 50. *Caffeo-tannic Acid*, $C_{14}H_8O_7$, was first observed by Pfaff, in the seeds and leaves of the coffee plant; it also occurs in the root of the *Chiococcu racemosa*, and in the leaves of the *Ilex paraguayensis*, S. Hil. It may be separated from coffee by fractional precipitation of the infusion with acetate of lead. The precipitate, at first falling, consists of citrate with caffeo-tannate of lead; but later on, the latter occurs alone, and can be washed with water and decomposed by SH_2 in the usual way. Caffeo-tannic acid thus obtained is a brittle, yellowish mass, easily powdered, and of feeble acid reaction. It is scarcely soluble in ether, but dissolves easily in water or in alcohol. The solution gives a dark-green colour with chloride of iron, or if dissolved in

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* Graham and Stenhouse found the following differences in the percentage of sugar between the raw and roasted coffees:—

	Raw. Per cent.	Roasted. Per cent.
Highest amount, ...	7·78	1·14
Lowest amount, ...	5·70	...
Average of twelve specimens grown in different places, ...	0·97	0·26

aqueous solution of ammonia, the alkaline earths, or the alkalies, a reddish-yellow or yellow colour. If caffeo-tannic acid be decomposed with 3 parts of solid potash, the end product is protocatechuic acid. If it be boiled with 5 parts of potash-lye (1·25 specific gravity) for three quarters of an hour, and then neutralised by sulphuric acid, caffeic acid ($C_9H_8O_4$) crystallises out, and can be obtained in straw-yellow prisms and plates by recrystallisation from hot water. It colours chloride of iron grass-green, is oxidised by nitric acid into oxalic acid, and is decomposed by potash into protocatechuic and acetic acids.

§ 51. *Coffee Fat.*—The coffee fat can be obtained from an alcoholic extract of coffee; part separates on cooling the fluid to 0°C., the rest on dilution with water. It is white, without odour, of a buttery consistence, melting at 37·5°C., and becomes rancid on exposure to the air. According to Rochleder (*Wien Akad. Ber.*, xxiv. 40), it contains the glyceride of palmitic acid and of an acid of the composition $C_{12}H_{24}O_2$.

The following are some analyses by O. Levesie of various commercial varieties of coffee:—

	Gummy Matter.	Caffeine.	Fat.	Tannic and Caffeo-tannic Acids.	Cellulose.	Ash.	Potash.	Phosphoric Acid.
Finest Jamaica Plantation, . . .	25·3	1·43	14·76	22·7	33·8	3·8	1·87	0·31
Finest Green Mocha,	22·6	0·64	21·79	23·1	29·9	4·1	2·13	0·42
Ceylon Plantation, .	23·8	1·53	14·87	20·9	36·0	4·0	...	0·27
Washed Rio, . .	27·4	1·14	15·95	20·9	32·5	4·5	...	0·51
Costa Rica, . .	20·6	1·18	21·12	21·1	33·0	4·9	...	0·46
Malabar, . . .	25·8	0·88	18·80	20·7	31·9	4·3	...	0·60
East Indian, . .	24·4	1·01	17·00	19·5	36·4	...	...	...

Some analyses of Dragendorff may be also quoted:—*

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* We give also a very elaborate analysis of coffee made by Payen, at a date when food analysis was not so well understood as now. It is probably a fair approximation as regards the more important constituents, but the percentage of ash can hardly be correct.

Cellulose, ...	34·000
Water (Hygros.), ...	12·000
Fat, ...	10 to 13·000
Glucose, Dextrine, &c., ...	15·500
Legumine, ...	10·000
Caffeate of Potash and Caffeine, ...	3·5 to 5·000
Nitrogenous substance, ...	3·000
Free Caffeine, ...	0·800
Concrete Essential Oil, ...	0·001
Aromatic Fluid Essential Oil, ...	0·002
Ash, ...	6·697

	Caffeine. Per cent.	Ash. Per cent.	Potash. Per cent.	Phosphoric Acid. Per cent.
1. Brown Preanger, ...	0·71	4·80	...	0·42
2. Mocha, yellow, very fine, .	0·64	4·06	2·13	0·42
3. Menado, yellow, . . .	1·22	4·03	...	0·39
4. ,, blue, . . .	1·38	4·11	...	0·36
5. Alexandrian Mocha, . .	0·84	4·19	...	0·44
6. Jamaica Plantagen, very fine,	1·43	3·83	1·87	0·31
7. Surinam, 1st quality (Java), .	1·78	4·39	...	0·56
8. Preanger, ...	0·93	4·36	...	0·35
9. Surinam, 2nd quality (Java), .	1·04	4·77	...	0·33
10. Ceylon Plantagen, . . .	0·78	4·02	...	0·31
11. Yellow Java, . . .	0·88	4·31	...	0·28
12. West Indian (Java), . .	1·22	4·21	...	0·32
13. Mysore, ...	1·23	4·20	2·12	0·31
14. Malabar, ...	0·88	4·27	...	0·60
15. Java, ...	2·21	4·01	...	0·41
16. Costa Rica, ...	1·18	4·94	...	0·46
17. Ceylon Plantagen, . . .	1·53	4·00	...	0·27
18. Washed Rio, ...	1·14	4·53	...	0·61
19. Native Ceylon, . . .	1·14	4·65	...	0·72
20. ,, ,, 1st quality, .	0·87	4·65	...	0·41
21. ,, ,, 2nd ,, .	1·54	4·80	...	0·44
22. African Mocha, . . .	0·70	4·70	2·80	0·38
23. Jamaica, ...	0·67	4·82	2·83	0·42
24. Native Ceylon, 3rd quality, .	1·59	4·87	2·60	0·40
25. Santos, ...	1·46	4·81	2·67	0·48

§ 52. *Analysis of Coffee.*—The hygroscopic moisture, theine, gum, astringent principles, and ash, are all determined precisely as in the case of tea.

The coffee fat may be conveniently estimated by putting a known quantity in the little apparatus figured (see Fig. 11). The *a* and *b* tubes are packed with glass wool; the one is connected with a flask, the other with an upright Liebig's condenser. The flask contains a small quantity of petroleum ether, which by means of a water-bath is distilled through the coffee, condensing perpetually, and falling back into the flask. When the process is finished, the petroleum is evaporated to dryness in a tared dish. As thus obtained, the fat is almost, but not quite, pure.

Fig 11.

§ 53. *Adulterations of Coffee and their Detection.*

The sophistications usually enumerated are: chicory, roasted wheat and beans, rye and potato flours, mangel-wurzel, acorns, and burnt sugar. The coffee is usually adulterated when in powder, but patents have been taken out for compressing ground coffee with chicory into the shape of berries.

The sophistication of coffee was at one time a regularly-organised industry; and there existed, ten years ago, two manufactories in France—one at Lyons and the other at Havre—expressly established for the purpose of mixing coffee with burnt cereals and the scorched outer covering of cocoa. Without venturing to assert that coffee is at the present time adulterated in England with chicory alone, it is certain that other admixtures are of the greatest rarity.

A preliminary examination will in a few minutes detect, so far as chicory is concerned, whether it has been added, or not. If the ground coffee be sprinkled on water, nearly the whole of it floats; if chicory be present, the chicory separates and sinks to the bottom, imparting a brown colour to the liquid. In this way, indeed, a tolerably complete separation of coffee and chicory may with care be obtained. The portions which sink to the bottom are, of course, examined microscopically. They are always soft to the touch, very different from the hard, gritty feeling of coffee particles; and put under the microscope, the difference of structure is at once apparent, for the loose, large cells of the chicory root, with dotted vessels and branching laticiferous ducts, are readily seen and appreciated.*

When chicory is mixed with coffee, the chemical composition of the mixture shows, in some particulars, a marked deviation from that of pure coffee.

Letheby's analysis of chicory is as follows:—

	Raw root.	Kiln-dried.
Hygroscopic Moisture,	77·0	15·0
Gummy Matter,	7·5	20·8
Glucose or Grape Sugar,	1·1	10·5
Bitter Extractive,	4·0	19·3
Fatty Matters,	0·6	1·9
Cellulose, Inuline, and Woody Matter,	9·0	29·5
Ash,	0·8	3·0

Composition of the roasted root:—	(1)	(2)
Hygroscopic Moisture,	14·5	12·8
Gummy Matter,	9·5	14·9

---

* Chicory is so readily detected that we scarcely require a direct chemical test. A. Franz has, however, pointed out that an infusion of coffee, when treated with copper acetate and filtered, yields a greenish-yellow filtrate; an infusion of coffee containing chicory yields, when similarly treated, a dark red-brown filtrate.—*Arch. Pharm.* [5], 298-302.

Glucose,	12·2	10·4
Matter like Burnt Sugar,	29·1	24·4
Fatty Matter,	2·0	2·2
Brown or Burnt Woody Matter,	28·4	28·5
Ash,	4·3	6·8

The ash of these had the following composition:—

Chloride of Potassium,	0·22	0·45
Sulphate of ,,	0·97	0·98
Phosphate of ,,	1·41	1·37
,, Magnesia,	0·90	0·53
,, Lime,	0·40	0·81
Carbonate of ,,	0·10	0·26
Alumina and Oxide of Iron,	0·20	0·20
Sand,	0·70	2·20

Chicory influences the composition of coffee as follows:—

(1.) It decreases the gum, the latter seldom rising in chicory to more than 15 per cent., whilst in coffee it has not been found less than 21 up to 28 per cent.

(2.) It increases the sugar, roasted coffee having seldom so much as 2 per cent. of sugar; whilst chicory, when roasted, usually has at least 8 or 9 per cent.

(3.) It decreases the fatty matter, the fat of chicory ranging from 1 to over 2 per cent., that of coffee from about 14 per cent. up to over 20 per cent.

(4.) It decreases the tannin and caffeo-tannic acids, chicory being destitute of tannin.

(5.) It decreases the caffeine, chicory possessing no alkaloid.

(6.) It profoundly modifies the constitution of the ash, especially by introducing silica, which is not a component of coffee ash. The main differences are thus, as follows:—

	Coffee Ash. Per cent.	Chicory Ash. Per cent.
Silica and Sand,		10·69 to 35·88
Carbonic Acid,	14·92	1·78 to 3·19
Sesquioxide of Iron,	0·44 to 0·98	3·13 to 5·32
Chlorine,	0·26 to 1·11	3·28 to 4·93
Phosphoric Acid,	10 to 11	5 to 6
Total Soluble Ash,	75 to 85	21 to 35

Mr. Allen has proposed to calculate the percentage of chicory in a mixture from the soluble ash data by the following formula:—

$$C = \frac{(100s - 1{\cdot}74)z}{3}$$

1·74 is assumed as the average soluble ash of chicory, 3 per cent. as that of coffee. This is of course only proposed as a rough guide, and, like all calculations of the kind, must not be rashly used.

By making standard infusions of pure coffee and chicory, and then taking the same weight of the suspected coffee, and comparing the colour, it is possible to obtain a very accurate idea of the quantity of chicory added.

Leebody recommends this to be done as follows :—Take 1 grm. of the unknown mixture, and 1 grm. of a standard mixture of equal parts of chicory and coffee ; remove all the colouring-matter from each sample, and make the extract of each up to the same bulk. Put 50 cc. of the filtered extract from the *unknown mixture* in a Nessler cylinder, and determine by trial how many cc. of the extract from the *standard* mixture, together with sufficient distilled water to make up the 50 cc., will give the same colour. In calculating the percentage of chicory present, closely accurate results are obtained in practice by assuming the tinctorial power of chicory to be three times that of coffee.—(J. R. LEEBODY, *Chemical News*, xxx. 243.)

Messrs. Graham, Stenhouse, and Campbell proposed to take the density of different infusions of coffee, &c., as a guide to its adulteration; and this is found in practice to work tolerably well, and to give approximative results. The following solutions were made by them by first treating the powder of the roasted substance with ten times its weight of cold water, boiling, and filtering, and determining the density at 60° F.:—

Spent Tan,	1002·14
Lupine Seed,	1005·70
Acorns,	1007·30
Peas,	1007·30
Mocha Coffee,	1008·00
Beans,	1008·40
Neilgherry Coffee,	1008·40
Plantation Ceylon Coffee,	1008·70
Java Coffee,	1008·70
Jamaica Coffee,	1008·70
Costa Rica Coffee,	1009·00
,, ,,	1009·05
Native Ceylon Coffee,	1009·00
Brown Malt,	1010·90
Parsnips,	1014·30
Carrots,	1017·10
Bouka,	1018·50
Yorkshire Chicory,	1019·10
Black Malt,	1021·20
Turnips,	1021·40
Rye-meal,	1021·60
English Chicory,	1021·70
Dandelion Root,	1021·90
Red-Beet,	1022·10

Foreign Chicory,	1022·60
Guernsey Chicory,	1023·20
Mangel-wurzel,	1023·50
Maize,	1025·30
Bread-Raspings,	1026·30

Allen (*Chemical News*, March 27, 1874) gives as the result of his estimations of the density of pure coffee 1008·7, and proposes the following formula, by which, when prepared as above, the proportion of chicory to coffee may be calculated. C represents the percentage of coffee, D the density of the solution :—

$$C = \frac{(1020{\cdot}6 - D)100}{12}$$

In regard to other adulterations, a great variety of starch-holding substances, with the cereals, may be entirely excluded, as certainly not present, if no dirty-blue or violet coloration is produced by iodine in an infusion of coffee. In order to apply this test properly, the infusion should be decolorised, which is most rapidly done by a solution of permanganate of potash. Coffee itself, as before stated, contains no starch.

Burnt sugar, or caramel, is usually detected by observing the rapid darkening of water on which a little coffee is sprinkled, and the particles (on examination in water by the microscope) reveal themselves by the absence of organised structure, and the coloured ring, arising from partial solution, round each.

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III.—COCOA AND CHOCOLATE.

§ 54. The cocoa of commerce is made from the roasted seeds * of the *Theobroma cacao*, a tree belonging to the natural order *Byttneriaceæ*, whole forests of which exist in Demerara. It is also more or less extensively grown in Central America, Brazil, Peru, Caraccas, Venezuela, Ecuador, Grenada, Essequibo, Guayaquil, Surinam, and some of the West Indian Islands; and its cultivation has also been attempted (in most cases successfully) in the East Indies, Australia, the Philippine Islands, the Mauritius, Madagascar, and Bourbon.

The principal kinds of cocoa in commerce are known under the names of Caraccas, Surinam, Trinidad, Grenada, Jamaica, Dominica, Guayaquil, Venezuela, Bahia, Brazil, and St. Lucia. The seeds are officinal in the French and Norwegian pharmacopeias. They are ovate, flattened, 2 to 2½ cm. [·7 to ·9 inch] long, and 1 to 1½ cm. [·39 to ·58 inch] broad, and covered with a thin red or grey-brown friable shell. The taste of the fresh seed is oily, bitter, and rather unpleasant.

The seeds, on being submitted to a kind of fermentation (technically called the *sweating* process), lose in a great measure this disagreeable flavour, and develop an aromatic smell. Seeds which have been subjected to this treatment are best suited for the manufacture of chocolate, while those which have been simply roasted are richer in cocoa-butter.

§ 55. *Microscopical Structure of the Seed.*—The seed, when deprived of the husk, consists for the most part of several irregularly-shaped angular divisions, filled with a large number of oval cells, within which is contained a peculiar starch, as well as a fatty matter. Near the surface these cells are angular, and of a pronounced red colour, but the tint is somewhat variable.

The starch-granules are perfectly round, normal measurement about 0·52 mm. [·00021 inch], and are often seen to have a somewhat obscure starred hilum. They strike a pronounced blue colour with iodine.

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* The seeds simply dried are also sold.

The husk contains from without inwards the following structures :—

(1.) A superficial layer of large, very characteristic tubular fibres, containing granular matter and little corpuscles.

(2.) A single layer of elongated cells, with their greatest diameter transversely to the axis.

(3.) Large angular cells in several layers ; those in the centre mucilaginous, constituting the greatest bulk of the envelope.

(4.) A very delicate membrane, formed of small cells, enclosing fatty matters. This membrane adheres to the almond, and portions of it may always be seen in the chocolates of commerce.

Another hyaline and fibrous structure connected with the last, and full of crystals, is usually described, as well as isolated, dark, elongated bodies. The whole structure, therefore, is complex in a high degree, but familiarity with the appearance presented by the different portions of the seeds is readily obtained.

§ 56. The *commercial varieties of Cocoa* are very numerous :—*Cocoa nibs* are simply the bruised roasted seeds deprived of their coverings ; and *flake cocoa* is composed of the nibs ground in a particular form of mill. The soluble cocoas are—ground cocoa, diluted with sugar and starches, *e.g.* :—

Epps' cocoa, according to an analysis advanced as evidence in the case of *Gibson* v. *Leafer*, is composed of cocoa 40 per cent., sugar 44 per cent., and starch 16 per cent.

Granulated cocoa, is mostly a mixture of nibs, arrow-root, and sugar ; *Homœopathic cocoa*, a preparation of the same kind without the sugar ; *Maravilla cocoa*, contains sugar and much sago flour ; and *Cocoa essence*, *cocoatine*, &c., consist of pure cocoa deprived of 60 to 70 per cent. of its fat.

The above are examples only. The analyst is liable to meet any day with some new patent cocoa, for the consumption of this food is greatly on the increase.*

§ 57. *Chocolate.*—In the manufacture of chocolate the cocoa-nibs are ground in a mill, the rollers of which are usually heated by steam, so as to soften the cocoa-butter ; and in this way a paste is formed which is mixed with refined sugar, and very often other substances, and pressed into moulds. Some of the receipts for chocolate are as follows :—

(1.) *French Chocolate.*—2 beans of Vanilla rubbed into a powder with sugar, and 1 lb. of best sugar to every 3 lbs. of cocoa nibs.

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* That the consumption of cocoa is increasing, is evidenced by the quantity imported—in round numbers, 10,000,000 lbs. in 1876, against 9,000,000 lbs. in 1875.

(2.) *Spanish Chocolate.*—(*a.*) Curaçoa cocoa 11, sugar 3, Vanilla $\frac{1}{16}$, cinnamon $\frac{1}{64}$, cloves $\frac{1}{128}$. (*b.*) Caraccas cocoa 10, sweet almonds 1, sugar 3, Vanilla $\frac{1}{64}$.

Vanilla Chocolate.—A chocolate paste highly flavoured with Vanilla, and generally with other spices as well. (*a.*) Caraccas cocoa 7, Mexican Vanilla $\frac{1}{16}$, cinnamon $\frac{1}{32}$, and sufficient cloves to flavour. (*b.*) Best chocolate paste 21, vanilla 4, cinnamon $\frac{1}{8}$, cloves and musk in small quantities.

The chocolates of English commerce yield but little cocoa-butter, since they are mostly prepared from the cake left after expression of the oil.

§ 58. The average chemical composition of cocoa, according to Mr. Wanklyn, is as follows:—

Cocoa Butter,	50·00
Theobromin,	1·50
Starch,	10·00
Albumen, Fibrin, and Gluten,	18·00
Gum,	8·00
Colouring Matter,	2·60
Water,	6·00
Ash,	3·60
Loss, &c.,	0·30
	100·00

The peculiar constituents of cocoa are then two, viz.—cocoa-butter and theobromin.

Cocoa-butter, Oleum theobromæ, specific gravity, 0·96 to 0·98;* melting point, 29° to 30°C.; solidifying point, 24°C., is a yellowish-white, concrete oil about the consistency of tallow, with a chocolate colour, and an agreeable taste. At common temperatures it is brittle, the fracture is smooth and equal, and examined by a lens it is somewhat crystalline. It is fully soluble at ordinary temperatures in two parts of ether, in half a part of benzole, as well as in 100 parts of cold and 20 parts of hot absolute alcohol; its solution is entirely neutral to test paper. If adulterated with tallow, wax, paraffin, or stearin, the specific gravity will be altered, and it will not dissolve to a clear solution in the quantity of ether named above. Pure cocoa butter does not become rancid, however long it is kept; but the admixture of most foreign fats impairs this property. Cocoa butter is usually said to consist of cocoa stearin, which separates in warty masses on evaporating an ethereal solution, and has a melting point of 65°C. with a little olein. Kingzett has, however, recently described two new fatty acids obtained from cocoa fat, one of

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* Its specific gravity was formerly given as from ·89 to ·91; but Flückiger, as well as Hirsch, has shown that this is too low.

which has the empiric formula $C_{64}H_{128}O_2$, and the subject appears to require further research. The best method of extracting the fat is to exhaust the nibs with ether in the apparatus figured at p. 109 (Fig 11).

Cocoa should contain at least 20 per cent. of cocoa fat; if less than that is found, it should be returned as adulterated.*

§ 59. *Theobromin*, $C_7H_8N_4O_2$.—This alkaloid was discovered in 1841 by Woskresensky, in the seeds of the *Theobroma cacao;* it principally resides in the cotyledons, and in smaller quantities in the seed-coverings. The average yield of theobromin appears to be 1½ per cent.

The original method of separation pursued by Woskresensky was—extraction on the water-bath with distilled water, filtering through linen, precipitating with sugar of lead, refiltering, freeing the filtrate from excess of lead by SH_2, evaporating to dryness, and subsequent purifying of the residue by solution in spirit, and treatment with animal charcoal. Mitscherlich, again, boils the cocoa with a weak solution of sulphuric acid in order to change the starch into sugar, saturates the fluid with carbonate of lead, and ferments it with yeast to destroy the sugar. On the conclusion of the fermentation, the fluid is boiled, neutralised with soda, filtered, concentrated by evaporation, and the impure brown theobromin which separates boiled in hot nitric acid. This nitric acid solution is precipitated by ammonia, again dissolved in nitric acid, and the nitrate obtained by evaporation. According to Mitscherlich, the quantity obtained in this way is much greater than by other processes.

A speedy method of determining, with very fair exactitude, the percentage of theobromin in cocoa, is to exhaust a weighed quantity with petroleum ether, mix the residue with a little burnt magnesia and water, evaporate to dryness at 60° to 70°C., and then exhaust the residue with boiling alcohol of 80 per cent., which dissolves out the theobromin. On driving off the alcohol by evaporation, the substance may be purified sufficiently for weighing purposes by washing with petroleum ether. Theobromin forms microscopic rhombic needles.

It is generally thought to sublime between 296° and 295°C. without decomposition, but this temperature is many degrees too high. The writer finds that a minute fragment, placed in the subliming cell elsewhere described, begins to give fine nebulæ at 134°C., and on examining the mists by a high power, they are resolved into extremely minute dots; distinct crystals are obtained at temperatures of 170°C. and above. Theobromin is

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* 20 per cent. is the standard of the Society of Analysts; but in the writer's opinion this is much too low, according to published analyses.

insoluble in petroleum ether, and not very soluble in ether, 1 part requiring 600 parts of boiling, and 1,700 parts of cold, ether. It is soluble in alcohol, 1 part requiring 47 parts of boiling, and 1,460 of cold, alcohol. Its solubility in water is stated to be 1 in 55 parts at 100°C., 1 in 600 parts at 20°, and 1 in 1,600 at 0°. It is somewhat soluble in chloroform and warm amyl alcohol, but with difficulty soluble in benzole.

Theobromin forms easily crystallisable salts. The simple neutral salts are decomposed by water, with the formation of basic salts, and lose their acid, if it is volatile, at 100°C. A hydrochloride of theobromin, $C_7H_8N_4O_2,HCl$; a nitrate, $C_7H_8N_4O_2,NHO_3$; a platinum salt, $C_7H_8N_4O_2,HClPtCl_2 + 2H_2O$, are all very definite crystalline compounds. A noteworthy salt is the nitrate of silver, which is formed by adding a solution of argentic nitrate to a solution of nitrate of theobromin; in a short time there separate silver-white needles, very insoluble in water, of the composition $C_7H_8N_4O_2$, $NHO_3 + AgNO_3$.

The other precipitants of theobromin are—phosphomolybdic acid (yellow) and chloride of gold (long needles). Tannic and picric acids only produce turbidity, while potass. mercuric iodide and potass. cadmium iodide do not precipitate. A characteristic reaction of theobromin is that produced by peroxide of lead and sulphuric acid. If peroxide of lead and diluted sulphuric acid are heated with theobromin, avoiding an excess of the oxidising agent, CO_2 is developed, and the colourless filtrate of sulphate of lead gives off ammonia with potash, separates sulphur on treatment with SH_2, stains the skin purple-red, and colours magnesia indigo-blue.

Theobromin is poisonous to kittens (and other animals of similar size) in such large doses as a gramme. It appears to be separated by the kidneys, and could probably be discovered in the urine of any person taking large quantities of cocoa. The method of research successfully used by Mitscherlich is as follows:—The urine is acidified with HCl, filtered, and to the filtrate, acidified with nitric acid, a solution of phosphomolybdate of soda is added. The precipitate is collected, and treated with baryta water until it is strongly alkaline, warmed, filtered, and the filtrate evaporated; the residue extracted with alcohol, refiltered, and the filtrate again evaporated. This last residue is dissolved in a drop of hydrochloric acid, and precipitated by ammonia. The alkaloid may now be collected and, if necessary, purified.

§ 60. *The Ash.*—The composition of the ash of cocoa seeds is stated by Mr. Wanklyn, from an analysis made in his laboratory, to be as follows:—

Composition of Ash of Cocoa-Seeds.

	Per cent.
Potash,	29·81
Chloride of Sodium,	6·10
Ferrous Oxide,	1·60
Alumina,	2·40
Lime,	7·72
Magnesia,	7·90
Phosphoric Acid,	24·28
Sulphuric Acid,	1·92
Carbonic Acid,	0·98
Silica,	5·00
Sand,	12·15

The percentages of ash found in cocoa, are given as follows :—

	Percentage of Ash.
Common Trinidad,	3·37
Very fine Trinidad,	3·62
Fair, good, fine Trinidad,	3·64
Fine Grenada,	3·06
Caraccas,	4·58
Bahia (Brazil),	3·31
Fine Surinam (small),	3·06
Mexican,	4·27
Dominican,	2·82
African,	2·68
Mean of the twelve being	3·39

Thus the lowest determination is 3·06, the highest 4·58 per cent. The nibs show a lower ash than the shell. The nibs of the Caraccas give 3·95 per cent. of ash, 2·00 being soluble and 1·95 insoluble in water. The nibs of Mexican seeds give 2·59 per cent. of ash, ·89 parts being soluble and 1·70 insoluble in water. The ash of the shell is rich in, but the nib almost devoid of, carbonates. Mr. Heisch has also recently examined the cocoas of commerce, with the results embodied in the following tables :—

Examination of Roasted Beans after Removal of the Husk.

	Husk.	Fat.	Nitrogen.	Albuminoids.	Ash.
Caraccas,	13·8	48·4	1·76	11·14	3·95
Trinidad,	15·5	49·4	1·76	11·14	2·80
Surinam,	15·5	54·4	1·76	11·14	2·35
Guayaquil,	11·5	49·8	2·06	13·03	2·50
Grenada,	14·6	45·6	1·96	12·40	2·40
Bahia,	9·6	50·3	1·17	7·40	2·60
Cuba,	12·0	45·3	1·37	8·67	2·90
Para,	8·5	54·0	2·00	12·66	3·05

	Ash. soluble in Water.	Ash soluble in HCl.	H_3PO_4 in Ash.	Moisture.	Starch, Gum, Cellulose, &c.
Caraccas, . . .	2·15	1·80	1·54	4·32	32·19
Trinidad, . . .	0·90	1·90	0·93	3·84	32·82
Surinam, . . .	0·80	1·85	1·23	3·76	28·35
Guayaquil, . .	1·75	1·75	1·87	4·14	30·47
Grenada, . . .	0·60	1·80	1·35	3·90	35·70
Bahia, . . .	0·90	1·70	1·26	4·40	35·30
Cuba, . . .	0·95	1·95	1·13	3·72	39·41
Para, . . .	1·40	1·65	1·00	3·96	26·33

The above analyses fully corroborate Mr. Wanklyn's statement as to the constancy of the percentage of phosphoric acid in cocoa ash. Mr. Heisch's highest determinate is 1·87, his lowest ·93, giving a mean of 1·28 per cent. phosphoric acid in the dry bean after removal of the husk.

§ 61. *Adulterations of Cocoa.*—The list of adulterations usually given is as follows:—Sugar, starches, Venetian red, brick-dust, and peroxide of iron. Some of these sophistications, such as the starches, may be detected by a preliminary microscopical examination, which in no instance should be neglected. The ordinary chemical examination consists in the extraction of the fat as before described (p. 116), the estimation of the percentage of ash in the ordinary way, its division into soluble and insoluble, and its content of phosphoric acid. By a simple estimation of the fat and the chief constituents of the ash, supplemented by the use of the microscope, all known adulterations can be detected. The amount of phosphoric acid in the ash of soluble cocoas may be taken as a basis of calculation of the amount of cocoa, and in the absence of foreign seeds, or other phosphate-producing substance, the calculation will be a fair approximation to the truth. The ash itself and the amount of phosphoric acid will, of course, be very notably diminished in the case of the soluble cocoas, and the percentage of the phosphoric acid will in such instances be a fair guide to the amount of foreign admixture. For example, suppose a soluble cocoa to yield an ash of 1·5 per cent., ·6 of which is due to phosphoric acid; taking as a basis of calculation, ·9 per cent.* of phosphoric acid in cocoa nibs:—

$$\frac{\cdot 6 \times 100}{\cdot 9} = 66 \cdot 6$$

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* The lowest percentage given by Mr. Heisch, and but little different from Mr. Wanklyn's.

That is, the mixture contains about 66·6 per cent. of cocoa. The amount of starch in cocoa may be determined in the ordinary way, as described at p. 16, but the process is somewhat tedious, and may be dispensed with, since the extract in cold water is always a guide to the adulteration of starchy substances. Cocoa nibs treated in this way give to water about 6·76 per cent. of organic matter and 2·16 of ash. The determination of theobromin may possibly be of use, but no sufficiently accurate and speedy process for technical purposes is as yet known.

§ 62. *Adulterations of Chocolate.*—Oil of almonds, cocoa-oil, beef and mutton fat, starches, cinnabar, chalk, and various other substances are usually enumerated; a few of these are, however, apocryphal.

The analysis of chocolate is conducted on exactly the same principles as that of soluble cocoa. If it is desired to separate the different constituents, the method recommended by A. Porrier may be used:—Extract the fat with ether, and the sugar with alcohol of 20°, and dissolve the starch out by boiling water. The liquid holding the starch is then decolorised by animal charcoal, and the starch precipitated by alcohol of 50 per cent., dried, and weighed. But as regards adulteration, the procedure recommended in the case of cocoa will be found quite efficient, and less cumbersome and tedious.

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PART V.

ALCOHOL — ALCOHOLIC LIQUIDS.

I.—ALCOHOL.

§ 63. The term *alcohol*, in its strict chemical sense, applies only to the neutral compounds of oxygen, carbon, and hydrogen, which by the action of acids form ethers. The principal alcohols are enumerated in the following table :—

TABLE EXHIBITING THE PROPERTIES OF THE PRINCIPAL ALCOHOLS.

Alcohols.	Formula.	Specific Gravity.		Vapour. Rel. Wt. H=1.	Boiling Point.	
		Liquid.	Vapour.		Fahr.	Cent.
1. Wood Spirit, or Methylic Alcohol,	CH_4O	0·798	1·12	16	149·9	65·5
2. Spirit of Wine, or Ethylic Alcohol,	C_2H_6O	0·7938	1·6133	23	173·	78·3
3. Tritrylic or Propylic, . . .	C_3H_8O	0·817	2·02	30	206·	96·7
4. Tetrylic or Butylic,	$C_3H_{10}O$	0·8032	2·589	37	233·	111·7
5. Fousel Oil, or Amylic, . . .	$C_5H_{12}O$	0·8184	3·147	44	269·6	132·0
6. Hexylic or Caproic,	$C_6H_{14}O$	0·833	3·53	51	299--309	148--154
7. Heptylic, . .	$C_7H_{16}O$	0·819	...	58	351·	176·7
8. Octylic or Caprylic,	$C_8H_{18}O$	0·823	4·5	65	356·	180·0
10. Laurylic, . .	$C_{12}H_{26}O$	...	...	...	...	...
16. Ethal or Cetylic, .	$C_{16}H_{34}O$	...	...	...	...	...
27. Cerotin or Cerylic,	$C_{27}H_{56}O$	...	...	...	...	...
30. Melissin or Mellisylic, . . .	$C_{30}H_{62}O$	...	...	...	...	...

Of these ethylic alcohol, wood spirit, and fousel oil are the three of most importance to the analyst.

§ 64. *Ethylic Alcohol*, C_2H_6O, specific gravity, 0·815 at 0°C., 0·79381 at 60°C. ; boiling point, 78·3°C. Absolute alcohol does not dissolve common salt, nor does it give a blue colour when digested with anhydrous sulphate of copper, if perfectly water-free. There is no cloudy appearance when mixed with water, denoting the absence of oily matters. It should be also perfectly neutral to test paper, and leave no residue on evaporation.

§ 65. *Rectified Spirit,* as defined by our own pharmacopeia, should be of specific gravity 0·838; by that of the Netherlands, 0·830 to 0·834; of Germany, Switzerland, and Norway, 0·8336; of Austria, 0·838; of France, 0·835 to 0·841. It should be neutral, colourless, volatilising without residue, and free from other alcohols. The proportion of alcohol in pure aqueous solution is usually found by specific gravity tables. The table on p. 125 answers all the ordinary purposes of the analyst.

Another method, sometimes called Gröning's, of arriving at the strength of dilute spirits, is based on the fact that the temperature of the vapour is an exact measure of the strength of the alcohol. The bulb of a thermometer is put (on the small scale) into a flask with a bilateral tube, and the temperature of the vapour carefully noted. The following table may be used:—

Table showing the Alcoholic Content by Volume of Boiling Spirits and of their Vapour. From the Temperature of the latter, as observed by a Thermometer. By Gröning.

Temperature of the Vapour (F.)	Alcoholic Content of the Distillate. Per cent.	Alcoholic Content of the Boiling Liquid. Per cent.	Temperature of the Vapour (F.)	Alcoholic Content of the Distillate. Per cent.	Alcoholic Content of the Boiling Liquid. Per cent.
170·0	93	92	189·8	71	20
171·8	92	90	192·0	68	18
172·0	91	85	194·0	66	15
172·8	90½	80	196·4	61	12
174·0	90	75	198·6	55	10
174·6	89	70	201·0	50	7
176·0	87	65	203·0	42	5
178·3	85	50	205·4	36	3
180·8	82	40	207·7	28	2
183·0	80	35	210·0	13	1
185·0	78	30	212·0	0	0
187·4	76	25			

The boiling-point is also a useful guide; for within certain limits the boiling-point of alcoholic liquids is not materially altered by admixture with saline and organic matter. A thermometer with a movable scale is employed. Before using it, the thermometer is immersed in boiling distilled water, and the 212°F. of the scale accurately adjusted to the level of the mer-

TABLE SHOWING THE DENSITIES AND VALUES OF SPIRITS AT 60°F., CORRESPONDING TO EVERY INDICATION OF SYKES' HYDROMETER.

Sykes' Hydrometer Indication.	Strength per cent.	Specific Gravity.	Per cent. of Absolute Alcohol.		Sykes' Hydrometer Indication.	Strength per cent.	Specific Gravity.	Per cent. of Absolute Alcohol.	
	O.P.		By Measure.	By Weight.		O.P.		By Measure.	By Weight.
0	67·0	·81520	95·28	92·78	51	11·4	·90551	63·54	55·70
1	66·1	·81715	94·78	92·08	52	10·0	·90732	62·74	54·89
2	65·3	·81889	94·31	91·42	53	8·6	·90913	61·94	54·09
3	64·5	·82061	93·84	90·78	54	7·1	·91107	61·09	53·23
4	63·6	·82251	93·33	90·07	55	5·6	·91299	60·24	52·38
5	62·7	·82441	92·80	89·36	56	4·2	·91479	59·43	51·57
6	61·8	·82622	92·29	88·67	57	2·7	·91666	58·58	50·73
7	60·9	·82800	91·77	87·99	58	1·3	·91839	57·78	49·94
8	60·0	·82978	91·25	87·30		U.P.			
9	59·1	·83151	90·74	86·63	59	0·3	·92037	56·86	49·04
10	58·2	·83323	90·23	85·96	60	1·9	·92228	55·96	48·17
11	57·3	·83494	89·72	85·30	61	3·4	·92408	55·10	47·33
12	56·4	·83661	89·21	84·65	62	5·0	·92597	54·19	46·46
13	55·5	·83827	88·70	84·00	63	6·7	·92798	53·22	45·53
14	54·6	·83993	88·17	83·33	64	8·3	·92984	52·30	44·65
15	53·7	·84153	87·67	82·70	65	10·0	·93176	51·36	43·76
16	52·7	·84331	87·10	81·99	66	11·7	·93367	50·39	42·84
17	51·7	·84509	86·51	81·26	67	13·5	·93586	49·34	41·86
18	50·7	·84680	85·95	80·58	68	15·3	·93758	48·31	40·90
19	49·7	·84851	85·39	79·89	69	17·1	·93949	47·29	39·96
20	48·7	·85022	84·81	79·19	70	18·9	·94135	46·29	39·04
21	47·6	·85205	84·19	78·44	71	20·8	·94327	45·20	38·04
22	46·6	·85372	83·61	77·74	72	22·7	·94518	44·09	37·03
23	45·6	·85537	83·04	77·07	73	24·7	·94709	42·96	36·01
24	44·6	·85700	82·47	76·39	74	26·7	·94899	41·82	34·98
25	43·5	·85878	81·85	75·66	75	28·8	·95092	40·63	33·92
26	42·4	·86055	81·21	74·92	76	31·0	·95288	39·40	32·82
27	41·3	·86229	80·59	74·19	77	33·2	·95484	38·10	31·68
28	40·2	·86402	79·97	73·47	78	35·6	·95677	36·76	30·50
29	39·1	·86574	79·34	72·75	79	38·1	·95877	35·32	29·24
30	38·0	·86745	78·71	72·03	80	40·6	·96068	33·90	28·01
31	36·9	·86915	78·08	71·32	81	43·3	·96259	32·41	26·73
32	35·7	·87099	77·40	70·54	82	46·1	·96457	30·77	25·32
33	34·5	·87282	76·71	69·77	83	49·1	·96651	29·08	23·88
34	33·4	·87450	76·08	69·06	84	52·2	·96846	27·31	22·38
35	32·2	·87627	75·41	68·32	85	55·5	·97049	25·39	20·77
36	31·0	·87809	74·72	67·55	86	59·0	·97254	23·41	19·11
37	29·8	·87988	74·03	66·79	87	62·5	·97458	21·39	17·42
38	28·5	·88179	73·29	65·98	88	66·0	·97660	19·41	15·78
39	27·3	·88355	72·60	65·23	89	69·4	·97857	17·46	14·16
40	26·0	·88544	71·86	64·43	90	72·8	·98057	15·51	12·56
41	24·8	·88716	71·17	63·68	91	76·1	·98261	13·58	10·97
42	23·5	·88901	70·43	62·89	92	79·2	·98452	11·85	9·56
43	22·2	·89086	69·69	62·10	93	82·3	·98657	10·04	8·08
44	20·9	·89268	68·95	61·32	94	85·2	·98866	8·28	6·65
45	19·6	·89451	68·21	60·53	95	88·0	·99047	6·83	5·48
46	18·3	·89629	67·47	59·76	96	90·7	·99251	5·25	4·20
47	16·9	·89822	66·67	58·92	97	93·3	·99448	3·80	3·03
48	15·6	·89997	65·93	58·15	98	95·9	·99658	2·31	1·84
49	14·2	·90182	65·14	57·34	99	98·2	·99851	·997	·793
50	12·8	·90367	64·34	56·52	100	...	1·00000	...	...

cury; it is then ready for an operation of several hours, or even an entire day, if no considerable variations of atmospheric pressure are experienced.[*]

Table exhibiting the Boiling-points of Alcohol and Water of the Given Strengths. By Gröning.

Boiling-point (F.)	Alcohol per cent. per Volume.	Boiling-point (F.)	Alcohol per cent. per Volume.
205·34	5	179·96	55
199·22	10	179·42	60
195·8	15	178·7	65
192·38	20	177·62	70
189·50	25	176·54	75
187·16	30	175·46	80
185·	35	174·92	85
183·38	40	174·2	90
182·12	45	173·14	95
181·58	50	172·	100

§ 66. *Proof Spirit,* a term in constant use for purposes of excise, is a diluted spirit, which was defined by Act of Parliament (58 George III.) to be "such as shall, at the temperature of 51°F. (10·5°C.), weigh exactly twelve-thirteenth parts of an equal measure of distilled water." According to Drinkwater it consists of—

Alcohol by weight, ...	49·24
Water by weight, ...	50·76
	100·00

and its specific gravity at 15·5°C. is 0·79381.

In the analysis of all spirits (seeing that the terms "proof" and "under proof" are used and known in the trade), the statements of results should always include the percentage of proof spirit.

§ 67. *Tests for Alcohol.*—The principal tests for alcohol are the following:—

(1.) *Production of Acetic Ether.*—To a distillate, or aqueous solution supposed to contain alcohol, some acetate of soda is

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In the present work the elaborate tables of Gay-Lussac, Tralles, &c., are not quoted, since every analyst is certain to have the ordinary chemical treatises containing them at hand.

added, and sulphuric acid in amount more than sufficient to decompose the acetate. The flask containing the mixture is connected with a Liebig's condenser, placed vertically, and boiled for a few minutes; any volatile vapour is condensed, and falls back again into the flask. On removing the cork, if acetic ether has been produced, it can readily be detected by its odour.

(2.) *Reduction of Chromic Acid or Bichromate of Potash to Oxide of Chromium.*—A crystal of chromic acid, placed in a test-tube, with a fluid containing alcohol warmed to a boiling temperature, is decomposed into the green oxide of chromium. Instead of chromic acid, a test-solution of one part of dichromate of potash dissolved in 300 parts of sulphuric acid, may be used. A portion of the liquid to be tried is mixed with twice its volume of concentrated sulphuric acid. On pouring a small quantity of this mixture into a quantity of the test solution, a deep green is produced where one fluid touches the other. This is a very good test in the absence of other reducing agents, such as formic acid, ether, &c.

(3.) *Dr. Edmund Davy's Test.*—Dr. Davy has proposed a test for alcohol founded on a colour reaction, and produced also by methyl, propyl, butyl, and amyl alcohols, ether and aldehyde. A solution of one part of molybdic acid in ten of strong sulphuric acid, is warmed in a porcelain capsule, and the liquid to be tested allowed to fall gently on it. If alcohol is present, a blue coloration appears either immediately, or in a few moments; the liquid gradually absorbs moisture from the air, and the colour disappears, but it may be reproduced by evaporation.*

(4.) *The Production of Iodoform.*—According to Lieben, one part of alcohol in 2000 of water can be detected by adding to some of the warmed liquid a little iodine and a few drops of solution of soda; again warming gently, and setting aside for a time, when a yellowish crystalline deposit of iodoform is obtained; under the microscope the latter presents the appearance of hexagonal plates, six-rayed, or other varieties of, stellar crystals: $C_2H_6O + 4I_2 + 6\,NaHO = CHI_3 + NaCHO_2 + 5NaI + 5H_2O$. The objection to this test is, however, that other alcohols, aldehyde, gum, turpentine, sugar, &c., give a similar reaction.†

(5.) *The Production first of Acetic Acid, then of Kakodyl.*—A

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* *Proceedings of the Royal Irish Academy* [2 ii., 579-582.]; *Journ. Chem. Soc.*, 7, 1877, p. 108.

† Rajewsky has found that the brain of a rabbit, which had been starved for two days before death, gave a marked reaction for alcohol with the iodoform test, and the same result was obtained from the muscles and tissues of rabbits. He therefore considers that alcohol always exists in the animal organism, or that it is produced during distillation.—*Pflüger's Archiv. für Physiologie*, xi., 122, 127.

very delicate test for alcohol, and one specially suited for its detection in the blood, &c., is recommended by Bucheim.*

The finely-divided substances are put in a tubulated retort, and, if acid, carefully neutralised. In the neck of the retort is placed a little porcelain or platinum boat, containing platinum black, and at each end there is a moistened piece of strongly-blued litmus-paper. On warming the retort, if alcohol be present, it is oxidised by the platinum black to aldehyde and acetic acid; hence, the hinder piece of litmus-paper will be reddened, the front one unchanged. If only a drop of acetic acid be present, it is possible to detect it in the following way:—The platinum black is washed, the washing water neutralised with potash, and dried after the addition of a few grains of arsenious acid. On warming the dry residue in a small glass tube, if even a very small admixture of acetic acid be present, the smell of kakodyl will be perceptible.

(6.) *The Action of Alcohol on Chloride of Benzole.*—Berthelot proposes as a test the action of alcohol on chloride of benzole. Very small quantities of alcohol decompose chloride of benzole and benzoic ether. Caustic potash, again, decomposes chloride of benzole, but *not* benzoic ether.

§ 68. *Separation of Alcohol from Animal Matters.*—In order to obtain alcohol from organic matters (*e.g.*, the contents of the stomach, or the tissues), the following process will be found convenient:—Solid matters, such as the tissues, are cut up as finely as possible, and placed with water in a retort attached to a suitable condenser. Most liquids require no previous preparation, and are merely poured into the retort or flask, as before described; but it is desirable in the treatment of *urine* to add a little tannic acid. About one-third to one-half of the liquid is distilled over into a flask closed by a mercury valve. The product is now made alkaline with caustic potash (which will fix any volatile acid, and expel any volatile alkali), and again distilled, about one-third being drawn over. The liquid is next neutralised with sulphuric acid, to fix volatile alkalies, and redistilled. This final distillate contains all the alcohol, but neither volatile acids nor alkalies. The liquid thus obtained may even now be too dilute to respond conveniently to tests, and it may therefore be digested for some hours with a little caustic lime, and then very slowly distilled. The distillate should finally be carefully measured or weighed, and divided into two parts, one of which serves for the application of the usual tests, the other (if alcohol be found) can be oxidised in the manner described at p. 131, and estimated as acetic acid volumetrically.

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* *Chem. Centralb.*, 1854, p. 428.

II.—ALCOHOLIC LIQUIDS.

§ 69. In the examination of alcoholic liquors, one of the analyst's first steps is to determine the percentage of alcohol, and the methods by which this is done are equally applicable (with slight modifications) to all liquids containing alcohol. The percentage is ascertained—

(1.) By distillation, and taking the specific gravity of the distillate.
(2.) By Tabarie's method, applied especially to wines and beers.
(3.) By Geissler's vaporimeter.
(4.) By oxidation into acetic acid, and by several other methods, which are, however, not much in use by the analyst.

(1.) *Distillation.*—A convenient quantity (*e.g.*, 100 cc. of beer or wine, 50 cc. of spirits, measured at 15·5°C.) is placed in a flask

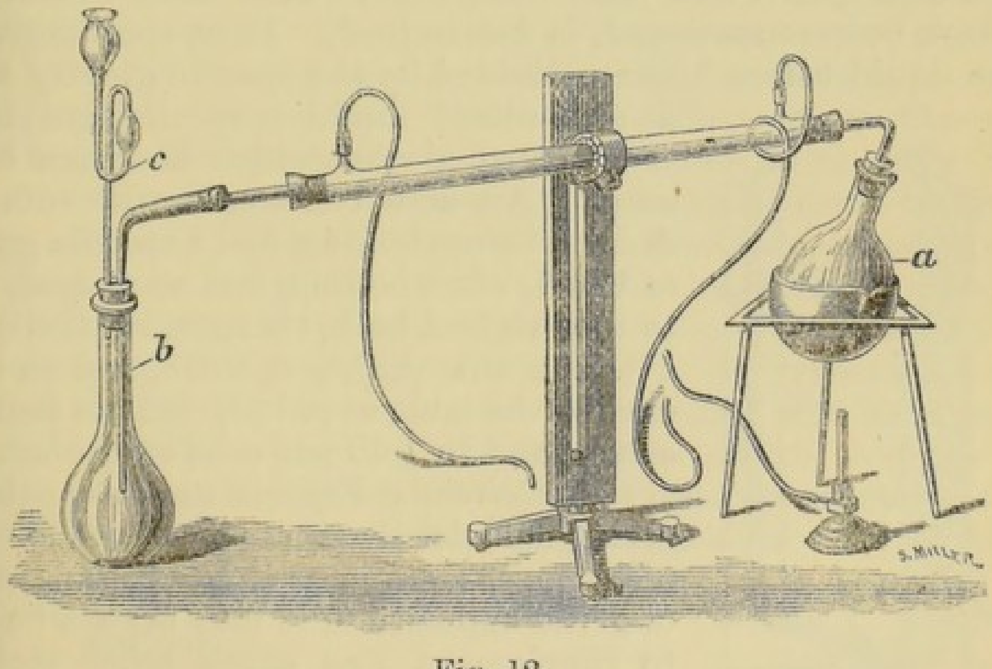

Fig. 12.

(*a*, Fig. 12), having a side tube connected by means of a cork to a Liebig's condenser. The distillate is received in a flask (*b*) provided with a doubly perforated cork, into which the bent tube of the condenser, as well as a tube provided with a mercury valve, to prevent loss, is adjusted; the latter may be readily made by putting a very small quantity of mercury into the bend of an ordinary thistle-head funnel (*c*). This precaution is only necessary when very small quantities are operated upon. Experiments with 50 cc. of spirit distilled into a flask unprovided with a valve, have shown that there is no appreciable loss; but distillation into an open vessel will always give results far too low. Beer and wine yield the whole of their alcohol when half is drawn over; spirits should be distilled nearly to dryness. In any case, the distillate should be made up to exactly the same bulk as the original liquid at the same temperature, its specific gravity taken in a proper specific-gravity bottle, and the percentage of alcohol obtained by reference to the tables given at p. 125. Spirits are best returned as containing so much *proof spirit*, by weight and by volume; wines and beers, so much alcohol per cent., by weight and by volume.

(2.) *Tabarie's method*, when properly performed, is sufficiently accurate for all practical purposes in the case of beers, wines, and similar liquids. The specific gravity is first accurately taken at 15·5°C.; a measured quantity—say 100 cc.—is then boiled long enough to evaporate away the whole of the alcohol, made up to the original bulk *at the same* temperature, and its specific gravity again determined. From these data the specific gravity of the liquid which, if it had been condensed, would have collected in the flask before-mentioned, is determined. Thus, specific gravity of the liquid before boiling, divided by the specific gravity of the de-alcoholised liquid = specific gravity of the diluted alcohol which has been boiled away. An actual example will suffice:—A beer, before boiling, had a specific gravity of 1·014; after boiling, and on making it up to the original bulk, its specific gravity was 1·0172; now $\frac{1{\cdot}014}{1{\cdot}0172} = {\cdot}9968$, and on reference to the table at p. 125, ·9968 is found to correspond to 1·68 per cent of alcohol.

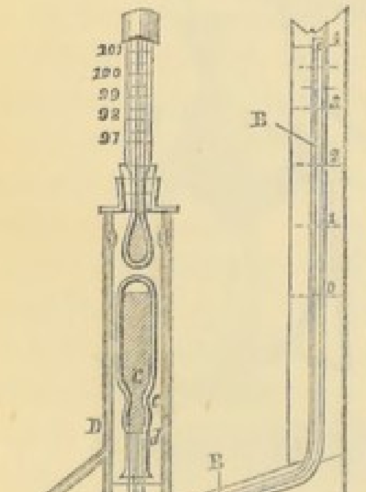

Fig. 13.

(3.) *Geissler's Vaporimeter* is capable of giving sufficiently accurate results for technical purposes, and as it has the advantage of great expedition, it may always be used to supplement and check other methods which take more time. It depends on the measurement of the tension or elastic force of the vapour of the liquid, as indicated by the height to which it raises a column of mercury. The apparatus (see Fig. 13) consists of four parts—viz., (1.) A brass vessel A, containing water; (2.) a doubly bent tube, BB, fastened to a scale; (3.) a cylindrical vessel C, which is filled with mercury and the fluid to be tested; (4.) a brass vessel D, in the upper part of which there is a thermometer.

By removing the bent tube and its connections from A, it may be turned upside down, and C detached; the alcoholic fluid is then poured in so as to fill the space between *c* and *d*, which, when the instrument is inverted, is empty. It is now connected with the bent tube, and adjusted exactly as in the figure, the water made to boil in A, when the mercury runs up to a certain height in the tube, and the percentage is directly read from the scale. Should the thermometer not register 100°C., certain corrections must be made, which is most conveniently done by a table, sold with the instrument. Care in this manipulation must always be taken to exclude air from the bulb.

(4.) *Oxidation into Acetic Acid* is an extremely accurate method of determining vinic alcohol, and is specially applicable to small quantities. Dr. Dupré recommends the following process:—* A small quantity of the distillate, representing about a gramme of alcohol, is put in a small strong assay-flask, and mixed with 10 cc. of an oxidising solution, composed of 147 grms. of bichromate of potash and 220 grms. of sulphuric acid, made up to 1,400 cc. by water. The flask is well stoppered by caoutchouc, and firmly tied down by canvas and string. It is then suspended upright in a water-bath (the neck being above the water), and heated for two hours between 80° and 90°C. The flask is next removed, and the excess of bichromate reduced by zinc and sulphuric acid; the solution is transferred to a small retort (adding some sulphuric acid and bits of tobacco pipe), and distilled over from a spermaceti-bath (see Fig. 12). It will be found necessary to distil at least thrice nearly to dryness, each time adding water to the contents. The united distillates contain acetic acid, the result of the oxidation of the alcohol. This acetic acid may be determined by a volumetric solution of soda, and the amount of alcohol to which it is equivalent calculated by the following short table:—

Acetic Acid.		Alcohol.
1	=	·7666
2	=	1·5332
3	=	2·2998
4	=	3·0664
5	=	3·8330
6	=	4·5996
7	=	5·3662
8	=	6·1328
9	=	6·8994
10	=	7·6666

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* It has been shown by Wanklyn that alcohol may also be oxidised into acetic acid very readily by an alkaline solution of permanganate of potash; it would appear that in this case there is no previous formation of aldehyde.

There are several other methods of estimating alcohol, but the above are the most practical and efficient; and whenever the amount of alcohol is important (as, for example, in the case of spirits) the analyst should determine it in at least two different ways. The specific-gravity methods presuppose the presence of ethylic alcohol only; but it is sometimes necessary to test fluids also for methylic and amylic alcohols. For these the following processes are available:—

§ 70. *Methylic Alcohol.*—100 cc. of the suspected spirit are distilled twice, having been rendered alkaline during the first process and acid during the second, about two-thirds being distilled over each time. The distillate is now shaken up with dry potassium carbonate, and, after standing over night, the upper layer is taken off by a syphon or pipette, and again twice distilled, about 15 cc. being driven over. This will contain any methylic alcohol present in the original 100 cc. A portion of the distillate is now diluted with water to a strength from 10 to 15 per cent., and in this diluted spirit the alcohol determined—(1.) By specific gravity; (2.) by Geissler's vaporimeter; and, (3.) by oxidation into acetic acid. If ethylic alcohol alone is present, all three methods fairly agree. The specific gravity will give the total amount of both alcohols, the specific gravity of aqueous methylic and ethylic alcohols being almost identical; but since methylic alcohol has a higher vapour tension than ethylic, Geissler's vaporimeter will give a higher result. The oxidation process will, on the other hand, give a lower result, for methylic alcohol yields water and CO_2, so that the acetic acid found is derived wholly from the ethylic alcohol, and the difference between the strength thus found and that derived from the specific gravity gives a rough indication of the proportion of methylic alcohol present. If the methylic alcohol is in sufficient quantity, instead of the usual slight vacuum on opening the flask, there is an escape of carbonic anhydride, and there is no reason why this gas should not be either absorbed or collected and estimated.

Dr. Dupré gives the following example. A pure whisky showed—

Strength by specific gravity, ...	9·83 per cent.
„ Vaporimeter, ...	9·75 „
„ Oxidation, ...	9·75 „

The same whisky, adulterated with 10 per cent of ordinary methylated spirit, and tested, gave—

Strength by specific gravity, . .	10·08 per cent.
,, Vaporimeter, . . .	10·45 ,,
,, Oxidation, . . .	9·50* ,,

The remainder of the distillate may be used in producing methyl aniline violet or oxalate of methyl.

The general process for the production of methyl aniline violet is as follows :—10 cc. of alcohol, with 15 grms. of iodine and 2 grms. of red phosphorus, are put into a small flask, and distilled into 30 or 40 cc. of water. The alcoholic iodide which settles to the bottom is separated by a pipette, and collected in a flask containing 5 cc. of aniline. If the action be too violent, the flask can be cooled with cold water; if too slow, a little heating may be necessary. At the end of an hour the crystals are dissolved in hot water and boiled, an alkaline solution is afterwards added, and the bases rise to the top in the form of an oily stratum, which may be separated by bringing the oil, by the addition of water, on a level with the neck of the flask. The oxidation of the bases may be effected in various ways, but best by pouring a cubic centimetre of the oily liquid on 10 grms. of a mixture formed of 100 grms. of quartz sand, 2 of chloride of sodium, and 3 of nitrate of copper. After incorporation it is introduced into a glass tube, and kept at 90°C. in a water-bath for eight or ten hours; it is ultimately exhausted by warm alcohol, thrown on a filter, and made up to 100°C. If the alcohol was pure the tint is red; if it contained 1 per cent. of methyl alcohol the colour, by the side of the preceding, is manifestly violet; with 2·5 per cent. the shade is a very distinct violet; and with 5 per cent. it is considerably darker. The process may be made quantitative by having volumetric solutions of methyl and ordinary alcohol. Very minute quantities of methyl alcohol may be detected by adding 5 cc. of the liquid to 95 cc. of water, and then again diluting 5 cc. of this liquid with 400 cc. of water, and heating it in a porcelain capsule. Fragments of white merino (free from sulphur), immersed in the liquid for half an hour, will remain white, if the alcohol was pure; if methyl was present, they will be of a violet tint.†

§ 71. *Oxalate of Methyl* may be obtained by mixing the distillate with half its bulk of sulphuric acid and double the quantity of hydropotassic oxalate. The whole should stand in the retort for twenty-four hours, and then be distilled. Crystals appear after a time in the cooler parts of the flask or retort;

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* Note on the Examination of Whisky and other Spirits for Methylated Spirit and Fousel Oil, by Dr. Dupré. *Analyst*, i., 1876, p. 4.

† A. Riche and Brady, *Comptes Rendus*, vol. xxx., p. 1096.

their composition is $(CH_3)_2C_2O_4$. It would also be quite possible to produce such compounds as the salicylate of methyl, &c.

§ 72. *Formic Acid.*—It has been already stated that methyl alcohol, when fully oxidised, is resolved into CO_2 and water. This takes place in two stages; first, formic acid is produced, and then this formic acid breaks up. Thus:—

(1.) Methyl Alcohol. Formic Acid.

$$CH_4O + O_2 = CH_2O_2 + H_2O$$

(2.) Formic Acid.

$$CH_2O_2 + O_2 = 2CO_2 + 2H_2O$$

It hence follows that if a spirit be distilled in the manner recommended by Dr. Dupré, and only partially oxidised, it is possible to get formic acid, which has some very characteristic properties. To obtain this result a small portion of the distillate, 2 to 4 cc., is taken, and 3 grms. of potassic dichromate are added, with an equal quantity of pure sulphuric acid, and four or five times as much water. This is allowed to act for twenty minutes, and then distilled; the liquid is alkalised with sodium carbonate, evaporated to half its bulk, acidulated with acetic acid, transferred to a test-tube, and then heated gently with a 5 per cent. solution of nitrate of silver. If formic acid has been produced, there is a distinct precipitate of metallic silver.

§ 73. *Fousel Oil* is the name given by most chemists to amylic alcohol; it may, however, be conveniently applied to the mixture of the higher homologues of ethylic alcohol. Dr. Dupré* detects fousel oil by oxidising one or two grammes of alcohol, previously distilled (if necessary) in the manner already described. When cool the flask is opened, the excess of dichromate reduced by zinc, and the acids produced distilled off. The acid distillate is neutralised with a standard solution of normal soda, the solution evaporated to a small bulk, and transferred to a retort. An amount of normal sulphuric acid, equal to one-twentieth of the normal alkali used, is now added, and the contents of the retort are distilled to dryness in an oil-bath, the temperature being allowed to rise to about 130°C. Water is then added, with a further quantity, one-twentieth, of normal acid, and the contents re-distilled to dryness. Some water is now poured on the dry residue in the retort, and it is again distilled, the latter operation being repeated three times. The distillates from these various operations are united, neutralised by carbonate of barium, the solution boiled, filtered, and evaporated to dryness, the residue dried at 130°C., and weighed. The barium salt is con-

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* *Op. cit.*

verted into sulphate in the usual manner, and the percentage of barium determined. The data are now at hand to determine the presence of fousel oil in the sample, and the approximate quantity. The barium salt of the acid produced by the oxidation of fousel oil, (Barium valerianate, $Ba(C_5H_9O_2)_2$,) contains 40·41 per cent. of barium. The barium salt of the acid derived from the oxidation of pure alcohol, (Barium acetate, $Ba(C_2H_3O_2)_2$,) contains 53·72 per cent. of barium. If the alcohol is free from fousel oil, the barium found will closely approximate the percentage mentioned; but if the higher alcohols are present, the percentage will be lower, and a fair approximation to the amount of fousel oil will be arrived at by estimating the salt as a mixture of baric acetate and valerianate, and calculating out the percentages on the usual principles.

III.—BEER.

§ 74. The most accurate definition of beer, as brewed in the present day, is that of a fermented saccharine infusion, to which has been added a wholesome bitter. The chief constituents of beer, stouts, and porters, are—

(1.) Water containing in solution (according to its origin) various salts. Distilled water is never used in brewing.
(2.) Alcohol.
(3.) Carbonic and acetic acids.
(4.) Malt extract, } Malt sugar, dextrine, albuminous constituents, and ash.
(5.) Bitter principles, occasionally derived solely from the hop, but very commonly supplemented by so-called "hop substitutes." Samples of the latter examined by the author all contained "quassia," and portions of the following plants were identified — Calumba, chirata, gentian, and wormwood.
(6.) The ash derived from the water, the malt, and the bitters.

To these must be added volatile and essential oils, vegetable gelatine, glucinic acid derived from the sugars, lactic acid, and, in porters, caramel and assamar.

The general composition of the chief ingredients of beer may be gathered from the following table, taken from Mr. Watts' dictionary :—

SPECIAL EXAMINATION OF CERTAIN BEERS.

Name of Beer.	Malt Extract. Per cent.	Alcohol. Per cent.	Carbonic Acid. Per cent.	Water. Per cent.	Analysed by
London Porter, Barclay & Perkins, ...	6·0	5·4	0·16	88·44	Kaiser.
London Porter, . . .	6·8	6·9	...	86·3	Balling.
,, ,, Berlin, .	5·9	4·7	0·37	89·0	Ziurek.
Burton Ale, ...	14·5	5·9	...	79·6	Hoffmann.
Scotch Ale, Edinburgh, .	10·9	8·5	0·15	80·45	Kaiser.
Ale, Berlin, ...	6·3	7·6	0·17	85·93	Ziurek.
Brussels Lambick, . .	3·4	5·5	0·2	90·90	Kaiser.
,, Faro, . . .	2·9	4·9	0·2	92·00	,,
Salvator Bier, München, .	9·4	4·6	0·18	85·85	,,
Bock Bier, ,, . .	9·2	4·2	0·17	86·49	,,
Bavarian Draught Beer (Schenk Bier, München), .	5·8	3·8	0·14	90·26	,,
Bavarian Store Beer (Lager Bier, München, 16 months old), ...	5·0	5·1	0·15	89·75	,,
Bavarian Store Beer, München,	3·9	4·3	0·16	91·64	,,
,, Draught Beer, Brunswick,	5·4	3·5	...	91·1	Otto.
Bavarian Beer (Waldschlösschen)	4·8	3·6	...	91·5	Fischer.
Prague Draught Beer, . .	6·9	2·4	...	90·7	Balling.
,, Town Beer (Stadt Bier),	10·9	3·9	...	85·2	,,
Sweet Beer, Brunswick, .	14·0	1·36	...	84·7	Otto.
Josty's Beer, Berlin, . .	2·6	2·6	0·5	94·3	Ziurek.
Werder's Brown Beer, Berlin,	3·1	2·3	0·3	94·2	,,
White Beer, Berlin, . .	5·7	1·9	0·6	91·8	,,
Bière Blanche de Louvain, .	3·0	4·0	...	93·0	Le Cambre.
Petermann (Louvain), . .	4·0	6·5	...	89·5	,,

The composition of beers, as a whole, varies in some degree according to the kind of ale or beer, according to the method of manufacture, and according to its age and preservation.

Pale Ale should be made from the finest and highest dried malt and the choicest hops, the bitter being in excess.

Mild Ale is a sweet, rather strong beer. *Table beer* is rarely sold—it is a weak watery ale.

Porter, as drunk in the metropolis, is a rather weak malt-liquor, coloured and flavoured with roasted malt. *Stout* is a richer and stronger description of porter.

Bavarian Beers in some degree derive their peculiar qualities from fermentation at a low temperature. They seldom contain more than two per cent. of alcohol, are only slightly bittered, have a fine aroma, and a peculiar flavour, said to be due to the solution of a minute fraction of the resinous matters used to caulk the casks.

Lambick and Faro Beers are made with unmalted wheat and barley malt. In fermentation the wort is self-impregnated, the process sometimes taking months, and being mostly of a bottom character. The beer contains a large quantity of lactic acid, and is very hard in consequence.

Of the constituents of beer, it will be necessary to notice fully the water, the malt extract, the bitters, and the ash.

§ 75. The *water used by the brewer* is mainly interesting to the analyst on account of the common salt held in solution, since in prosecutions for the addition of salt the defence generally is, that the latter is a natural component of the beer. Thus, Dr. Bottinger's analysis of the constituents of the water used at Messrs. Allsopp's brewery is as follows :—

	Per Gallon.
Chloride of Sodium, ...	10·12
Sulphate of Potash, ...	7·65
,, Lime, ...	18·96
,, Magnesia, ...	9·95
Carbonate of Lime, ...	15·51
,, Magnesia, . . .	1·70
,, Iron, ...	0·60
Silica, ...	0·79
	65·28

Messrs. Bass and Co.'s water (according to an old analysis of Cooper) contains chlorine equal to a little over 10 grains of common salt per gallon, and all published analyses of water used in breweries give quantities of salt under 14 grains per gallon. However, since breweries, as a rule, use hard spring water, it is quite possible for the water in particular localities to contain a much larger percentage of salt than the quantity mentioned above.

§ 76. *Malt Extract.*—The constituents of barley and also of malt are given in the accompanying table ; but of these it is the ash alone which will remain, comparatively speaking, unchanged ; for by the action of mashing a very large portion of the dextrine and starch becomes changed into sugar.

Composition of Barley and Malt.

	Barley.	Malt.		
	Air-dried.	Air-dried.	Kiln-dried, pale.	Kiln-dried, amber.
Produce of Torrefaction, .	0·0	0·0	7·8	14·0
Dextrine, . . .	5·6	8·0	6·6	10·2
Starch, ...	67·0	58·1	58·6	47·6
Sugar, ...	0·0	0·5	0·7	0.9
Cellulose, . . .	9·6	14·4	10·8	11·5
Albuminous substances, .	12·1	13·6	10·4	10·5
Fatty substances, . .	2·6	2·2	2·4	2·6
Ash, &c., . . .	3·1	3·2	2·7	2·7
	100·0	100·0	100·0	100·0

Barley contains dextrine, starch, albuminous substances, and a small quantity of fat, together with cellulose, and the ordinary saline constituents of seeds. Malt, varying a little in composition according to the heat of the final operations of the maltster, differs from barley in containing a small quantity of sugar (derived from transformation of a portion of the starch), rather more dextrine, and altogether less organic matter, the loss on malting being usually represented as—

Water, ...	6·00
Saline matter, ...	0·48
Organic matter, ...	12·52
	19·00

in 100 per cent. barley.

The constituents of barley are thus given by Oudemann:—

Dried Barley.

Starch, ...	65·7
Dextrine, ...	5·5
Gluten insoluble in water, soluble in alcohol, .	0·3
Soluble albuminous bodies coagulable by heat, .	0·3
" " not coagulable, . .	1·9
Albuminous bodies insoluble in water or in alcohol,	9·3
Fatty substances, ...	2·5
Cellulose, ...	9·4
Ash, ...	3·1
Lime, &c., ...	2·0

According to Thomson, the following is the relative composition of the ash of malt and barley:—

	Barley.	Malt.
Potash,	16·00	14·54
Soda,	8·86	6·08
Lime,	3·23	3·89
Magnesia,	4·30	9·82
Ferric Oxide,	0·83	1·59
Phosphoric Acid, P_2O_5,	36·80	35·34
Sulphuric Acid, (SO_3),	0·16	0·0
Chlorine,	0·15	Trace.
Silica,	29·67	28·74

Valentine and O'Sullivan have recently disputed the correctness of Oudemann's and the older analyses in the following points:—Oudemann finds from 5 to 8 per cent. of dextrine, Mr. O'Sullivan no dextrine at all; the small percentages of sugar generally quoted—viz., up to 1·0 per cent., Mr. O'Sullivan gives at from 16 to 20 per cent.; and the authors have compiled the following table, stating that each item has been estimated directly, and not by difference:—

COMPOSITION OF PALE MALT.

		(1.		(2.)
Starch,		44·15		45·13
Other Carbo-hydrates (of which 60 to 70 per cent. consist of fermentable sugars), Inulin (?) and a small quantity of other bodies soluble in cold water,		21·23		19·39
Cellular matter,		11·57		10·09
Fat,		1·65		1·96
Albuminoids—				
(*a.*) Soluble in alcohol of specific gravity ·820, and in cold water,	·63	...	·46	...
(*b.*) Soluble in cold water and at 68°C.,	3·23	...	3·12	...
(*c.*) Insoluble in cold water, but soluble at 68° to 70°C.,	2·37	...	1·36	...
(*d.*) Insoluble at 68° to 70°C., but soluble in cold water (albumen proper),	·48	...	·37	...
(*e.*) Insoluble in cold water, and at 70°C.,	6·38	...	8·49	...
	——	13·09	——	13·80
Ash,		2·60		1·92
Water,		5·83		7·47
		100·12		99·76

A sugar, "maltose," is obtained by the action of malt extract on starch; it has a specific rotatory power of + 150°, and 100 parts of it are equal to 65 parts of glucose in reducing cupric oxide. It forms a hard, white, crystalline mass, consisting of needles which lose their water in a current of air at 100°C. Maltose may be estimated by Fehling's solution, 10 cc. of Fehling being equivalent to 0·075 grm. malt sugar. [1 of metallic copper = ·85227 maltose.]

§ 77. *Beer Bitters.*—If the analyst should find the beer bittered by any substance other than hop, his verdict as to whether it is an adulteration, or not, will depend altogether on the nature of the substance added; for since the repeal of the hop duty in 1862, and the consequent return of the trade to other bitters, anything harmless in the way of a bitter is perfectly legal. If, however, such poisons as picric acid, picrotoxin, or colchicine, should be found, there can be no difference of opinion as to the course the analyst should pursue.

With regard to these, picric acid has certainly been discovered, and picrotoxin is strongly suspected, but as yet the latter has not been proved to be a common adulterant. The evidence as to the reputed occurrence of colchicine is unsatisfactory. Vangeldern, a short time ago, obtained from a mixture of genuine hops and the gummy matter of beer a substance giving the reactions of colchicine, so that a mistake is possible.

§ 78. *Hops.*—Hops are the catkins of the *Humulus lupulus*, and consist of imbricated scales enclosing the so-called nut. The scales themselves are covered with aromatic superficial glands, which are designated "yellow powder," or lupulin. Freed as far as possible from the lupulinic grains, the scales consist of astringent matter, chlorophyl, gum, colouring matter, and ash. The lupulin itself, according to Dr. Yves, contains the following matters:—

Volatile Oil,	?
Tannin,	4·16
Extractive,	8·33
Bitter principle,	9·16
Wax,	10·00
Resin,	30·00
Lignin,	38·33
Loss,	·02
	100·00

This analysis does not include the oil of hops, which is a very important constituent of the hop, and may be obtained by distilling the fresh flowers, or the lupulin.

The resin and bitter principle of the hop are to the brewer the most important constituents, its commercial value being directly dependent on them. According to some recent analyses made by Mr. Porter, the substances capable of solution in ether (viz., the oil, resin, and bitter principle) vary in different samples from 8·8 to a little over 17 per cent.*

§ 79. *Lupulite, or true Lupulin* (a substance isolated by Lermer in 1863), can be obtained in rhombic prisms by treating fresh hops with four times their weight of ether, distilling the ether off, then adding to the extract alcohol of 90 per cent. (which leaves the wax undissolved), and again taking up the alcoholic extract with ether. The ethereal solution is repeatedly shaken with strong potash-lye to get rid of the resin, and lastly with pure water to take up the bitter matter. It is precipitated from the aqueous solution by sulphate of copper, the composition of the precipitate being $C_{16}H_{25}CuO_4$; and crystals are obtained by dissolving the precipitate in ether, decomposing with SH_2, and evaporating the ethereal filtrate in a stream of carbonic acid gas.

A principle very bitter, but not crystalline, can also be obtained by adding to the aqueous extract of the lupulin grains a little lime, and then treating with alcohol. The solution is to be evaporated, the mass treated with water, and the solution again evaporated to dryness. On washing this residue with ether, a white uncrystallisable, bitter principle—soluble in 20 parts of water, very soluble in alcohol, and but slightly so in ether—is obtained; it is probably a derivative of Lermer's lupulite.

Lermer's Lupulite crystallises in glittering, rhombic, brittle prisms, tasteless in themselves, but with a very bitter flavour, and an acid reaction when dissolved in alcohol. They are insoluble in water, but dissolve easily in alcohol, ether, chloroform, bisulphide of carbon, benzole, and turpentine; exposed to the air, they soon become yellow and partly amorphous.

The ash of the hop differs but little from the ashes of foliar organs generally, the relative proportion of each constituent varying within somewhat wide limits, according to the particular variety. (See table on next page.)

Oil of Hops, according to the researches of Wagner, consists chiefly of an oxygen-holding oil, $C_{10}H_{18}O$, containing in solution a camphor boiling at 175°C. The specific gravity of the oil itself is 0·968. It begins to boil at 125°C., and successive portions can be separated by fractional distillation, the last passing

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* On the Examination of Hops, by W. E. Porter, F.C.S. *Analyst*, August, 1877; January, 1878.

CONSTITUENTS OF THE ASH OF HOP CONES.

	WAY AND OGSTON.			E. WATTS.
	Bentley Variety.	Golding Variety.	Grape Variety.	Grape Variety.
Potash,	11·98	24·88	25·56	19·41
Soda,	...	...	...	0·70
Lime,	17·93	21·59	18·47	14·15
Magnesia,	5·94	4·69	5·27	5·34
Alumina,	...	...	...	1·18
Ferric Oxide,	1·86	1·75	1·41	2·71
Sulphuric Acid,	7·01	7·27	11·68	8·28
Chlorine,	...	...	...	2·26
Silica,	22·97	19·71	9·99	17·88
Carbonic Acid,	5·44	2·17	4·54	11·01
Phosphoric Acid,	21·38	14·47	17·58	14·64
Chloride of Potassium,	5·45	...	4·34	...
,, Sodium,	...	3·42	0·12	...
Charcoal and Loss,	...	...	...	2·44
	99·96	99·95	98·96	100·00
Ash per cent. of Dry Hops,	8·07	5·95	7·21	...
,, ,, Fresh ,,	7·27	5·22	6·22	6·5

over at 235°C.; one-sixth distils over between 125° and 175°C., and is of a pale colour and quite clear; about half passes over between 175°C. and 225°C., and is also very clear; but the remainder is yellow, and the residue in the retort has the appearance of a brown turpentine.

The crude oil is brownish-yellow, and very sparingly soluble in water, one part requiring more than 600 times its weight for complete solution. It does not contain sulphur, as previously asserted by Payen and Chevallier, nor does it reduce ammoniacal solution of silver. Oxidation by nitric acid produces valerianic acid and a yellow acid resin; if dropped on melted caustic potash, valerianate, carbonate of potash, and a hydrocarbon are the results. The oil appears to be neither narcotic nor poisonous, twenty drops having had no action whatever on a kitten (*W. Keil*); but the wonderful preservative properties ascribed to it by older writers are very problematical.

A few other bitter principles, some of which have actually been found, and the remainder are supposed to exist, may be now conveniently described. (For *Picrotoxin* and *Colchicum* the reader is referred to the second portion of this work.)*

§ 80. *Absynthin*, $C_{40}H_{28}O_8HO$.—The bitter principle of wormwood, *Artemisia absynthium*. It may be extracted from the hot aqueous extract of wormwood by precipitation with tannic acid, evaporating the tannate to dryness with oxide of lead, and extracting the dried residue by alcohol, and subsequent purification with animal charcoal. Absynthin dissolves easily in alcohol and ether, with difficulty in hot water, and is scarcely soluble in cold. When obtained from alcoholic solution it is usually in the form of pale-yellow drops, which gradually become crystalline; it has a peculiar odour and extremely bitter taste, and its reaction is neutral. It reduces a hot ammoniacal solution of silver nitrate, but an alkaline tartrate of copper solution remains unchanged by it. It is dissolved by caustic potash with the production of a brown colour. Concentrated sulphuric acid produces first a brown colour, passing into a green-blue; as water is added, the colour becomes darker, until grey flocculent particles are separated. Boiling with dilute acids produces resinous products, but no sugar.

The bitter principle, according to some observers, is a direct cerebral excitant; according to others, a pure tonic. It is used occasionally in medicine, in doses from ½ grain to 2 grains, and the herb producing it is officinal in the Continental pharmacopeias.†

§ 81. *Aloin*—$C_{16}H_{18}O_7$ (TILDEN), $C_{17}H_{18}O_7$ (STENHOUSE), $C_{15}H_{16}O_7$ (E. SCHMIDT)—may be obtained by treating aloes with dilute sulphuric acid, removing the deposit of resin, and evaporating to a syrup. The crystals thus obtained are yellow needles, soluble in water and alcohol, and possessing a bitter taste. The amount of crystallisation water varies from 5·89 to 14·29 per cent.; if anhydrous, the melting point of the crystals is from 146° to 148°F. [70° to 80°C.]; if hydrous, sulphuric acid colours it first

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red, then orange, and it is dissolved by caustic potash with the production of a purple-red colour. The action of nitric acid produces chrysammic, picric, and oxalic acids, with the addition of carbonic anhydride; that of zinc dust, methylanthracene and anthraquinone.*

§ 82. *Cnicin*, $C_{42}H_{56}O_{15}$, was discovered by Nativelle in the leaves of the *Cnicus benedictus;* it is found also in the *Centaurea calcitrapa*, and in other composite plants. It forms transparent silky crystals, neutral, without smell, of very bitter taste, melting at a high temperature, but not subliming. Its solution turns the plane of polarisation to the right $[a]\ r = 130°68$. It is scarcely soluble in cold water, better in boiling, soluble in all proportions in alcohol and wood spirit, almost insoluble in ether. Cold sulphuric acid gives with cnicin a red solution, becoming violet on the addition of water, and yellow on the addition of ammonia. Cold concentrated hydrochloric acid dissolves it with the production of a green colour; on heating, brown drops separate, which solidify into a yellow resin.†

§ 83. *Daphnin*, $C_{31}H_{38}O_{19}$, a crystalline principle discovered by Vauquelin, 1817, in the bark of the *Daphne alpina*, L., and *D. mezereum*, L. It forms long rectangular prisms, or fine needles, and crystallises with 4 atoms of water. Its reaction is neutral, its taste bitter. When anhydrous it melts at about 200°C. to a colourless fluid, which again becomes crystalline on cooling; if the heat is continued, it sublimes as daphnetin, $C_{10}H_{14}O_9$. This substance presents itself in fine, colourless, rhombic prisms, melt-

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ing about 250°C.; it has a bitter taste, with a weak acid reaction, and is easily soluble in boiling water, with the production of a yellow colour; it dissolves also in boiling alcohol, but is very little soluble in ether.

Daphnin dissolves slightly in cold water, easily in hot; it is also very soluble in hot alcohol, but is not dissolved at all by ether. In solutions of the caustic and the carbonated alkalies it dissolves with the production of a yellow colour, and is also easily soluble in acetic acid. On boiling with a dilute acid, daphnin breaks up into daphnetin and sugar, and emulsin and fermentation with yeast have a similar effect. An aqueous solution of chloride of iron produces, when cold, a blue colour, and if the liquid is boiled, a dark yellow precipitate. Nitric acid colours it red.*

§ 84. *Gentianin*, $C_{14}H_{10}O_5$, discovered by Henry and Caventou in 1821, but first prepared pure by Trommsdorff, is found, like gentiopicrin, in the root of the *Gentiana lutea*, L. It forms long, pale-yellow, silky needles, without smell or taste, which may be sublimed above 300°C. without decomposition. Its solubility, according to Leconte, is as follows:—1 part requires of cold water 5000 parts, of boiling, 3850 parts; of cold absolute alcohol 455 parts, of boiling 62·5 parts; of cold ether 2000 parts, for solution. Concentrated sulphuric acid dissolves it with a yellow colour; on dilution with water it separates unchanged; on being boiled with dilute sulphuric acid there is no change. If treated with pure nitric acid (1·43 specific gravity), a dark-green solution is obtained, and on adding water carefully dinitro-gentianin, $C_{14}H_8(NO_2)_2O_5 + H_2O$, separates out as a green powder. If similarly treated with strong nitric acid, and subsequent addition of water to the solution, yellow microscopical prisms are separated, probably *trinitro-gentianin*. Gentianin reduces nitrate of silver.†

§ 85. *Gentiopicrin*, $C_{20}H_{30}O_{12}$, first prepared pure by Kromayer in 1862, is a glucoside found in the fresh root of the *Gentiana lutea*. It crystallises in colourless needles, with 1 atom of water of crystallisation. The crystals effloresce in the air, and lose

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their transparency, becoming white and opaque. The anhydrous crystals melt between 120° and 125°C. to a brown fluid, which coagulates amorphously, and at higher temperatures is fully destroyed. Water dissolves it easily, but it is insoluble in absolute alcohol and in ether, though, on the other hand, weak alcohol is an excellent solvent for it. One of the best tests for its presence is the action of concentrated sulphuric acid, giving in the cold a colourless solution, but producing with slight warming a carmine-red colour, and precipitating on the addition of water in grey flocks. It reduces an ammoniacal solution of silver nitrate, and on boiling with dilute sulphuric acid splits up into sugar and gentiogenin.

Gentiogenin, $C_{14}H_{16}O_5$, is an amorphous, yellow-brown powder, of neutral reaction and bitter taste, not easily soluble in cold water, but dissolving readily in alcohol and ether.*

§ 86. *Menyanthin*, $C_{30}H_{46}O_4$, a glucoside obtained pure by Ludwig and Kromayer in 1861, from the *Menyanthes trifoliata*, L. As hitherto prepared, menyanthin is an amorphous, terebinthinate mass, becoming slowly solid on drying over sulphuric acid. It has a neutral reaction, and its taste is strongly and purely bitter. It softens at 60° to 65°, and melts at 10° to 15° to a thin, clear fluid, which again solidifies to a hard transparent mass; by stronger heating it is entirely destroyed. Concentrated sulphuric acid gives with it a yellow-brown colour, which on standing becomes violet-red, and grey flocks are separated on the addition of water. By heating with dilute sulphuric acid it splits up into sugar and menyanthol.

Menyanthol is an oil having an acid reaction, and an odour like that of oil of almonds; it is changed by the air (as well as by melting with potash) into a crystalline acid capable of being sublimed.†

§ 87. *Quassiin*, $C_{10}H_{12}O_3$, a bitter principle, discovered in 1835 by Winckler, in the bark of the *Quassia amara*, L., and *Picræna excelsa*, L. It forms white, opaque, glittering crystals, without odour, and of extremely bitter taste. On heating, it melts and solidifies as a transparent yellow mass; at decomposition temperatures it burns like resin, if exposed to the air. Tannic acid precipitates it from an alcoholic solution in thick, white flocks; cold concentrated sulphuric acid dissolves it, without the pro-

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duction of colour; and on dilution with water it is apparently precipitated without change.*

§ 88. *The Ash of Beer.*—The ash of beer contains the mineral constituents that previously existed partly in the water, partly in the hop, and partly in the malt used. It would appear that the ferric oxide, a certain proportion of phosphoric acid, a small portion of the lime and magnesia, with a great part of the silica, remain undissolved, and do not pass into the beer; the rest are dissolved.

The following table gives the average composition of the beer ash of commerce:—

	Beer Ash.
Potash,	37·22
Soda,	8·04
Lime,	1·93
Magnesia,	5·51
Iron Oxide,	traces.
Sulphuric Acid,	1·44
Phosphoric Acid,	32·09
Chlorine,	2·91
Silica,	10·82

The table on next page may be also useful, showing analyses of ash by Walz and Dickson (*Dictionary of Chemistry, Arts, and Manufactures*, edited by Vincent).

§ 89. *Analysis of Beer.*—The ordinary full analysis of beer determines—

(1.) The alcohol.
(2.) The carbonic acid.
(3.) The volatile and fixed acids.
(4.) The percentage of malt extract, and, if necessary, its composition.
(5.) The hop resin and glycerine.
(6.) The nature of the bitter used.
(7.) The general composition of the ash, and especially its chlorides.

(1.) *The alcohol* is found most accurately by the distillation process described at p. 129, but it is often determined in the following manner:—Shake up the beer well in a flask, so as to deprive it of as much carbonic acid as possible, then take the specific gravity at 15·5°C., and boil a third of the beer away in an open beaker. To make up the boiled beer to exactly the

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ASH OF BEERS.

	London Beer.	Munich Beer.	Speyer Beer.	Scotch Ale, 14 Samples.	Scotch Porter, 2 Samples.	Dublin Porter, 2 Samples.	London Porter, 5 Samples.
Potash, ...	38·35	36·58	37·68	3·2 — 29·8	18·9 — 20·9	21·4 — 32·0	4·9 — 31·1
Soda, ...	7·68	9·03	6·59	20·9 — 38·5	33·8 — 38·8	24·0 — 42·7	21·8 — 50·8
Lime, ...	2·45	1·48	2·98	0·2 — 2·0	1·3 — 1·6	0·8 — 1·5	0·8 — 6·9
Magnesia, . . .	3·78	5·64	4·66	0·1 — 5·6	0·2 — 1·4	0·2 — 1·2	0·1 — 1·2
Sulphuric Acid, . .	1·36	1·68	2·56	1·6 — 19·2	2·2 — 6·4	2·8 — 10·1	1·6 — 12·2
Chlorine, . . .	2·75	3·14	2·14	4·3 — 18·25	7·4 — 11·4	6·9 — 10·1	6·5 — 14·5
Silica, ...	9·87	9·96	10·29	4·6 — 19·1	13·3 — 18·6	6·9 — 19·7	8·25 — 19·7
Phosphoric Acid, . .	33·76	31·69	33·10	6·0 — 25·7	12·2 — 18·8	7·9 — 20·0	9·3 — 20·6
	100·00	100·00	100·00				

original quantity again, take the specific gravity, and calculate as described at p. 130.

(2.) *The carbonic acid* which the beer holds dissolved is most readily estimated by placing 100 cc. (or any convenient quantity) in a flask, provided with a caoutchouc stopper, carrying a tube twice bent at right angles, which is connected with a smaller flask, containing strong ammonia water, into which the tube dips. This second flask must also carry a caoutchouc stopper, which should be doubly perforated, the one hole for the tube already mentioned, the other provided with a short, wide tube, packed with glass wool moistened with ammonia water. The beer must first be gently warmed and ultimately boiled, when the whole of the carbonic acid is absorbed by the ammonia. A sufficient quantity of a solution of calcium chloride is now added, the liquid boiled until all free ammonia is expelled, and the calcium carbonate thrown on a filter and washed. Lastly, the washed calcium carbonate is dissolved in either standard or decinormal acid, according to the quantity, a little cochineal solution is added, and the acid titrated back. 2 cc. of decinormal acid equal 10 mgrms. of carbonate of lime, or 4·4 mgrms. of CO_2. This simple process is applicable to all liquids from which carbonic anhydride can be expelled by boiling.

(3.) *Volatile and Fixed Acids.*—The acetic acid is obtained by distilling the beer to dryness, and estimating the acidity of the filtrate by decinormal solution of soda. Should the residue in the flask or retort be still acid, a little water should be added, and the distillation again continued to dryness; any acid now remaining is certain to be a fixed acid, probably lactic. It may be estimated by titration, and returned as lactic. The equivalent of dry lactic acid is 90; hence 1 cc. of d. n. soda = 9 mgrms. of lactic acid. Should it be specially necessary to determine the percentage of lactic acid, a sufficient quantity of beer—say 300 cc.—is taken, evaporated to a small bulk, diluted with a little water, filtered, and mixed with a little sulphuric acid; pure carbonate of baryta is now added, and the whole warmed on the water-bath for some time. The liquid is then freed from the precipitate of sulphate of baryta by filtration, and the precipitate well washed with hot water. This filtrate is evaporated to a syrup, and treated, when cold, in a tube or separating-funnel with a mixture of one part of sulphuric acid, one of water, one of alcohol, and ten of ether; the ethereal layer is separated in the usual way, and evaporated. The lactic acid thus obtained is still impure, and it is best to dissolve in water, saturate with freshly-precipitated carbonate of zinc, and estimate as zinc lactate, the latter containing 54·49 per cent. of anhydrous lactic acid. In most cases, however, the error will not be great, if the total acidity of the beer is taken directly without distillation, and returned as acetic acid.

(4.) *The Malt Extract.*—The extract of beer can be determined by evaporating down a carefully measured quantity, and weighing the dry residue. In order to do this with any approach to accuracy, the smallest possible quantity should be taken—5 cc. or 5 grms. is quite sufficient. This small quantity, spread out as a thin film on the bottom of a tolerably capacious platinum dish, can be thoroughly dried over the water-bath in two or three hours, while if such quantities as 25 cc., 50 cc., or 100 cc. are taken, to get the extract completely dry is very tedious, and usually requires a higher temperature than 100°C. It is, however, found in practice much more convenient to dispense with this drying altogether, the alcohol and carbonic acid being driven off, as before described, the beer made up to its first bulk, the specific gravity taken, and the amount of malt extract determined by the aid of the following tables. If the beer has been distilled, the residue in the retort or flask can be made up to the original bulk, brought to the proper temperature, and treated as just described.

The alcoholic strength, the acetic acid, and the amount of malt extract being known, the analyst can now give a fairly approximate estimate of the amount of malt originally used in the brewing of the beer. To do this it is necessary to calculate the "original gravity" of the beer. The specific gravity of the alcoholic distillate (or, if an indirect process has been used, the specific gravity of the alcoholic strength) subtracted from 1000, gives a number called the "spirit indication." The degrees of gravity lost are then ascertained by the aid of the following tables, using the first if the beer has been distilled, and the second if the evaporating process has been used. The degrees of gravity thus found are added to the specific gravity of the boiled beer, and the number thus obtained is called "the original gravity of the wort." On reference to Table I., the amount of malt extract is determined, which corresponds to this original gravity.

TABLE I.—SPECIFIC GRAVITY AND STRENGTH OF MALT EXTRACT.

Specific Gravity.	Malt Extract.	Specific Gravity.	Malt Extract.	Specific Gravity.	Malt Extract.	Specific Gravity.	Malt Extract.
1,0000	0,000	1,0047	1,175	1,0094	2,350	1,0141	3,525
1,0001	025	48	200	95	375	142	550
2	050	49	225	96	400	143	575
3	075	1,0050	250	97	425	144	600
4	100	51	275	98	450	145	625
5	125	52	300	99	475	146	650
6	150	53	325	1,0100	500	147	675
7	175	54	350	101	525	148	700
8	200	55	375	102	550	149	725
9	225	56	400	103	575	1,0150	750
1,0010	250	57	425	104	600	151	775
11	275	58	450	105	625	152	800
12	300	59	475	106	650	153	825
13	325	1,0060	500	107	675	154	850
14	350	61	525	108	700	155	875
15	375	62	550	109	725	156	900
16	400	63	575	1,0110	750	157	925
17	425	64	600	111	775	158	955
18	450	65	625	112	800	159	970
19	475	66	650	113	825	1,0160	4,000
1,0020	500	67	675	114	850	161	025
21	525	68	700	115	875	162	050
22	550	69	725	116	900	163	075
23	575	1,0070	750	117	925	164	100
24	600	71	775	118	950	165	125
25	625	72	800	119	975	166	150
26	650	73	825	1,0120	3,000	167	175
27	675	74	850	121	025	168	200
28	700	75	875	122	050	169	225
29	725	76	900	123	075	1,0170	250
1,0030	750	77	925	124	100	171	275
31	775	78	950	125	125	172	300
32	800	79	975	126	150	173	325
33	825	1,0080	2,000	127	175	174	350
34	850	81	025	128	200	175	375
35	875	82	050	129	225	176	400
36	900	83	075	1,0130	250	177	425
37	925	84	100	131	275	178	450
38	950	85	125	132	300	179	475
39	975	86	150	133	325	1,0180	500
1,0040	1,000	87	175	134	350	181	525
41	025	88	200	135	375	182	550
42	050	89	225	136	400	183	575
43	075	1,0090	250	137	425	184	600
44	100	91	275	138	450	185	625
45	125	92	300	139	475	186	650
46	150	93	325	1,0140	500	187	675

TABLE I.—*continued.*

Specific Gravity.	Malt Extract.	Specific Gravity.	Malt Extract.	Specific Gravity.	Malt Extract.	Specific Gravity.	Malt Extract.
1,0188	4,700	1,0235	5,875	1,0282	7,024	1,0329	8,170
189	725	236	900	283	048	1,0330	195
1,0190	750	237	925	284	073	331	219
191	775	238	950	285	097	332	244
192	800	239	975	286	122	333	260
193	825	1,0240	6,000	287	146	334	292
194	850	241	024	288	170	335	316
195	875	242	048	289	195	336	341
196	900	243	073	1,0290	219	337	365
197	925	244	097	291	244	338	389
198	950	245	122	292	268	339	413
199	975	246	146	293	292	1,0340	438
1,0200	5,000	247	170	294	316	341	463
201	025	248	195	295	341	342	488
202	050	249	219	296	365	343	512
203	075	1,0250	244	297	389	344	536
204	100	251	268	298	413	345	560
205	125	252	292	299	438	346	584
206	150	253	316	1,0300	463	347	609
207	175	254	341	301	488	348	633
208	200	255	365	302	512	349	657
209	225	256	389	303	536	1,0350	681
1,0210	250	257	413	304	560	351	706
211	275	258	438	305	584	352	731
212	300	259	463	306	609	353	756
213	325	1,0260	488	307	633	354	780
214	350	261	512	308	657	355	804
215	375	262	536	309	681	356	828
216	400	263	560	1,0310	706	357	853
217	425	264	584	311	731	358	877
218	450	265	609	312	756	359	901
219	475	266	633	313	780	1,0360	925
1,0220	500	267	657	314	804	361	950
221	525	268	681	315	828	362	975
222	550	269	706	316	853	363	9,000
223	575	1,0270	731	317	877	364	024
224	600	271	756	318	901	365	048
225	625	272	780	319	925	366	073
226	650	273	804	1,0320	950	367	097
227	675	274	828	321	975	368	122
228	700	275	853	322	8,000	369	146
229	725	276	877	323	024	1,0370	170
1,0230	750	277	901	324	048	371	195
231	775	278	925	325	073	372	219
232	800	279	950	326	097	373	244
233	825	1,0280	975	327	122	374	268
234	850	281	7,000	328	146	375	292

TABLE I.—*continued.*

Specific Gravity.	Malt Extract.	Specific Gravity.	Malt Extract.	Specific Gravity.	Malt Extract.	Specific Gravity.	Malt Extract,
1,0376	9,316	1,0423	10,452	1,0470	11,571	1,0517	12,690
377	341	424	476	471	595	518	714
378	365	425	500	472	619	519	738
379	389	426	523	473	642	1,0520	761
1,0380	413	427	547	474	666	521	785
381	438	428	571	475	690	522	809
382	463	429	595	476	714	523	833
383	488	1,0430	619	477	738	524	857
384	512	431	642	478	761	525	881
385	536	432	666	479	785	526	904
386	560	433	690	1,0480	809	527	928
387	584	434	714	481	833	528	952
388	609	435	738	482	857	529	976
389	633	436	761	483	881	1,0530	13,000
1,0390	657	437	785	484	904	531	023
391	681	438	809	485	928	532	047
392	706	439	833	486	952	533	071
393	731	1,0440	857	487	986	534	095
394	756	441	881	488	12,000	535	119
395	780	442	904	489	023	536	142
396	804	443	928	1,0490	047	537	166
397	828	444	952	491	071	538	190
398	853	445	976	492	095	539	214
399	877	446	11,000	493	119	1,0540	238
1,0400	901	447	023	494	142	541	261
401	925	448	047	495	166	542	285
402	950	449	071	496	190	543	309
403	975	1,0450	095	497	214	544	333
404	10,000	451	119	498	238	545	357
405	023	452	142	499	261	546	381
406	047	453	166	1,0500	285	547	405
407	071	454	190	501	309	548	428
408	095	455	214	502	333	549	452
409	119	456	238	503	357	1,0550	476
1,0410	142	457	261	504	381	551	500
411	166	458	285	505	404	552	523
412	190	459	309	506	428	553	547
413	214	1,0460	333	507	452	554	571
414	238	461	357	508	476	555	595
415	261	462	381	509	500	556	619
416	285	463	404	1,0510	523	557	642
417	309	464	428	511	547	558	666
418	333	465	452	512	571	559	690
419	357	466	476	513	595	1,0560	714
1,0420	381	467	500	514	619	561	738
421	404	468	523	515	642	562	761
422	428	469	547	516	666	563	785

TABLE I.—*continued.*

Specific Gravity.	Malt Extract.	Specific Gravity.	Malt Extract.	Specific Gravity.	Malt Extract.	Specific Gravity.	Malt Extract.
1,0564	13,809	1,0604	14,761	1,0643	15,674	1,0682	16,581
565	833	605	785	644	697	683	604
566	857	606	809	645	721	684	627
567	881	607	833	646	744	685	650
568	904	608	857	647	767	686	674
569	928	609	881	648	790	687	697
1,0570	952	1,0610	904	649	814	688	721
571	976	611	928	1,0650	837	689	744
572	14,000	612	952	651	860	1,0690	767
573	023	613	976	652	883	691	790
574	047	614	15,000	653	907	692	814
575	071	615	023	654	930	693	837
576	095	616	046	655	953	694	860
577	119	617	070	656	976	695	883
578	142	618	093	657	16,000	696	907
579	166	619	116	658	023	697	930
1,0580	190	1,0620	139	659	046	698	953
581	214	621	162	1,0660	070	699	976
582	238	622	186	661	093	1,0700	17,000
583	261	623	209	662	116	701	022
584	285	624	232	663	139	702	045
585	309	625	255	664	162	703	067
586	333	626	278	665	186	704	090
587	357	627	302	666	209	705	113
588	381	628	325	667	232	706	136
589	404	629	348	668	255	707	158
1,0590	428	1,0630	371	669	278	708	181
591	452	631	395	1,0670	302	709	204
592	476	632	418	671	325	1,0710	227
593	500	633	441	672	348	711	250
594	523	634	464	673	371	712	272
595	547	635	488	674	395	713	295
596	571	636	511	675	418	714	318
597	595	637	534	676	441	715	340
598	619	638	557	677	464	716	363
599	642	639	581	678	488	717	386
1,0600	666	1,0640	604	679	511	718	409
601	690	641	627	1,0680	534	719	431
602	714	642	650	681	557	1,0720	17,454
603	738						

TABLE II.—FOR USE IF THE DISTILLATION PROCESS HAS BEEN USED.

Degrees of Spirit Indication.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	0·0	0·3	0·6	0·9	1·2	1·5	1·8	2·1	2·4	2·7
1	3·0	3·3	3·7	4·1	4·4	4·8	5·1	5·5	5·9	6·2
2	6·6	7·0	7·4	7·8	8·2	8·6	9·0	9·4	9·8	10·2
3	10·7	11·1	11·5	12·0	12·4	12·9	13·3	13·8	14·2	14·7
4	15·1	15·5	16·0	16·4	16·8	17·3	17·7	18·2	18·6	19·1
5	19·5	19·9	20·4	20·9	21·3	21·8	22·2	22·7	23·1	23·6
6	24·1	24·6	25·0	25·5	26·0	26·4	26·9	27·4	27·8	28·3
7	28·8	29·2	29·7	30·2	30·7	31·2	31·7	32·2	32·7	33·2
8	33·7	34·3	34·8	35·4	35·9	36·5	37·0	37·5	38·0	38·6
9	39·1	39·7	40·2	40·7	41·2	41·7	42·2	42·7	43·2	43·7
10	44·2	44·7	45·1	45·6	46·0	46·5	47·0	47·5	48·0	48·5
11	49·0	49·6	50·1	50·6	51·2	51·7	52·2	52·7	53·3	53·8
12	54·3	54·9	55·4	55·9	56·4	56·9	57·4	57·9	58·4	58·9
13	59·6	60·0	60·5	61·1	61·6	62·2	62·7	63·3	63·8	64·3
14	64·8	65·4	65·9	66·5	67·1	67·6	68·2	68·7	69·3	69·9
15	70·5	...	...	...	...	...	...	...	...	...

TABLE III.—FOR USE IF THE EVAPORATION PROCESS IS ADOPTED.

Degrees of Spirit Indication.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	0	0·3	0·7	1·0	1·4	1·7	2·1	2·4	2·8	3·1
1	3·5	3·8	4·2	4·6	5·0	5·4	5·8	6·2	6·6	7·0
2	7·4	7·8	8·2	8·7	9·1	9·5	9·9	10·3	10·7	11·1
3	11·5	11·9	12·4	12·8	13·2	13·6	14·0	14·4	14·8	15·3
4	15·8	16·2	16·6	17·0	17·4	17·9	18·4	18·8	19·3	19·8
5	20·3	20·7	21·2	21·6	22·1	22·5	23·0	23·4	23·9	24·3
6	24·8	25·2	25·6	26·1	26·6	27·0	27·5	28·6	28·5	29·0
7	29·5	30·0	30·4	30·9	31·3	31·8	32·3	32·8	33·3	33·8
8	34·3	34·9	35·5	36·0	36·6	37·1	37·7	38·3	38·8	39·4
9	40·0	40·5	41·0	41·5	42·0	42·5	43·0	43·5	44·0	44·4
10	44·9	45·4	46·0	46·5	47·1	47·6	48·2	48·7	49·3	49·3
11	50·3	50·9	51·4	51·9	52·5	53·0	53·5	54·0	54·5	55·0
12	55·6	56·2	56·7	57·3	57·8	58·3	58·9	59·4	59·9	60·5
13	61·0	61·6	62·1	62·7	63·2	63·8	64·3	64·9	65·4	66·0
14	66·5	67·0	67·6	68·1	68·7	69·2	69·8	70·4	70·9	71·4
15	72·0	...	...	...	...	...	...	...	...	...

From the malt extract the amount of malt used is calculated, 32·0 of malt equalling 21·0 of extract; or, instead of referring to the malt extract tables, 1000 may be subtracted from the original gravity, and the remainder multiplied by ·0025, which will equal the total amount of malt extract per gallon in pounds weight.

EXAMPLES.

(1.) An ordinary Mild Ale.

	1000·0
Specific gravity of alcoholic distillate =	993·6
Spirit indication, . .	6·4

This spirit indication on reference to Table II., equals 26·0.

Gravity of boiled beer . . . =	1·014·2
Add, ...	26·0
Original gravity, . .	1·040·2

Now, in reference to Table I., 1·0402 correspond to 9·950 parts of extract in 100, or ·9950 lbs. per gallon.

Or, if from the original gravity . .	1·0402
Be subtracted	1·000
And the number obtained . . .	402
Be multiplied by	·0025
The product equals	1·005

which does not materially differ from the amount obtained from the tables.

(2.) A beer, by the evaporation process, indicated 9·7 per cent. of alcohol. On reference to the specific gravity tables (p. 125), the specific gravity corresponding to this strength is ·9896.

	1000·0
	989·6
Spirit indication . . =	10·4

This, according to Table III., corresponds to 47·1.

The gravity of the boiled beer was .	1016·2
Add	47·1
Original gravity . .	1063·3

corresponding, according to the tables, to 1·5441 lbs. of malt extract to the gallon. The amount of malt used in the two examples is found thus—

$$(1.)\quad \frac{\cdot 9901 \times 320}{210} = 1\cdot 508 \text{ lbs. of malt to the gallon.}$$

$$(2.)\quad \frac{1\cdot 5441 \times 320}{210} = 2\cdot 3526 \text{ lbs. of malt to the gallon.}$$

If the beer should have a somewhat large proportion of acetic acid (as in old and hard beers), it will be necessary to take into account the loss of gravity by acetic acid. This complicates the calculation, and is only occasionally required.

The loss of gravity by acetic acid is obtained by the use of the following table (see Table IV). Let us suppose ·36 per cent. of acetic acid to have been found in Example 1; from this subtract ·10 per cent., the amount which may be taken as incidental to healthy fermentation, and allowed for in the table. Thus,

Total acetic acid present, ...	·36
Deduct	·10
Acetic acid to be taken account of, . .	·26

This ·26, according to the table, equals ·34, the number to be added to the spirit indication.

Spirit indication from alcohol, . . .	6·4
,, ,, from acetic acid, . .	·34
Total spirit indication, . .	6·74

The rest of the calculation is as before.

It may be desirable to examine the malt extract further, and specially with a view to ascertaining whether grape sugar has been used in place of malt, or not. This may be done, according to Haarstick, by taking advantage of the fact that most, perhaps all, of the grape sugars of commerce contain Béchamp's amylin, a substance of great rotatory power, and one, moreover, not destroyed by fermentation.

The samples of beer were examined by Haarstick as follows:—1 litre of beer was evaporated to a syrup, to which alcohol of 90 per cent. was added, drop by drop, from a burette with constant agitation, until a volume of about 300 cc. had been used. The separation of dextrine was completed with 95 per cent. alcohol, until the filtrate did not show the least turbidity when mixed with an equal bulk of 95 per cent. alcohol. The mixture

TABLE IV.—FOR ASCERTAINING THE VALUE OF THE ACETIC ACID.

Excess per cent. of Acetic Acid in the Beer.	Corresponding Degrees of Spirit Indication.									
	·00	·01	·02	·03	·04	·05	·06	·07	·08	·09
·0	...	·02	·04	·06	·07	·08	·09	·11	·12	·13
·1	·14	·15	·17	·18	·19	·21	·22	·23	·24	·26
·2	·27	·28	·29	·31	·32	·33	·34	·35	·37	·38
·3	·39	·40	·42	·43	·44	·46	·47	·48	·49	·51
·4	·52	·53	·55	·56	·57	·59	·60	·61	·62	·64
·5	·65	·66	·67	·69	·70	·71	·72	·73	·75	·76
·6	·77	·78	·80	·81	·82	·84	·85	·86	·87	·89
·7	·90	·91	·93	·94	·95	·97	·98	·99	1·00	1·02
·8	1·03	1·04	1·05	1·07	1·08	1·09	1·10	1·11	1·13	1·14
·9	1·15	1·16	1·18	1·19	1·21	1·22	1·23	1·25	1·26	1·28
1·0	1·29	1·31	1·33	1·35	1·36	1·37	1·38	1·40	1·41	1·42

was then left at rest for twelve hours, filtered, and the greater part of the alcohol distilled off. The remainder was evaporated to dryness on a water-bath, the solid portion dissolved in distilled water, and the solution diluted to a litre, and fermented with yeast at 20°, until all the sugar had been destroyed. The fermentation was completed on the fourth day, and the result of the process was, that beers prepared without grape sugar gave a solution of no rotatory power, while those prepared with grape sugar turned the plane of polarisation 2·0° to 3·4° to the right, as observed in Hoppe's scale.

(5.) *The Hop Resin and Glycerine.*—Griessmayer[*] estimates the hop resin and glycerine by concentrating the beer to one-third of its bulk, and shaking it up with petroleum ether; this, on separation and evaporation, leaves the hop resin. The liquid now freed from hop constituents is made alkaline by baryta water, or, better, by barium alcoholate, and shaken up several times with a mixture of two parts of alcohol and three of ether; the latter, on being separated and evaporated in the usual way, leaves the glycerine.

(6.) *The Nature of the Bitter used.*—This is the most difficult part of the investigation, and requires a very considerable amount of practical knowledge. In most cases it is sufficient to use some of the special processes hereafter described, and restrict the inquiry to proving the absence of picric acid, of picrotoxin, and of any other specially noxious substance which may be suspected. Should, however, the analyst desire to examine the beer generally for various organic principles, the elaborate process worked out by Dragendorff (see *Index*) is decidedly the best. About 600 to 1000 cc. of the beer are evaporated to a syrupy consistence, and sufficient strong alcohol is added to precipitate the dextrine. The whole is filtered, and after standing some hours, the filtrate acidulated with sulphuric acid, and shaken up successively with petroleum ether, benzine, chloroform, and (if salicin be sought) amylic alcohol.

Or, the beer may be precipitated with acetate of lead, filtered, the excess of lead thrown out by sulphuric acid, and treated with the solvents as described. If inquiry be made as to the nature of the residue left by these different solvents in beer simply made from hops and malt, it appears that—

(1.) The *petroleum ether* extracts—

(*a.*) An amorphous, slightly bitter substance, soluble in ether and alcohol, and partially soluble in water; this is derived from both hops and malt;

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[*] *Deut. Chem. Ges. Ber.*, xi. 292, 293.

(*b.*) A substance precipitable by basic acetate of lead; and one

(*c.*) Becoming red by Fröhde's reagent; both derived from the hop.

(*d.*) A substance derived from the hop alone, becoming red with sulphuric acid and sugar.

(2.) *Benzine* extracts the same substances, and in addition—

(*e.*) A substance derived from the hop, which precipitates tannin;

(*f.*) A substance derived from the malt, becoming dark-brown on the addition of sulphuric acid.

(3.) *Chloroform* extracts (*a.*), (*b.*), and (*e.*), and also (*f.*), a substance partly precipitated by potassium iodide and phosphomolybdic acid;

(*g.*) A substance reducing ammoniacal solution of silver nitrate;

(*h.*) A substance crystallisable from ether. All of these are derived from the malt.

The normal reactions of the substances being known, the following scheme will be found useful, always bearing in mind that few chemists, should they obtain any of the reactions mentioned, would conclude from this alone that the substance is actually present. The reaction would be considered as an *indication only to be supplemented by other evidence.* Unless this is remembered and acted upon, the most unfortunate errors may be committed by the inexperienced. The beer is most conveniently shaken up with the solvent in the flask figured p. 74; the ether and benzine will float at the top, the chloroform will gravitate to the bottom; in either case separation is tolerably easy. It will, however, be found a good plan, in the first place, to separate the liquids rather roughly—*i.e.*, to draw off the ether, benzine, and chloroform layers, with some of the adjacent liquid, to wash this in the same flask with water, to withdraw the solvent from the water as completely as possible by the separating flask, and if this (as sometimes happens) is not very feasible, to evaporate the impure liquid to dryness in a water-bath, and exhaust the residue with the original solvent. The latter may be, in the first place, concentrated over hot water, and then portions distributed between two or three watch-glasses, and evaporated to dryness.

I. THE ACID SOLUTION.

Petroleum Residue.

(*a.*) It is amorphous, colours sulphuric acid first brown, then violet, and finally red violet. *Traces of Absynthin.*

(*b.*) It is amorphous, colourless, having a hot taste, reddening the skin, and colouring sulphuric acid brownish-red. *Traces of Capsicin.*

(*c.*) It is amorphous, green, is coloured by sulphuric acid and sugar, and gives no precipitate with ammoniacal silver solution. *Resin of the Juniper berries.*

(*d.*) It is crystalline, yellow, and becomes blood-red on warming with cyanide of potash. *Picric acid.*

Benzine Residue.

A.—Crystalline residue.

It is not bitter, caustic potash colours it purple-red, sulphuric acid first red, then orange. *Aloetin.*

B.—Amorphous residue.

a.—The residue soluble in water; does not trouble or reduce gold chloride solution in the cold.

(*a.*) Tannin does not precipitate the solution in water residue sharp tasting.

1. Sulphuric acid colours it red brown. *Capsicin.*
2. Sulphuric acid colours it brown. *Daphne bitter.*

(*b.*) Tannin precipitates the solution in water, the residue somewhat bitter.

I. Basic lead acetate causes a weak turbidity, sulphuric acid and sugar scarcely redden.

1. Iron chloride colours the watery solution, on warming, brownish-green; taste slightly bitter. *Gentian bitter.*
2. Iron chloride colours the watery solution brown; taste peculiar, almost unsupportably bitter. *Quassiin.*

II. Basic lead acetate strongly precipitates, sulphuric acid and sugar colour it gradually a beautiful cherry-red; taste bitterish. *Cnicin.*

b.—The residue soluble in water; does not trouble solution of gold chloride in the cold, but reduces it on warming.

(*a.*) Tannin causes a faint turbidity in the watery solution, ammoniacal silver solution is not reduced. Heated with diluted sulphuric acid, an ericinol smell is developed. Fröhde's reagent colours it black-brown, sulphuric acid and sugar beautiful red. *Ledum bitter.*

(*b.*) Tannin precipitates the watery solution, ammoniacal solution of silver is reduced. Heated with diluted sulphuric acid, a weak smell of menyanthol is developed. *Trifolium bitter.*

c.—The residue soluble in water, precipitates in the cold chloride of gold, but does not reduce it upon warming. Heated with diluted sulphuric acid (1 of acid to 5 of water), it gives a weak benzoic acid smell. *Centaurea bitter.*

d.—The residue soluble in water, precipitates in the cold chloride of gold, which it reduces upon warming. Sulphuric acid dissolves it first brown, then gradually violet, after the addition of water quickly a beautiful violet. Hydrochloric acid of 1·135 specific gravity colours it first green, then a beautiful blue. *Absynthin.*

CHLOROFORM RESIDUE.

A.—Chloride of gold does not precipitate, and is not reduced.

a.—Tannin gives no precipitate, the residue has a pungent taste. Sulphuric acid colours it dark-brown red, it reddens the skin. *Capsicin.*

b.—Tannin precipitates.

(*a.*) Basic lead acetate gives a decided precipitate. Heated with diluted sulphuric acid it is first troubled, then it becomes brown-red, and develops a weak smell of benzoic acid. *Cnicin.*

(*b.*) Basic acetate of lead gives little or no precipitate.

I. *Sulphuric acid colours brown.*

1. Residue bitter.

aa. Strongly bitter. *Quassiin.*

bb. Residue somewhat bitter. *Gentian bitter.*

2. Residue tasting pungent. *Daphne bitter.*

II. *Sulphuric acid colours but slightly yellow, or not at all.* *Colocynth bitter.*

B.—Chloride of gold does not precipitate in the cold, but is reduced in the warm.

a.—Tannin does not precipitate.

1. Intoxicates fish, tastes bitter. *Picrotoxin.*

2. Is tasteless or slightly bitter, caustic potash colours it red-brown. *Constituent of Aloes.*

b.—Tannin precipitates.

(*a.*) Ammonia solution of silver is reduced. Heated with dilute sulphuric acid, as well as with Fröhde's reagent, there is a strong smell of menyanthol. *Menyanthin.*

(*b.*) Ammoniacal solution of silver is not reduced. With concentrated sulphuric acid and sugar, after long standing, a splendid carmine red develops; heated with diluted sulphuric acid, as well as with Fröhde's reagent, an intense ericolin smell is developed. *Ericolin.*

C.—Chloride of gold precipitates in the cold, and is not reduced by the application of heat. Nitric acid colours violet. *Colchicine.*

Heated with sulphuric acid, an odour somewhat like trifolium is developed, then the solution becomes red-brown, and the smell similar to benzoic acid. *Centaurea bitter.*

D.—Chloride of gold precipitates in the cold and reduces in the warm. Sulphuric acid colours brown, then the solution becomes gradually dirty violet. *Wormwood bitter.*

If necessary to go farther, search may be made for the alkaloids by rendering the liquid weakly alkaline by carbonate of soda or by ammonia.

II. THE ALKALINE SOLUTION.

I. RESIDUE OBTAINED BY SHAKING UP WITH BENZINE.

(1.) It dilates the pupil of a cat.

(*a.*) Platin chloride does not precipitate the aqueous solution. A solution in sulphuric acid gives on warming a peculiar smell. *Atropine.*

(*b.*) Platin chloride precipitates. *Hyoscyamin.*

(2.) It does not dilate the pupil.

(*a.*) The sulphuric acid solution gives with oxide of cerium or bichromate of potash a blue colour. *Strychnine.*

(*b.*) The sulphuric acid solution gives a red colour with nitric acid solution. *Brucin.*

II. RESIDUE OBTAINED FROM SHAKING IT UP WITH AMYLIC ALCOHOL.—(This need only be done if salicin be suspected.) On warming with sulphuric acid and bichromate of potash, a smell of salicylic acid is developed. *Salicin.*

A very good process, only aiming at the identification of a few principles, is recommended by Enders ; it is as follows :—

The beer is evaporated to a syrup, the dextrine separated by mixing it with three or four times its volume of alcohol, the liquid filtered, and the sugar precipitated by ether. The filtered ether-alcohol solution is evaporated, the residue dissolved in alcohol, mixed with water, and precipitated by means of acetate of lead. The precipitate is filtered, the filtrate put on one side. The washed precipitate is then separated from lead by SH_2, the lead sulphide filtered and washed with alcohol, and the filtrate (as well as the alcohol washing of lead sulphide) evaporated together. The residue is dissolved in chloroform, and the solution warmed with water until all the chloroform is driven off. The *hop bitter*, which remains insoluble, is filtered off, and the filtrate evaporated to dryness. The lupulin in it should taste bitter and have an acid reaction; it is soluble in alcohol, ether, and chloroform; is not precipitated when in solution in weak spirit by tannic acid, but is precipitated by acetate of lead. Ammoniacal solution of silver is not reduced by it. The filtrate of the first lead precipitate is freed from lead by SH_2, the lead sulphide filtered off and washed with hot water, the excess of SH_2 driven off by warming, and then tannin added to the filtrate. If no precipitate occurs, absynthin, quassiin, and menyanthin are absent. Any precipitate is filtered, dried with carbonate of lead, boiled with alcohol, evaporated, and, lastly, treated with ether. The latter agent dissolves absynthin, which is also soluble in alcohol, and in much hot water; from the latter solution it is precipitated by tannic acid, but not by lead acetate; it is soluble in sulphuric acid, and on careful addition of water to this solution a *violet-blue colour* is produced. Absynthin reduces an ammoniacal solution of silver. Ether leaves menyanthin and quassiin undissolved. Both are soluble in alcohol, and the latter behaves towards tannic acid and acetate of lead like absynthin. Menyanthin reduces ammoniacal solution of silver, quassiin does not.

Picrotoxin* may be specially tested for by some one of the following processes :—

Herapath's Process.—Mix the beer with acetate of lead in excess; filter, and transmit sulphuretted hydrogen through the filtrate. Filter again, concentrate the filtrate, and treat it with animal charcoal, which has the property of absorbing the picrotoxin. Wash the animal charcoal, dry at 212°F., and boil with alcohol; this dissolves out the picrotoxin, from which it may be obtained in tufts of crystals.

Depaire's Process.—Mix with 1 litre of beer finely powdered rock salt (which throws down the resinous and extractive matters), and shake the liquid with ether; an impure picrotoxin crystallines on separating the ether and evaporating it: or the beer may be simply acidulated with hydrochloric acid and agitated with ether, the ether separated and evaporated as before.

Schmidt's Process.—1. Evaporate the beer in a water-bath to a syrupy consistence, mix it with tepid water till it is perfectly liquid, so as to bring the volume to a third of the liquid used; heat

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* Picrotoxin is fully described in the second portion of this work. (See *Index*.

and shake with animal charcoal. Let it stand several hours, filter, and heat slightly; precipitate by basic acetate of lead, and again filter. The liquid should now be of a yellow wine-colour; if not, re-filter through animal charcoal. Add from 5 to 10 cubic centimetres of amylic alcohol, and shake briskly several times at intervals; after twenty-four hours the amylic alcohol, containing the greater part of the picrotoxin, collects on the surface. The remainder is subsequently eliminated by fresh treatment with amylic alcohol. Collect the limpid layers of this alcohol, and leave the rest to evaporate spontaneously. On the sides of the capsule a yellowish ring forms, and this contains the picrotoxin mixed with resinous substances.

2. *Isolation of the Picrotoxin.*—First, dissolve the resinous product in weak alcohol, evaporate to dryness, recover by a little boiling water containing a small quantity of H_2SO_4, boil to expel any volatile matter, add a little animal black to eliminate all extractive and resinous matter, and, lastly, filter. Evaporate inodorous liquid, and when a fresh bitter taste is developed, shake up with ether; this redissolves the picrotoxin, and collects into a distinct layer on the surface of the liquid. Treat again with ether, and the whole of the picrotoxin is eliminated; finally, the ethereal liquids are mixed, a little alcohol is added, and the whole is evaporated. The white or yellowish ring formed consists of picrotoxin, which then has only to be dissolved in alcohol to furnish the immediate principle in the form of well-defined crystals. These crystals, however, will not be obtained unless the solution be quite free from resinous substances; if not free, and if, for instance, the ethereal solution is of a yellow colour, it must be recovered with water and treated by charcoal, as above described.

Schmidt was able to detect by this process 0·04 of picrotoxin in a bottle of beer which had been adulterated with eight grains of Indian berry.*

Dragendorff has modified the method of Schmidt, by adding an excess of acetate of lead, precipitating this by SH_2, and with the lead sulphide getting rid of some colouring matter. The sulphide of lead may be washed and dried, and then boiled with ether, to recover any picrotoxin which has gone down with it.

By the following process the animal charcoal may be dispensed with altogether:—The beer is first evaporated to a syrup, then 4 to 5 vols. of alcohol of 90 to 94 per cent. are added. After maceration for twenty-four hours at a low temperature, the alcoholic extract is evaporated, the residue acidified with diluted

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* M. Schmidt, *Chem. News*, March 12, 1864, p. 122.

SO_4H_2, and treated several times with amyl alcohol or chloroform; but previously to this the fluid should be shaken up several times with benzine, which does not remove any picrotoxin. The rest of the process is similar to that of Schmidt.

§ 90. *Special Tests for Picric Acid.*—If picric acid alone should be sought for, the quickest way is to agitate the beer in the separating flask, described p. 74, with half its volume of amylic alcohol. On separating and evaporating the alcohol, if picric acid be present a yellow residue will be left, and can be identified by the action of potassic cyanide, as described below. It will not be worth while testing specially for picric acid if the beer, on being treated with subacetate of lead, loses nearly all its bitter taste; but if, on the contrary, it continues bitter, picric acid, or some other bitter not precipitable by acetate of lead, is present.

Another test frequently proposed for picric acid is to soak some pure wool in the beer, first gently warmed over the water-bath and acidulated with HCl, when the picric acid will stain the wool yellow. The wool thus stained may next be warmed with aqueous ammonia, the liquid filtered, concentrated to a small bulk, and a few drops of a solution of potassic cyanide added, when, if picric acid be present, a red colour (potassium isopurpurate) will be produced. Picric acid may be also recognised, if present, by spectroscopic examination : the dried extract is exhausted either by amyl alcohol or ether, and the solution examined, comparing any spectrum obtained with that given by a solution of the acid.

§ 91. *Salicylic Acid* is used occasionally in brewing. If the beer, concentrated to a small bulk, is acidified with hydrochloric acid and shaken up with ether, the latter solvent will extract the organic acid, and it may be identified by the colour it gives with ferric chloride, and by its physical properties.

§ 92. (7.) *The Ash.*—The analysis of the ash of beer differs in no degree from an analysis of ash in general, and is carried out in the principles detailed, pp. 4-7. The substances to which the analyst's attention is specially directed are—the amount of salt, the presence or absence of iron (often added in the form of sulphate to porter), alum, and lead.* Of these the only one necessary to allude to further here is the salt.

The salt in beer is determined with sufficient accuracy by charring in a platinum dish the extract from 70 cc. of beer (it is not well to burn to a complete ash, for in so doing there is always a considerable loss of chlorides). The charred mass is boiled up with successive portions of distilled water, filtered, and

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* Many firms now use large copper coolers, but no injurious amount of copper appears to have been as yet detected in beers.

the filtrate made up to a known bulk, from which a convenient fractional portion is taken, and titrated with a solution of nitrate of silver (4·79 grms. to the litre), 1 cc = 1 mgrm. of chlorine, using as an indicator neutral chromate of potash. The chlorine found is calculated and expressed as common salt, every mgrm. of salt, when 70 cc. are taken, being equivalent to 1 grain in the gallon. Mr. Griffin's convenient measure, the septem or one-hundredth of a gallon, may, of course, be used, and grains instead of grammes—each grain measure of nitrate of silver being made to correspond to one-tenth of a grain of common salt per gallon. Should the amount thus found indicate more than 50 or 60 grains per gallon, a second determination of chlorine should be made by the more accurate gravimetric method of weighing the chlorine as chloride of silver. It may even be advisable to make a qualitative and quantitative examination of the soluble portion of the ash; for, if called as a witness, the analyst must be prepared to state positively the amount of chloride of *sodium;* nor can he well do this simply from the soluble chlorine, for that may represent other chlorides besides sodium. The writer has as yet seen no reason to change the limit usually fixed of 50 grains of salt per gallon—anything over should be returned as adulterated.

The amount of salt derived from the hops and malt can approximatively be determined, as Mr. Gatehouse has shown,—* First, for the malt: by taking the original gravity, as before described (p.157), obtaining thence the quantity of malt originally used in the beer, and reckoning the malt to contain ·025 per cent. of salt (and certainly no malt will be found to exceed this). Then, for the hops: the possible maximum of salt in hops is ·345 per cent. The quantity used in brewing being seldom, if ever, more than 20 lbs. per quarter of malt for bitter beer, and generally less than half this amount for strong beer, and this weight of malt giving at least 72 gallons, the salt derived from the hops cannot in bitter beer exceed 6·7 grains, and in strong beer 3·35 grains per gallon.

Thus, to take the first example (p. 157), the original gravity of which was 1·0402, corresponding by the tables to 9·950 lbs. of malt extract per gallon. Since 320 of malt equal 210 of extract, and there are 7000 grains in the pound—

$$\frac{9{\cdot}950 \times 320 \times {\cdot}025 \times 7000}{210 \times 100}$$

= 2·65 grains of salt per gallon as the possible maximum from

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* The Amount of Salt in Beer. *Analyst*, No. 20, 1877.

the malt, the beer in question not being a bitter beer. Add to this 3·35 as possible maximum amount of salt from the hops—

2·65	from malt,
3·35	from hops,
6·00	salt possible from both malt and hops.

Now, if the composition of the water used in brewing be known, one-third more than the actual quantity of salt in the water present may be added to the number representing the salt from the hops and malt, and the data are then complete for the analyst to form his judgment. The amount of salt in the water used will, however, only occasionally be known.

The numbers used in the above calculations being constants, the process is shortened by simply deducting 1000 from the original gravity, and multiplying by ·066 the result, giving the salt in grains per gallon. Thus, taking an example from Mr. Gatehouse's excellent paper:—*

		Per cent.
Beer found to contain alcohol,		5·2
Malt extract,		7·38
Specific gravity of alcohol equals ·9911; the spirit indication therefore equals 8·9, giving an original gravity,		38·6
Gravity of boiled beer,		1030.6
Original gravity of wort,		1069·2
Salt due to malt alone	69·2 × 066 =	4·567
Salt due to hops,		3·350
Salt due to water, unknown.		
Possible total due to malt and hops,		7·917
The amount of salt actually found being 8·55		

It has been suggested that the concrete sugar† so largely and legitimately used by brewers, sometimes contains a considerable

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* *Op. cit.*

† It is possible for arsenic to be found in beers manufactured from glucose, for in certain kinds of the latter arsenic is occasionally discovered, the substance probably having been introduced by the use of an arsenical sulphuric acid in the process of manufacture. The darker in colour the glucose, the more likely is it to be arsenical; thus, M. Ritter found—

	Grm.	
In White Glucose,	0·0105	arsenic per kilogramme.
„ Yellow „	0·0170	„ „
„ Black „	0·1094	„ „

Clouet, in the examination of a very large number of arsenical glucoses, ound as a minimum 0·0025 grm., as a maximum 0·0070 grm., and as a nean 0·0051 grm., metallic arsenic per kilogramme. (T. Clouet, Du glucose rsenical. *Ann. d'Hygiène Publique*, xlix., Jan., 1878.)

amount of chlorides. If samples are found, occasionally, with more than a trace of chloride, it is because the sugar itself has been prepared for the brewers; nor can there be any difference whether the brewer adds the salt as salt, or first mixes it with sugar. However, analytical proof of sufficient chlorides *naturally* present in concrete sugar, to raise the salt in beer made from ordinary materials to over 50 grains per gallon, is wanting; and all the evidence in its favour has been derived from loose statements.

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IV.—WINE.

§ 93. *Constituents of Wine.*—Wine is the fermented juice of the grape, with such additions only as are essential to the stability, or keeping of the liquid (*Dupré*). The principal constituents of wine are enumerated in the table on pp. 172, 173.* The remaining constituents are glycerine, formic, succinic, malic, propionic, and other organic acids, compound ethers, one or more colouring matters, traces of tannin, albuminous substances, and so-called extractives.

§ 94. *Adulterations of Wine.*—The adulterations of wine bought at a fair price from respectable firms do not appear numerous; but, on the other hand, low-priced wines (especially such as are retailed to the poor, and are supplied to workhouses) are often of extremely bad quality, and sometimes entirely fictitious.† Thus, Ports are fortified with brandy, coloured by various ingredients, plastered with gypsum and mixed with inferior wines; salt of tartar and œnanthic ether are often added to give an appearance of age, alum to increase the brilliancy of hue; and occasionally (as an impurity, or as an unintentional adulterant) lead and other metals are detected. Sherries, again, are plastered and fortified to a considerable extent, and Clarets, Madeira, and Champagnes are all subject to somewhat similar sophistications.

§ 95. *Analysis of Wine.*—A complete analysis of wine embraces the following:—

1. Determination of alcohol.
2. Percentage of solid residue.
3. Estimation of succinic acid and glycerine.
4. ,, volatile and fixed acids.
5. ,, ethers.
6. ,, sugar.
7. ,, albuminous matters and ammonia.
8. ,, tannin.
9. Examination of the colouring matters.
10. Estimation and analysis of ash.

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* Drawn up by Dr. Dupré. *Proceedings of Society of Public Analysts*, i., 1876, p. 77.

† Dr. A. Cameron has found in Port wine supplied to Irish workhouses 12 per cent. of solid residue, one-half of which was composed of grape sugar. According to Maumené, the Russian military pharmacopeia contains the following receipt for making a Port wine:—Cider, 3 kilogrms.; kino, ·008 kilogrm.; Old Hock, with cider, 3 kilogrms.; brandy, 1 kilogrm.; nitric ether, alcoholised, ·008.

WEIGHT IN GRAMMES OF SOME OF THE CHIEF
VOLUMES) OF THE UNDER-

Particulars of Wines analysed.			Specific Gravity.	Absolute Alcohol.	Free Fixed Acid as Tartaric Acid.	Free Volatile Acid as Acetic Acid.	Total Free Acid as Tartaric Acid.	Real Tartaric Acid.
	Doz.	Vintage.						
Hock, white,	30s.	1862	993·43	95·6	3·48	0·57	4·20	...
,, ,,	40s.	1859	993·48	92·0	4·20	1·14	5·62	2·550
,, ,,	120s.	1857	992·81	104·4	4·31	0·93	5·37	0·675
Claret, .	15s.	1865	995·58	85·3	4·24	1·47	6·08	0·675
,, .	48s.	1865	995·03	120·0	4·24	1·74	6·41	1·875
,, .	66s.	1861	994·73	85·3	3·23	1·80	5·48	1·838
Hungarian, red,	21s.	...	992·07	113·6	3·56	2·49	6·68	0·600
,, white,	34s.	...	992·88	95·4	5·33	1·47	7·16	0·675
,, ,,	42s.	...	993·09	94·9	4·74	1·80	6·99	0·375
Greek wine, ,,	20s.	...	994·56	107·2	3·41	3·00	7·16	0·675
,, ,, ,,	28s.	...	992·25	124·5	4·54	1·68	6·64	...
,, ,, ,,	36s.	...	993·17	138·9	2·33	1·77	4·54	0·300
Sherry, .	22s.	1865	994·09	172·0	2·70	1·53	4·61	0·187
,,	high price,	1860	997·93	178·1	3·08	1·68	5·18	0·262
,,	,, ,,	1857	998·30	184·0	2·81	1·62	4·84	0·150
Madeira, E.I.,	60s.	...	993·94	177·5	3·26	1·68	5·36	0·300
,, .	high price,	1812	994·15	180·0	4·20	3·27	8·25	...
Port, .	32s.	1864	1004·76	185·6	3·08	0·84	4·13	0·225
,,	high price,	1854	997·42	175·3	3·54	1·07	4·88	0·225
,,	,, ,,	1842	986·95	182·6	2·66	1·08	4·01	0·150
Marsala, .	16s.	old	996·65	167·1	1·88	1·11	3·26	...
,, .	20s.	very old	999·65	168·9	2·25	1·38	3·98	0·150

nstituents of 1 Litre (1000 cc. or 1000
ntioned Wines (Dupré).

	Grape and Fruit Sugar.	Total amount of Ash.	Carbonate of Potassium.	Sulphates and Chlorides.	Phosphate and Carbonate of Calcium.	Total amount of Phosphoric Acid.	Alcohol in Fixed Ethers.	Alcohol in Volatile Ethers.	Total Alcohol in Ethers found.	Total Alcohol in Ethers calculated.	Proportion per cent. of Alcohol found to Alcohol calculated.
·63	...	1·95	0·58	0·76	0·60	0·32	0·132	0·230	0·362	0·360	100·5
·55	0·12	1·70	0·07	0·78	0·85	0·30	0·199	0·239	0·438	0·458	95·7
·60	1·12	1·45	0·14	0·46	0·85	0·35	0·225	0·239	0·464	0·493	94·3
·40	4·31	2·08	0·66	0·95	0·48	0·33	0·155	0·197	0·352	0·476	74·0
·33	2·04	2·25	0·66	1·05	0·55	0·30	0·186	0·248	0·430	0·581	74·6
·00	0·95	2·00	0·38	0·99	0·63	0·30	0·166	0·216	0·382	0·429	88·8
·85	1·47	1·85	0·41	0·91	0·53	0·35	0·151	0·358	0·509	0·656	77·6
·20	0·61	1·75	0·14	0·81	0·80	0·25	0·186	0·271	0·457	0·613	74·5
·13	0·24	1·88	0·12	0·90	0·85	0·25	0·162	0·273	0·435	0·596	73·0
·30	2·00	2·25	0·07	1·18	1·00	0·25	0·224	0·214	0·438	0·690	63·6
·42	1·12	3·05	0·41	2·01	0·62	0·25	0·384	0·179	0·563	0·707	79·6
·50	3·64	3·75	0·21	2·49	1·05	0·45	0·245	1·207	0·453	0·530	85·1
·00	25·65	4·50	0·07	3·63	0·80	0·18	0·206	0·216	0·422	0·639	66·1
·50	29·70	5·50	0·18	4·41	0·95	0·25	0·290	0·391	0·681	0·749	90·8
·44	35·10	5·13	0·07	4·18	0·88	0·13	0·262	0·469	0·731	0·722	101·2
·47	20·80	3·90	0·27	2·52	1·10	0·42	0·305	0·382	0·687	0·774	88·7
·41	16·29	3·59	0·17	1·93	1·49	0·50	0·460	0·773	1·233	1·207	102·1
·57	43·31	2·48	0·48	1·34	0·65	0·35	0·302	0·128	0·430	0·620	69·4
·90	22·84	2·58	0·66	1·37	0·55	0·33	0·351	0·220	0·571	0·697	84·9
·01	10·10	2·10	0·69	0·86	0·45	0·33	0·283	0·331	0·614	0·595	103·2
·83	32·40	2·25	0·21	1·54	0·50	0·18	0·256	0·189	0·445	0·447	99·3
·48	37·60	3·13	0·55	1·92	0·65	0·23	0·333	0·216	0·549	0·550	99·8

1. *Alcohol.*—Wines, in regard to their alcoholic content, may be divided into two classes—viz., *natural wines,* the strength of which has not been increased by the addition of spirit; and *fortified wines,* such as those of Spain and Portugal, which absolutely *require* the addition of a certain amount of spirit to preserve them. Natural wines contain as a minimum 6 per cent., and as a maximum a little over 12 per cent., of absolute alcohol by weight. The percentage of alcohol in fortified wines depends, of course, entirely on the operator; it appears to range usually from 12 to 22 per cent. by weight. The alcohol is returned as ethylic, but there are always traces of the higher homologous alcohols—*e.g.*, propylic, butylic, and amylic. If the analyst desire to estimate the different proportions of these, a large quantity of wine must be distilled, the distillate re-distilled in fractions, and ultimately oxidised into the corresponding acids, the latter being more easily separated than the alcohols. The method of determining the alcohol in wine differs in no essential feature from the processes described at p. 129.

2. *The Solid Residue.*—The dry extract from pure natural wines is from 1·5 to 3 per cent.; the presence of sugar in fortified wines may raise the extract to 6·8 or 10 per cent. The solid residue may be taken by simply evaporating 10 cc. to dryness, which can be done rapidly, without any decomposition of the solids, by using a large flat platinum dish, and thus spreading the 10 cc. out in a thin layer. This method is, however, somewhat inconvenient, and causes a loss of glycerine; therefore, the indirect process for beer, given at p. 130, may be employed instead, wine extract being considered equal in density to malt extract.* But in wines containing much ash (since the mineral constituents of the latter seriously affect specific gravity, containing in a given specific gravity about twice as much substance in solution as a sugar solution of the same gravity), it is necessary to subtract from the percentage of extract thus estimated, the percentage of ash found in the same wine; or if the amount of extract without the ash is required, twice the percentage of ash has to be subtracted from the percentage found. Duprè and Thudichum give the following examples:

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* A. Gautier (*Annales d'Hygiène Publique,* t. xlvii., 118, 1877) has recommended in all cases, the evaporation of 5 cc. of wine on a watch-glass, in a vacuum, without the application of artificial heat. This method takes from two to six days, according to the temperature, for completion, so that it is scarcely applicable for technical purposes; but it is evident that a heat of 30°C., whilst greatly expediting the process, would in no way impair its accuracy.

Ronenthaler, 1859 (£15 Ohm).

	Per cent.
Specific gravity of de-alcoholised wine, ...	1008·01
Percentage of sugar (see table, p. 151), . . .	2·041
Percentage of ash found, ...	0·170
Total solid constituents, ...	1·871
To find total solids minus ash, subtract again . .	0·170
Total solid constituents, ...	1·701

Sherry, 1865.

Specific gravity of de-alcoholised wine, ...	1017·56
Percentage of sugar from specific gravity (see table, p. 151), ...	4·467
Percentage of ash found, ...	0·515
	3·952
Subtract ash, ...	0·515
Total solids constituents, ...	3·437

The extract and amount of alcohol being known, it is in certain instances possible to detect the *watering* of wine; although such a diagnosis can only be made when the analyst is intimately acquainted with the kind of wine under examination, and in some cases with the characters of the particular vintage. The Bordeaux wines, according to Girardin and Pressier, give almost always the same amount of extract, varying only within the limits of 20 to 20·8 grms. the litre; and the proportion of alcohol also is fairly constant, viz., from ·005 to ·015, the mean being ·010 per litre. From these data they calculated the amount of genuine wine present in any samples. Thus, supposing the extract in a Bordeaux wine to be 14·5, then

$$\frac{1000 \times 14\cdot5}{20\cdot0} = x, \text{ or } 725\cdot00$$

i.e., the litre contains 725 cc. of wine, the rest being alcohol and water. To know the quantity of alcohol added, it is necessary to ascertain how much the 72·5 parts of wine contain of absolute alcohol:—

$$100 : 10 :: 72\cdot50 : x$$

$$x = 7\cdot25.$$

If the absolute alcohol is found, for example, to be 0·11, then, subtracting 7·25 from 11, it is supposed that 3·75 of alcohol has been added.

That this process, as applied to the Bordeaux wines, is in the main correct, is supported by the fact that the Rouen wine-merchants have frequently paid duty on the excess of alcohol, &c., which Girardin and Pressier found in their wines.*

3. *Estimation of Succinic Acid and Glycerine.*—Half a litre to a litre of wine is decolorised with animal charcoal, filtered, and the charcoal well washed with water; the filtrate and washings are then evaporated down in the water-bath, and the drying finished in a vacuum. The residue, when dry, is treated with a mixture of one part of strong alcohol and 2½ parts of rectified ether. The latter is driven off by floating the dish in warm water, and the whole evaporated again on a water-bath. The residue is now neutralised with lime-water, which combines with the succinic acid, and forms succinate of calcium. The glycerine is dissolved out by alcohol and ether, and weighed either directly or by loss. The succinate of calcium remaining behind is impure, and should be well washed with spirit before weighing. Every 100 parts of calcic succinate equals 75·64 of succinic acid ($H_2C_4H_4O_4$); and since Pasteur has shown that 112·8 parts of grape sugar (107 of cane) yield about 3·6 of glycerine and 0·6 parts of succinic acid, it follows that in a natural wine the glycerine would amount to about one-fourteenth part of the alcohol present. It is also evident that a careful determination of the glycerine in a natural wine, and its proportion to the alcohol present, combined with the percentage of dry extract, will greatly help to solve the question as to whether water has, or has not, been added.

4. *Acids in Wine.*—All wines possess an acid reaction, due to acids which are conveniently divided into *volatile* and *fixed.* The volatile acid of sound wine, according to Pasteur, never exceeds 2 to 3 decigrms. per litre; in wines a little deteriorated much higher values may be found. Dr. Dupré puts the amount of volatile acid, expressed in terms of acetic acid, as 0·3 to 0·6 per cent. by weight in volume. About one-fourth of the total acidity in white natural wines should be due to volatile acids, and in red and fortified wines the volatile should not amount to more than about one-third of the total acidity. The non-volatile acids appear to be chiefly malic and tartaric (sometimes part of the tartaric being replaced by succinic); the former, according to Dupré, predominating in pure natural wines, and largely so in fortified liquors; whilst in plastered wines it is often present to the total exclusion of tartaric acid.

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* Soubeiran; *op. cit.*

The principal volatile acid is acetic, but it is always accompanied by formic, propionic, butyric, and other members of the series. The general method of estimation is to take from 10 to 20 cc. of the wine suitably diluted, and titrate with d. n. soda, using tincture of logwood as an indicator, the result being the *total acidity*. On now evaporating the wine on the water-bath to a syrupy extract, diluting and again titrating, the loss of acidity corresponds to the *volatile acid*, the latter being expressed in terms of acetic acid, the non-volatile as tartaric acid.

A very different and highly ingenious method of diagnosing and estimating volatile acids has been proposed by E. Duclaux. As this is applicable not to wines alone, but also to beers, sour milk, and in fact to all liquids developing acids of the acetic series, it will be described at length.

Estimation of Volatile Acids by the Method of E. Duclaux.—The process depends upon the regularity with which the different volatile acids distil. If in a retort of from 250 to 300 cc. be introduced 110 cc. of a mixture of acetic acid and water, and 100 cc. (that is $\frac{10}{11}$) be distilled, the quantity of acid which has come over is found to be 80 per cent. of the whole, or very nearly so. Further, if the 100 cc. be successively titrated, in every 10 cc. the successive numbers thus obtained (indicating the proportion of acid passing in these equal volumes) are the same, whatever may be the quantity of acid operated upon, provided the acid is pure; but it *varies very sensibly should there exist even feeble traces of the fatty acids.* It is then sufficient to study the course of the distillation of the acids in order to know their nature. In a general way, foreign matters exercise only a slight influence; but it is always best to eliminate them as far as possible by operating on a first or second distillation.

For the titration, M. Duclaux uses lime-water standardised by sulphuric acid. The size of the retort does not exercise the great influence which might be expected; but it is well to use one of about 300 cc. capacity, for the experiments on which the tables are founded were conducted in retorts which varied from between 250 to 350 cc. The slight difference in the results from a retort of 800 cc., as compared with one of 300 cc., may be gathered from the following table, which represents the distillation of 110 cc. of a dilute acetic acid.

The two series of numbers, A and B, are obtained by titrating each 10 cc., until 100 cc. have come over; the acetic acid in the A series being worked out in percentage of the whole acid found n the entire distillate, and that in the B series in the quantity of acid existing in the retort.

ESTIMATION OF ACETIC ACID.

	Retort of 800 cc.		Retort of 300 cc.	
	A.	B.	A.	B.
1.	7·2	5·5	7·4	5·9
2.	14·7	11·2	15·3	12·2
3.	22·7	16·9	23·5	18·7
4.	31·2	23·7	32·1	25.6
5.	40·2	30·6	41·2	32·9
6.	49·9	32·9	50·9	40·6
7.	60·2	45·8	61·3	48·9
8.	71·9	54·7	72·5	57·9
9.	85·3	64·8	85·2	67·9
10.	100·0	75·9	100·0	79·8

It would appear that the quantity of acid which vaporises at a given moment, is proportional to that which exists in that same moment in the heated liquid; and when the quantities of water distilled increase in an arithmetical progression, the quantities of acid increase in a geometrical progression.

Let y be the quantity of acid existing at any moment in the volume λ of the liquid remaining in the retort; the quantity of acid dy, which will volatilise with the volume $d\lambda$ of the liquid will be evidently first proportional to $d\lambda$ and then to y. Thus—

$$dy = xyd\lambda$$

whence may be educed (calling y the total weight of acid existing at the commencement in the volume L of the liquid),

$$ly - l\mathrm{Y} = l\frac{y}{\mathrm{Y}} = -\mathrm{K}\,(\mathrm{L} - \lambda)$$

giving

$$y = \mathrm{Y}e^{-x\,(\mathrm{L} - \lambda)}$$

Let a be called the quantity $\mathrm{Y} - y$ of acid which distils when

$$\mathrm{L} - \lambda = l = \mathrm{L}\frac{l}{\mathrm{L}}$$

has been removed from the liquid; then we have

$$a = \mathrm{Y}\left(1 - e^{\frac{-x\mathrm{L}l}{\mathrm{L}}}\right) = \mathrm{Y}\left(1 - e^{-m\frac{l}{\mathrm{L}}}\right)$$

The following table shows that acetic acid obeys this law; the figures in the second column are calculated by the formula

$$a = 102\left(e^{\frac{0{\cdot}0615l}{11}} - 1\right)$$

	a found.	*a* calculated.		*a* found.	*a* calculated.
1.	5·9	5·2	6.	40·5	40·5
2.	12.2	12·2	7.	48·7	48·7
3.	18·8	18·7	8.	57·9	57·8
4.	25·6	25·4	9.	67·7	66·6
5.	32·9	32·7	10.	79·8	76·3

Butyric acid obeys the same law; but it has a method of distillation in some sense inverse to that of acetic acid, and passes in greater abundance in the first portions. The following table gives the experimental and the calculated numbers found in distilling a mixture of butyric acid and water, in the manner before described.

The formula for calculation is—

$$147{\cdot}5\left(1 - e^{\frac{-0131l}{11}}\right)$$

	A.	B.	B calculated.
1.	16·8	16·1	16·8
2.	31·9	31·1	31·4
3.	45·4	44·3	44·4
4.	57·7	56·1	55·8
5.	67·9	66·2	66·1
6.	77·2	75·3	75·1
7.	85·0	82·9	83·2
8.	91·4	89·2	90·3
9.	96·4	94·0	96·6
10.	100·0	97·5	102·4

It is thus seen that the numbers are very different from those of acetic acid, and that nearly the whole of the acid is obtained.

Metacetic acid.—Formula for calculation—

$$m = 357\left(1 - e^{\frac{-0{\cdot}033l}{11}}\right)$$

	A.	B.	B calculated.
1.	11·3	10·5	10·8
2.	22·8	21·1	21·4
3.	34·0	31·5	31·5
4.	44·6	41·4	41·4
5.	55·3	51·3	51·1
6.	65·4	60·6	60·3
7.	74·7	69·5	69·3
8.	84·0	78·0	78·0
9.	92·5	85·8	86·5
10.	100·0	92·8	95·3

Valerianic Acid.—

	B.		B.
1. . .	24·5	6. . .	85·7
2. . .	44·5	7. . .	89·7
3. . .	59·5	8. . .	92·8
4. . .	71·3	9. . .	95·4
5. . .	79·5	10. . .	96·9

Formic Acid.—

$$f=30{\cdot}2\left(e\frac{0{\cdot}1194l}{11}-1\right)$$

	A.	B.	B calculated.
1. . .	5·5	3·5	3·5
2. . .	11·9	7·6	7·3
3. . .	18·5	11·8	11·6
4. . .	25·7	16·3	16·3
5. . .	34·0	21·6	21·6
6. . .	43·1	27·3	27·5
7. . .	53·1	33·7	34·1
8. . .	65·2	41·4	41·4
9. . .	79·8	50·7	49·7
10. . .	100·0	63·5	58·8

Passing from the single acids to the behaviour of mixed volatile acids, it is found that each acid distils in the same proportion as if it existed individually in the liquid. Thus, Duclaux found a mixture of equivalent quantities of butyric and acetic acids behave as follows :—

	A.	B.	B calculated.
1. . .	12·7	11·4	11·4
2. . .	24·8	22·1	22·1
3. . .	35·9	32·0	32·1
4. . .	46·4	41·4	41·6
5. . .	56·3	50·3	50·5
6. . .	65·7	58·6	58·9
7. . .	74·5	66·4	67·0
8. . .	83·1	74·1	74·4
9. . .	91·4	81·6	82·2
10. . .	100·0	89·3	90·0

A mixture of 2 of butyric to 1 of acetic acid, when distilled, gave the following series :—

	A.	B.	B calculated.
1. . .	14·0	12·8	12·8
2. . .	26·1	25·1	24·8
3. . .	35·5	36·2	35·9
4. . .	50·6	46·4	46·1
5. . .	60·6	55·5	55·3
6. . .	69·8	63·9	63·9
7. . .	78·4	71·7	71·8
8. . .	86·0	78·7	79·1
9. . .	93·1	85·2	85·6
10. . .	100·0	91·6	92·0

Hence it follows, that it is possible to obtain from fractional distillation a knowledge of the nature and quantity of the volatile acids existing in the liquid. Theoretically, ten different equations might be educed, and ten volatile acids determined; but in practice this is not possible; and should there be even three volatile acids, it is better to make a new distillation after a partial saturation, which will almost completely arrest one of the acids, and let only two pass into the receiver.

As an example of the method of calculation, the following table gives the results of the distillation of a certain wine, A and B having the same signification as before:—

	A.	B.	M.	N.
1. . .	9·6	8·6	1·2	3·2
2. . .	19·2	17·3	1·1	3·1
3. . .	28·8	26·0	1·0	3·0
4. . .	38·4	34·7	1·0	2·8
5. . .	48·2	43·5	1·0	2·5
6. . .	57·9	52·2	1·0	2·5
7. . .	67·8	61·1	1·0	2·2
8. . .	77·9	70·2	1·0	2·1
9. . .	88·5	79·9	1·0	1·6
10. . .	100·0	90·2	1·1	1·3

From the B series there should be acetic acid mixed with either metacetic or butyric acids. In order to know which of the two is present, a double calculation is necessary. Turning to the tables giving the numbers obtained for the first 10 cc. in the distillation of pure acetic and pure butyric acids (p. 179), we find for the former 5·9, for the latter 10·5; then, by the following equation, the numbers in the column M are obtained—

$$8{\cdot}6x + y = 5{\cdot}9x + 10{\cdot}5y$$

$$\frac{y}{x} = 1{\cdot}2$$

Analagous calculations give for $\frac{y}{x}$ the series of numbers contained in N, if butyric acid is thought to be present; it now becomes evident, that the mixture was formed of equivalent parts of acetic and metacetic acid. In order, however, to avoid long calculations, it is better to make tables of reference with various mixtures, so that in most experiments the quantities will fall somewhere near those given in the tables, and at all events be a guide. In the following tables A and B have the same signification as before, and 110 cc. are supposed to be distilled in the manner described, in a retort of about 300 cc. capacity:—

A MIXTURE OF ACETIC (a), AND BUTYRIC ACID (b).

/	$\frac{a}{b} = \frac{56\frac{1}{2}}{28} = \frac{20}{1}$		$\frac{a}{b} = \frac{10}{1}$		$\frac{a}{b} = \frac{840}{168} = \frac{5}{1}$		$\frac{a}{b} = \frac{4}{1}$		$\frac{a}{b} = \frac{2}{1}$		$\frac{a}{b} = \frac{34}{35} = \frac{1}{1}$		$\frac{a}{b} = \frac{796}{582} = \frac{1}{2}$		$\frac{a}{b} = \frac{1}{4}$	
	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.
1. .	7·9	6·4	8·6	7·0	9·5	7·9	9·8	8·2	11·3	9·6	12·7	11·4	14·0	12·8	15·5	14·5
2. .	16·3	13·2	17·4	14·2	19·0	15·8	19·5	16·2	22·0	18·9	24·8	22·1	26·1	25·1	29·5	27·7
3. .	24·8	20·1	26·2	21·4	28·3	23·6	29·1	24·2	32·4	27·8	35·9	32·0	39·5	36·2	42·2	39·5
4. .	33·6	27·2	35·2	28·8	37·7	31·4	38·5	32·1	42·3	36·3	46·4	41·4	50·6	46·4	53·6	51·2
5. .	42·7	34·5	44·5	36·3	47·1	39·2	47·8	39·8	52·2	44·7	56·3	50·3	60·6	55·5	63·9	59·9
6. .	52·2	42·2	54·1	44·1	56·6	46·1	57·5	47·8	61·4	52·7	65·7	58·6	69·8	63·9	73·1	68·6
7. .	62·2	50·4	64·1	52·3	66·3	55·3	67·0	55·7	70·7	60·6	74·5	66·4	78·4	71·7	81·2	76·2
8. .	73·1	59·2	74·8	61·1	76·5	63·8	77·0	64·1	79·9	68·5	83·1	74·1	86·0	78·7	88·3	82·8
9. .	85·4	69·2	86·4	70·6	87·4	72·9	87·9	73·1	89·4	76·7	91·4	81·6	93·1	85·2	94·5	88·6
10. .	100·0	81·0	100·	81·7	100·	83·4	100·	83·3	100·	85·8	100·	89·3	100·	91·6	100·	93·8

Mixtures of Acetic Acid (*a*) and Metacetic Acid (*m*).

	$\frac{a}{m}=\frac{668}{326}=\frac{2}{1}$		$\frac{a}{m}=\frac{334}{326}=\frac{1}{1}$	
	A.	B.	A.	B.
1. . .	9·1	7·7	9·7	8·5
2. . .	18·4	15·6	19·4	17·0
3. . .	27·8	23·6	29·2	25·6
4. . .	37·3	31·6	38·9	34·1
5. . .	46·9	39·8	48·6	42·7
6. . .	56·6	48·0	58·6	51·4
7. . .	66·6	56·5	68·5	60·1
8. . .	77·0	65·2	78·6	68·9
9. . .	88·0	74·6	89·1	78·2
10. . .	100·0	84·8	100·0	87·7

Mixtures of Acetic Acid (*a*), or of Butyric Acid (*b*), with Valerianic Acid (*v*).

	$\frac{a}{v}=\frac{593}{118}=\frac{5}{1}$		$\frac{a}{v}=\frac{296}{236}=\frac{5}{4}$		$\frac{b}{v}=\frac{291}{236}=\frac{5}{4}$	
	A.	B.	A.	B.	A.	B.
1. . .	11·1	9·1	16·3	14·3	20·6	20·0
2. . .	20·8	17·2	30·3	26·5	38·3	37·0
3. . .	30·5	25·1	42·4	37·0	52·9	51·0
4. . .	39·9	32·8	52·5	45·9	64·6	62·4
5. . .	48·9	40·3	61·3	53·6	74·5	71·9
6. . .	57·9	47·7	69·3	60·5	82·1	79·3
7. . .	67·2	55·4	76·6	66·9	88·2	85·2
8. . .	77·0	63·4	84·0	73·4	93·2	90·0
9. . .	87·5	72·2	91·5	80·0	96·9	93·3
10. . .	100·0	82·4	100·0	87·4	100·0	96·8

It now only remains to apply the preceding principles to the examination of wines. 275, or 550, or 825 cc., according as the wine is more or less rich in alcohol, is agitated strongly (or a current of air passed through the liquid), in order to free it from carbonic acid gas. It is next distilled to ten-elevenths, air drawn through the apparatus, and the distillate titrated by lime-water. A slight excess of lime-water is next added, and the

MIXTURES OF ACETIC ACID (a) WITH FORMIC ACID (f).

	$\frac{a}{f} = \frac{593}{293} = \frac{2}{1}$		$\frac{a}{f} = \frac{296}{293} = \frac{1}{1}$		$\frac{a}{f} = \frac{296}{586} = \frac{1}{2}$	
	A.	B.	A.	B.	A.	B.
1. . .	6·6	4·9	6·1	4·3	6·0	4·1
2. . .	14·0	10·4	13·5	9·5	13·2	9·2
3. . .	22·1	16·3	21·1	14·8	20·6	14·3
4. . .	30·2	22·3	28·9	20·3	28·6	19·9
5. . .	39·1	28·9	37·8	26·6	37·1	25·7
6. . .	48·5	35·9	43·8	33·0	46·4	32·2
7. . .	59·2	43·8	57·2	40·3	56·5	39·3
8. . .	70·6	52·3	68·9	48·5	68·4	47·5
9. . .	83·8	62·0	82·7	58·2	81·9	56·9
10. . .	100·0	74·0	100·0	70·4	100·0	69·4

liquid is concentrated by evaporation to about 250 cc., in order to get rid of the alcohol; 1 grm. of glycerine is now added, and sufficient tartaric acid, to put the fatty acids at liberty.

The tartrate of lime is allowed to crystallise, and the liquid decanted and made up with the washing water to 275 cc., after having added sufficient tartaric acid to ensure that on completion of the distillation, the residue will be nearly as acid as at the end of the first operation—1 grm. of tartaric acid per litre suffices for this. The liquid is now distilled anew to ten-elevenths, and the whole distillate titrated; the relation between the quantity of lime-water necessary now, and that of the first saturation, will serve to show the quantity of volatile acid existing in the wine in question.

This new liquid is submitted to the same operations as before, adding nothing save the quantity of tartaric acid exactly necessary. The acid liquid is made up to 165 cc., of which 150 cc. are distilled over, 50 cc. out of the 150 cc. are titrated, the remaining 100 are made up to 110 cc. with water, and submitted to fractional distillation, titrating every 10 cc. of the distillate. The numbers found will conduct directly, by a simple calculation, to the knowledge of the quantity and nature of the volatile acids in the wine. Thus, taking a wine, the results of the distillation of which are given in a tabular form at p. 181:—

275 cc. of this wine were distilled to 250 cc.; these 250 cc. required for neutralisation 316 cc. of lime-water of 30·6 [*i.e.*, 30·6 cc. = 0·075 acid acetic]; the second distillation has given 83·2 per cent. of the acid employed. Hence, for 275 cc.—

$$316 \text{ cc.} \times \frac{100}{83\cdot2} = 379 \text{ cc. of lime-water.}$$

The third and last distillation showed in the liquid equal parts of acetic and metacetic acid; the proportions in which these acids pass over are, as has been shown, $\frac{93}{80}$; denoting the proportion in which they exist in the wine by $\frac{y}{x}$

$$\left(\frac{0\cdot93}{0\cdot80}\right)^3 \frac{x}{y} = \frac{100x}{66y} = \frac{1}{1}$$

There were then present in the wine, 100 of acetic acid against 66 of propionic acid. In dividing the volume of lime-water used—viz., 1378 cc.—in proportional parts to 100 and 66, and valuing the corresponding quantities of the two acids, it is found that 1 litre of the wine contained 1·960 of acetic, and 1·810 grm. of metacetic acid.

In order to discover, by this method, valerianic acid, which, it would appear, exists in many sound wines (in about the proportion of 6 mgrms. per litre), it is necessary to distil a considerable quantity of wine, and then to saturate the distillate to nine-tenths or nineteen-twentieths. In this way, acetic and valerianic acid pass almost alone into the receiver. For instance, 7·7 litres of the wine alluded to before (p. 181), were distilled, and 10 grms. of lime salts obtained; sulphuric acid was added, representing nearly one-fortieth of the lime salt, and then the partially-decomposed salt distilled, when the following numbers were obtained :—

	A.	B.	$\frac{a}{v}$
1.	10·5	8·7	6·1
2.	20·5	16·9	6·1
3.	29·3	24·1	6·8
4.	38·1	31·4	6·9
5.	46·8	38·6	7·2
6.	55·6	45·9	7·5
7.	64·8	53·4	7·4
8.	75·2	62·0	7·5
9.	86·6	71·4	6·5
10.	100·0	82·4	6·0

The numbers in the columns A and B correspond in no way to mixtures of acetic acid with butyric or propionic. With valerianic acid, on the contrary, there is a relation constant enough, as the fourth column shows, the slight irregularities arising probably from a trace of butyric acid.

Estimation of Tartaric Acid and Bitartrate of Potash.—This is best estimated by the method suggested by Berthelot :—20 cc. of wine are mixed with 100 cc. of equal volumes of alcohol and ether in a well-stoppered flask. The same process is employed to another 20 cc., but with the addition of potash in sufficient quantity to neutralise about one-fifth of the free acid present. Both bottles are allowed to stand two or three days, and at the end of the time, owing to the insolubility of bitartrate of potash in strong alcohol, there will be a deposit of that salt in both bottles. The first will represent the bitartrate of potash present as such ; the second, the whole of the tartaric acid which the wine contains. There is, however, always a small quantity of bitartrate in solution, about ·004 grm., equalling ·21 d.n. soda, and this amount must be added to that found. The precipitates from both bottles are collected on separate filters, washed with the alcohol-ether mixture, dissolved in water, and titrated with soda solution.

Direct Estimation of Malic Acid.—100 cc. of wine are precipitated with lime-water, added only in slight excess ; the filtrate is evaporated down to one-half, and absolute alcohol added in excess ; the resulting precipitate, consisting of malate and sulphate of lime, is then collected on a filter, washed, and weighed. If, now, the sulphate of lime in this sample be estimated by solution in water, and precipitation of the sulphuric acid by baric chloride, &c., and the amount subtracted from the total weight of the precipitate, the remainder equals malate of lime.

5. *Estimation of Ethers in Wine.*—The compound ethers in wine may be divided into volatile and non-volatile. It is especially the volatile ethers that impart a character to the wine, and give it bouquet and odour. The proportion of volatile to fixed ethers is very small in unfortified wines, but the reverse is the case with fortified wines. The total amount of ethers is extremely small ; Dr. Dupré gives as the highest proportion he has yet met with, about one part of compound ether in 300 parts of wine. The ethers themselves are, of course, derived from conversion of the alcohols, the ultimate amount depending entirely on the relative proportion of alcohols, acid, and water present, and not being dependent on the *nature* of the alcohols or acids. If, as sometimes happens, an excess of compound ether is added to a wine, decomposition will at once begin, until ultimately the wine will contain no more than it would otherwise have reached in the natural order of things. An estimation of the ethers is, therefore, of the greatest possible importance, as it enables the analyst to judge of the age, character, &c., of the wine.

Berthelot has given the following formula for the calculation of the amount of alcohol present in the compound ethers of wine :—

$$y = 1{\cdot}17\text{A} + 2{\cdot}8$$
$$x = \frac{y \times a}{100}$$

A is the percentage of alcohol by weight in the wine; a the amount of alcohol equivalent to the total free acid (reckoned as acetic) contained in 1 litre. It, hence, follows that if the amount of alcohol present as ether, found by experiment, fairly agrees with the calculated amount, etherification is complete, and the wine must be of a certain age; if the compound ethers exceed the proper amount, the probability is that it is an artificial wine; and, lastly, if the amount of ethers is below the theoretical standard, either etherification is not complete, on account of its youth, or alcohol has been recently added.

Dr. Dupré, taking advantage of the fact that all ethers (when treated with an alkali) break up into their respective acid and alcohol, indirectly estimates both the volatile and non-volatile ethers as follows :—

250 cc. of wine are distilled, with special precautions against loss, until 200 cc. have come over; the distillate is now made up to 250 cc., and 100 cc. of this titrated. Another 100 cc. are decomposed by alkali (a known amount), and again titrated. The second 100 cc. will, of course, be more acid than the first, and therefore the amount of *volatile* ether can be estimated from such increase. The *fixed* ether is determined by evaporating down to 50 or 60 cc. in an open dish on the water-bath; the residue, which, of course, contains *no alcohol*, is rendered alkaline with sodium hydrate, some tannin added, and the whole slowly distilled; the fixed ether present is resolved into an acid and an alcohol, and the latter distilled over; the distillate is rendered slightly acid by sulphuric acid, redistilled, and the second distillate (which may amount to 20 or 25 cc.) oxidised into acetic acid in a closed flask by potassic bichromate; the acetic acid is distilled over and titrated as described at p. 131.

6. *The Estimation of Sugar in Wine* is carried out on the principles described at sect. 2, p. 7.

7. *Albuminoid Substances.*—The albuminoid substances in wine may be estimated by Mr. Wanklyn's well-known ammonia process :—5 cc. of the wine are put in a half-litre flask, and made up with water to 500 cc.; $\frac{1}{100}$ (*i.e.*, 5 cc.) of this is distilled with a little water and pure carbonate of soda (ammonia pure),

and the ammonia in the distillate estimated by the colorimetric process known as Nesslerising. An alkaline solution of permanganate of potash is then added, and the operation repeated—the ammonia coming over now being the result of the breaking-up of albuminoid bodies. It would appear that in *white* wines the albuminous matters are very small in amount; while in *red*, and most *young* wines, there is an excess of albuminous matters, which decreases with age; hence, in experienced hands, a determination of this kind may help to distinguish between old and new.

Thudichum and Dupré found in certain wines the following amounts of ammonia:—

	Ammonia free. Per cent.	Ammonia albd. Per cent.
Ingelheimer, red, ...	0·0051	0·3730
Port, 1851, ...	0·0046	0·0888
Sherry, 30 years in bottle, .	0·0073	0·1807
Madeira, ...	0·0021	0·1581
Merstemer, ...	0·0021	0·3550
Natural Port, ...	0·0019	0·0527
Port, 1865, ...	0·0012	0·1760

8. *The tannin* of wine may be estimated by the methods described at p. 99.

9. *Estimation of the Colouring matter of Wine.*—The colouring matter of red wines has been termed *œnolin*, or *œnocyanin*, and has also received other names. Glenard has assigned to it the formula $C_{10}H_{10}O_5$; but it is doubtful whether it has ever yet been separated in a state of absolute purity. The process used by Glenard was—precipitation with lead acetate, exhaustion of the washed, dried, and powdered precipitate, first, with anhydrous ether saturated with HCl, then with pure ether; and, lastly, extraction with alcohol, from which the œnolin was obtained by evaporation as a bluish-black powder insoluble in ether, almost insoluble in pure water, but more readily dissolved in acidulated water; acidulated alcohol dissolving it easily. The blue colour is turned red by acid. Œnolin, according to Vaserine,* may be separated from wine by mixing the latter with lime to the consistency of a paste, which is drained on a funnel. The residue, containing the colouring matter, is mixed with alcohol of 95 per cent., and treated with sufficient sulphuric acid to neutralise the lime and decompose the compound of lime with the colouring matter. The solution is filtered from calcium sulphate, and on evaporation leaves œnolin as a black powder. Solutions of œnolin show, when examined by the spectroscope, certain bands, and the

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* *Bull. Soc. Chim.* [2], xxix. 109, 110.

application of this instrument to the investigation of wines is indispensable. In no case, however, should the analyst trust to descriptions or plates; the only safe course is to have in readiness tinctures of colouring matters of different strength and different ages, as well as samples of wine artificially coloured.

The colour of white wines is due to oxidised tannin; it takes long to develop; hence, the manufacturer not unfrequently adds a little caramel. Should this be the only addition, it would be injudicious to consider the wine adulterated.

The artificial colouring of wines by elder-berry, logwood, cochineal, aniline, &c.,* is said to exist, at all events, on the Continent; and it is a fact that a few home-made, low-priced wines, almost entirely fictitious, are passed off by the aid of the same or similar substances; but with regard to the ordinary foreign wines in English commerce, there is no reliable evidence whatever that any adulteration of this kind has been practised. Nevertheless, it is absolutely necessary to be acquainted with the best and most recent methods for the discovery of such frauds.

Dr. Dupré, taking advantage of the fact that the colouring matter of wine † only dialyses to a minute extent, and that the colouring matters of Brazil logwood and cochineal readily dialyse, separates the latter colouring matters from the wine by dialysis. The same chemist has suggested a still more convenient and practical process—viz., the staining of a jelly. The jelly is made by dissolving 5 grms. of gelatine in 100 cc. of warm water, and pouring the solution into a square flat mould made of paper. From this cake cubes about $\frac{3}{4}$ inch square are cut with a sharp wet knife, and are immersed in the wine, taken out after the lapse of from twenty-four to forty-eight hours, washed slightly, and sections cut, in order to see how far the colouring principles have penetrated. If the wine is pure, the colour will be confined almost entirely to the edges of the slice, or will not have penetrated beyond $\frac{1}{16}$ to $\frac{1}{8}$ inch; most other colouring matters rapidly permeate and colour the jelly.

(1.) *Colouring matters penetrating slowly into the jelly:*

Colouring matter of pure wine.
,, ,, Rhatany root.

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* Soubeiran says: "At Fismes, in the neighbourhood of Rheims, there as been manufactured for more than a century (since 1741) a colouring gent composed of elder-berries, alum, and water, in different proportions, the rolonged use of which can only have injurious consequences on the health, n account of the alum. Unfortunately, the production of this colouring gent (*teinte*) was encouraged by a royal decree of 1781. . . . Recent nalyses have shown that this *liqueur de Fismes* contains from 20·8 to 57·56 rms. per litre of alum."—*Dict. des Falsifications.* Paris, 1874.

† The colouring matter of Rhatany root has the same property.

(2.) *Colouring matters penetrating rapidly into the jelly:*

Rosaniline.
Cochineal.
Logwood.
Brazil-wood.
Indigo.
Litmus.
Red Cabbage.
Beetroot.
Malva sylvestris.
Althea officinalis.

The jelly may be examined spectroscopically, good results being obtained in the case of rosaniline, red cabbage, and beetroot; and may be also tested with reagents—*e.g.*, dilute ammonia dissolves much colour from the slice, if the colour should be derived from logwood or cochineal; on the other hand, the ammonia remains colourless in the case of rosaniline, red cabbage, and beetroot.

A simple method for the detection of certain colouring matters is that of Lammatine:—Shake 100 parts of the wine with 100 of coarsely-powdered peroxide of manganese, and then pass through a double filter; if pure, a colourless filtrate will result. The process is said to answer well in the case of logwood and cochineal, but to fail with aniline.

A general method, applicable to fuchsine and other colouring matters, is based upon the fact that a great many of the colouring matters which may be used for purposes of wine adulteration (such as caramels, ammoniacal cochineal, sulphindigotic acid, logwood, and the lichen reds), are precipitated by acetate of lead; whilst fuchsine, if present in considerable quantity, is only partially thrown down. Those which are not precipitated may be separated by agitating the filtrate with amyl alcohol.

The lead precipitate may be treated by dissolving out cochineal, sulphindigotic acid, and fuchsine, by a solution of potassic carbonate [2 : 100]. From this liquid the fuchsine is separated by neutralisation with acetic acid and agitation with amyl alcohol, the rose-coloured liquid obtained being identified as a solution of fuchsine by the spectroscope. On now acidifying the liquid with sulphuric acid, the carminamic acid from the cochineal is removed by means of amyl alcohol, and identified by its three bands—viz., one between D and E in the red, the second in the green, and the third in the blue. The indigo remaining may be detected by the blue colour, and absorption band between C and D. The original lead-precipitate, insoluble in potassic carbonate, is treated with a 2 per cent. solution of potassium sulphide, which dissolves the colouring matter of logwood and that of the wine itself. Logwood may, however, be tested for directly in the wine by the addition of calcium carbonate and two or three drops of lime-water. In the case

	N.	C
te from	To 1 cc. of clarified wine add 1 cc. of aluminium acetate of 2° B. Colour of liquid.	To 1 cc. wine add potassium (obtained alum to a alumina Filter the
	Wine lilac. *Aramon* is	Lilac, faintl

of a natural wine, the filtered liquid is almost colourless, but is of a fine red colour if logwood is present. Lastly, the lichen red may be obtained by washing the insoluble portion left after treatment with potassium sulphide, and dissolving it in alcohol, when a red colour and a definite absorption band reveal its presence.

For the detection of fuchsine simply, Bouillon (*Comptes rendus*, lxxxiii. 858, 859) recommends half a litre of the wine to be evaporated down to 120 cc., with the addition of 20 grms. of barium hydrate. It is then filtered, and the filtrate shaken up with ether; the ether is separated, a drop of acetic acid, a little water, and a small piece of white silk, are added, and (if an appreciable amount of fuchsine is present) the silk assumes a pink colour immediately; if not, the liquid must be concentrated nearly to dryness.

Lastly, M. A. Gautier* has proposed a method aiming at a systematic detection of every probable colouring matter likely to be added to wine. How far the whole, or any portion, of this elaborate system will be followed and confirmed by chemists, remains to be seen.

The following abstract of M. Gautier's paper is taken from the *Analyst*, i., 1877:—

M. Gautier's Process for Detecting Colouring Matters in Wine.

Preliminary Preparation of the Sample.—The wine to be examined is mixed with one-tenth its volume of white-of-egg, previously diluted with one and a half times its bulk of water, well shaken, and, after standing for half an hour, filtered. If the wine is very poor in tannates, a few drops of a fresh aqueous solution of tannin should be added previous to the agitation with albumen. The filtrate is treated with dilute sodium bicarbonate until its reaction is *very* feebly acid. All the reactions of Table B. must be made on this liquid, except those for indigo, which are executed upon the albuminous precipitate.

Table B.—SYSTEMATIC PROCESS TO BE FOLLOWED FOR THE DETECTION OF THE NATURE OF FOREIGN COLOURING MATTERS ADDED TO WINES.

A. Having placed aside the filtrate from the albuminous precipitate, the precipitate is washed until the washings are almost colourless.

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* *Bull Soc. Chim.*

Two cases may present themselves :—

(*a.*) The precipitate after washing remains wine-coloured, lilac, or maroon; *wine, natural, or adulterated with the greater part of the substances usually employed.* Pass on to C.

(*b.*) The precipitate is of a very deep wine-colour, violet-blue, or bluish; *wines from the deepest coloured grapes, or wines coloured with indigo.* Proceed to B.

B. The precipitate is washed with water, then with alcohol of 25 per cent., a part is then removed and boiled with alcohol of 85 per cent.

(*a.*) The filtrate is *rose,* or *wine-coloured.* A portion of the precipitate is removed from the filter, suspended in water, and carefully saturated with dilute potassium carbonate. The colour changes to brown or blackish-brown; *natural wines, or adulterated with substances other than indigo.* Pass to C.

(*b.*) The filtrate is *blue.* A portion of the precipitate suspended in water and treated with dilute potassium carbonate affords a deep blue liquid, which changes to yellow by an excess of the reagent. *Various preparations of indigo. Indigo.*

C. 2 cc. of wine are treated with 6 to 8 cc. of a $\frac{1}{200}$ solution of sodium carbonate, which must be added in slight excess (1 cc.) after the change of colour.

(*a.*) The liquid becomes *lilac,* or *violet,* sometimes the liquid becomes only winey, or dashed with violet. *Brazil-wood, cochineal, Portugal berries, fuchsine . . . . wines of certain sorts, fresh beetroot, logwood, both elders, whortleberries* (myrtille), *Portugal berries.* Pass to D.

(*b.*) The liquid becomes bluish-green, sometimes with a faint lilac tint, *wine, hollyhock, privet, whortleberries, logwood, Portugal berries, fuchsine.* Pass to M.

(*c.*) The liquid becomes greenish-yellow without any blue or violet, *beetroot* (old or fermented decoction), *whortleberries, certain rare varieties of wine.* Pass to L.

D. The liquid C. *a.* is heated to boiling.

(*a.*) The liquid remains wine-violet, rose, or wine-lilac, or becomes a brighter lilac; *logwood, Brazil wood, cochineal, certain varieties of wine.* Pass to E.

(*b.*) The colour disappears, or changes to a yellow, or maroon, or reddish tint, *wine, fuchsine, both elders; whortleberries, Portugal berries, fresh beetroot.* Pass to F.

E. Treat 4 cc. of the wine with 2 cc. of each of a 10 per cent. solution of alum, and a 10 per cent. solution of crystallised sodium carbonate. Filter.

(*a.*) Clear yellowish-green lake (which may be bluish from mixtures of wines containing aramon), filtrate colourless, becom-ng very slightly yellow on warming; its own volume of luminium acetate at 2° B. almost wholly decolorises it. On cidification with acetic acid, after treatment with its own olume of barium-hydrate (saturated solution), the wine becomes lear greenish-yellow, *maroon, pure or mixed.*

(*b.*) Greenish-blue lake, or dirty yellowish-green, according to he varieties present, sometimes very slightly winey. Filtrate right-rose, gradually decolorised on warming, though retaining tinge of lilac; not decolorised by lime-water in the cold. ochineal.

(*c.*) Winey-violet lake, which darkens on exposure to the air. iltrate bottle-green, or grey faintly red (if much logwood is resent). The filtrate becomes green on warming. Logwood.

(*d.*) Lilac, or maroon-lilac lake. Filtrate greyish with tint of aroon. On boiling, this filtrate becomes fine old wine coloured. razil wood.

F. Treat 4 cc. of the wine with alum and sodium carbonate as explained at E.), add to the mixture two or three drops of ery dilute sodium carbonate, and filter.

(*a.*) The filtrate is lilac or winey, *Portugal berries, fresh beetroot.* ass to G.

(*b.*) The filtrate is bottle-green, or reddish-green, *wine, fuchsine, lack elder, whortleberries, beetroot.* Pass to H.

G. Treat 2 cc. of the wine with subacetate of lead solution of ensity 15° B. Shake. Filter.

(*a.*) The filtrate is rose, which persists even when made slightly lkaline; it slowly disappears on boiling. Lime-water destroys he rose colour. Portugal Berries.

(*b.*) The filtrate is yellowish, or brownish-red. Fresh Beet- oot.

H. The alum-lake obtained from F. (*b.*) was—

(*a.*) Deep blue. On treating the clarified wine with a few rops of aluminium acetate solution, it becomes a decided violet, r wine violet. *Both elders.* Pass to I.

(*b.*) Bluish-green, green, or faintly rose-tinted, *wine, whortle- erries, beetroot, fuchsine.* Pass to J.

I. After the test H. (*a.*) treat a fresh quantity of 2 cc. with ·5 to 2 cc. (according to its acidity and the depth of its colour) f an 8 per cent. solution of sodium bicarbonate charged with arbonic acid.

(*a.*) The liquid remains lilac for a moment, then changes to reenish-grey blue. Another specimen treated with sodium arbonate (according to C.), and heated to boiling, becomes dark reenish-grey. Black Elder.

(*b.*) The liquid retains a lilac tint, or becomes grey with mixture of maroon, or dirty lilac. Another specimen treated with sodium carbonate (as at C.) tends to discolour on heating, the green being replaced by red. DWARF ELDER.

J. Treat 5 cc. of the clarified wine with a slight excess of ammonia, heat to boiling, and after cooling shake with 10 cc. of ether, decant and evaporate the ether, and treat the residue left on evaporation with acetic acid.

(*a.*) The liquid becomes red. FUCHSINE.

(*b.*) The liquid does not become red, *wine, whortleberries, fresh beetroot.* Pass to K.

K. Another specimen is treated according to C. with sodium carbonate.

(*a.*) The colour darkens or becomes red on heating, *whortleberries, fresh beetroot.* Pass to L.

(*b.*) The greenish or bluish-green liquid, possibly having a winey tinge, has a tendency to discolour on heating. *Natural wine.*

L. Treated with sodium bicarbonate according to the rules given at I.

(*a.*) The liquid is deep grey, slightly greenish, green, sometimes green with very slight lilac tint.

The clarified wine, treated with an equal volume of saturated baryta water, filters after standing for fifteen minutes, dirty yellow, or slightly greenish.

With an equal volume of aluminium acetate of 2° B. it gives a lilac wine-coloured filtrate.

With a few drops of aluminate of potash no change of colour. With sodium carbonate, employed as at C., the liquid tends to lose its colour on heating. With barium peroxide, used according to Table A., column P., the liquid is faintly rose-tinted, with or without an orange-coloured deposit on the barium peroxide. NATURAL WINE.

With the general characters above indicated, if with baryta water it affords a madeira-coloured filtrate, changing to buff on acidulation with acetic acid; if with borax it becomes deep-green with a bluish cast; if with alum and sodium carbonate (as at E.) a deep bottle-green with bluish tinge, and a precipitate falls, and if with aluminium acetate it remains rose-coloured with no change to violet-blue. TEINTURIER.

(*b.*) The liquid is reddish-yellow or brown-lilac. By treatment with acetate of alumina the filtrate is clear lilac. With a few drops of aluminate of potash the colour becomes that of the skin of an onion, and with a larger quantity of the reagent the colour is green, tinged with maroon. With sodium carbonate (employed as at C.) the fluid passes to yellowish or greyish-yellow with tinge of red. With barium peroxide, flesh-coloured liquid with considerable orange-coloured deposit in contact with the peroxide. BEETROOT, *fermented or not.*

(*c.*) The liquid is yellowish-grey, with tinge of green or red. With baryta water the filtrate is yellowish olive-green. With aluminium acetate the filtrate is bluish-violet, or violet-lilac. With aluminate of potash, fresh rose, becoming yellowish-green, with an excess of reagent. With sodium carbonate (as at C.) the fluid becomes deep grey on heating. With barium peroxide the fluid is bleached, or remains but very slightly roseate, with a trace of orange deposit in contact with the peroxide. WHORTLEBERRIES.

M. The mixture of wine and alkaline carbonate C. (*b.*) is heated to boiling.

(*a.*) The mixture becomes lilac-violet, or violet. LOGWOOD.

(*b.*) The mixture tends to become decolorised, or changes to yellowish-green, or dark green, or maroon green, *natural wines, whortleberries, both elders, privet, Portugal berries, fuchsine.* Pass to N.

N. Treat the wine with alum and sodium carbonate, as directed at E., and filter.

(*a.*) The colour of the filtrate is lilac. *Portugal berries.*

(*b.*) The filtrate changes to bottle-green, or reddish-green. *Natural wines, whortleberries, hollyhock, privet, both elders, fuchsine.* Pass to O.

O. Treat 2 cc. of the clarified wine with 3 or 4 cc. of a saturated solution of borax, according to the intensity of the colour of the wine.

(*a.*) The liquid remains wine-lilac, or with some violet tinge, *both elders, privet, whortleberries.* Pass to P.

(*b.*) The fluid becomes bluish-grey-flax-blossom, greenish or bluish-grey, with very faint trace of lilac, *pure wine, whortleberries, hollyhock, fuchsine.* Pass to R.

P. Treat a new portion of wine with sodium bicarbonate (as directed at I).

(*a.*) The tint, at first lilac, changes afterwards to grey, slightly brownish, or to maroon. If a new portion be treated with sodium carbonate, according to C., and then heated to boiling, it becomes clearer, and loses its green tint.

The lake obtained according to E. is deep blue-green. DWARF ELDER.

(*b.*) The specimen remains grey, tinged with green, bottle-green, or yellowish. Sometimes (black elder) it acquires a lilac tint, which almost immediately disappears, changing to a greenish-grey-blue, *whortleberries, black elder, privet.* Pass to Q.

Q. Treat a specimen of the wine with alum and carbonate of soda (as directed at E.). Shake the mixture, and after a few moments throw it on a filter.

(*a.*) The lake remaining on the filter is deep green-blue; the filtrate is clear bottle-green. A sample treated with sodium carbonate (as at C.) darkens and becomes grey, slightly greenish, on heating to boiling. BLACK ELDER.

(*b.*) The lake is clear bluish or greenish. The filtrate is clear bottle-green. A sample treated with sodium carbonate (as at C.), and heated to boiling, changes to dirty yellowish. PRIVET.

(*c.*) The lake is ash-green faintly rose-tinted. The filtrate is bottle-green, with tint of maroon. A sample treated with sodium carbonate (according to C.) becomes deep grey on being heated to boiling. WHORTLEBERRIES.

R. Treat a specimen of the wine with ammonia and ether, as directed at J.

(*a.*) The ether being decanted and evaporated, the fluid residue becomes rose-coloured on treatment with acetic acid. FUCHSINE.

(*b.*) The liquid left after the evaporation of the ether does not become red on acidification with acetic acid, *natural wines, hollyhock, whortleberries.* Pass to S.

S. A sample is treated with its own bulk of a solution of aluminium acetate of 2° B.

(*a.*) The colour of mixture remains winey, *natural wines, whortleberries*; differentiate between them, as directed at L. (*a*), and L. (*c*).

(*b.*) The colour of the mixture becomes violet-blue, *hollyhock, whortleberries.* Pass to T.

T. A specimen is treated with alum, and sodium carbonate (as at E.), and after a few moments filtered.

(*a.*) The lake is clear green, slightly bluish, and rose-tinted, filtrate is bottle-green, with little maroon. With borax (as at O.), particularly if the sample has been concentrated, the liquid is grey with trace of lilac. 2 cc. of the liquid treated with 3 cc. of dilute ammonia (1 vol. of liq. ammonia with 10 vols. of water), and the mixture diluted with its own bulk of water, gives a liquid which is yellowish-grey, greenish or greenish-grey. The other characteristics as at L. WHORTLEBERRIES.

(*b.*) The lake is green, slightly bluish, quite free from rose, filtrate clear bottle-green. With borax the liquid is greenish blue-grey. With ammonia (as above), dark bottle-green. With aluminium acetate (as at S), bluish-violet coloration. HOLLYHOCK.

Although somewhat difficult, this systematic method serves for the discovery of several colouring matters mixed in one wine, if the indications of Tables A. and B. are carefully observed, and followed. It is always desirable to determine the presence of fuchsine by the special reactions given further on. By means of Table B. the presence of one or several of the colouring matters may be detected, but before deciding, it is as well to verify by repeating, for the substances so found, the reactions of Table A. on the sample; and also the more special characteristics given further on, for the identification of those substances.

SPECIAL REACTIONS FOR THE DETECTION OF CERTAIN OF THE COLOURING MATTERS MIXED WITH WINES.

Brazil Wood.—Even a very strong clarification (two or three times more albumen than mentioned at the head of Table B.) does not wholly decolorise the adulterated wine. It becomes yellow-buff, which on exposure to the air gradually changes to red. If a wine that has been adulterated with Brazil-wood is clarified, and then a skein of scoured silk, washed with dilute tartaric acid, be soaked in it for twenty-four hours, and then withdrawn, washed, and dried at 60° to 70°, the silk will be found to be dyed lilac-maroon, or red. In pure wine, the skein remains wine-coloured or lilac.

If the dyed silk be now dipped into dilute ammonia, and heated to 100° for a moment, it becomes lilac-red, if Brazil-wood was present; but deep grey, with scarcely a tinge of its original colour, if the wine were pure. If the ammonia be replaced by lime-water, the skein changes to ash-grey, if Brazil-wood were present, but to a dark, dirty yellowish-red, if the wine were pure. Finally, if the skein be dipped into aluminium acetate, and then heated to 100°, it retains its wine-red lilac colour. This reaction differentiates Brazil-wood from logwood.

Logwood.—If the colour due to logwood is in excess in the wine, ammonia gives it a shade of violet; if the proportion of logwood is small, the reactions B, L, N, of Table A., which are very delicate, should be tried.

Treated with a skein of silk, prepared in the manner described for Brazil-wood, it dyes lilac-red, or maroon, which dilute ammonia changes to violet-blue tinged with grey, and which by acetate of aluminium becomes bluish-violet.

Cochineal.—The lilac, or roseate tints due to the reactions A, B, H, K, of Table A., are very sensitive, the last being very characteristic; the only substance likely to be confounded with it being the phytolacca (Portugal berries), which is differentiated by the reaction B. of the same table.

A skein of scoured silk, mordanted with aluminium acetate, soaked in the clarified wine for twenty hours, is dyed of a wine violet colour, analogous to that of pure wine, on being dried at 100°. The colour does not change, even at 100°, by cupric acetate (exclusion of fuchsine); but if the skein be dipped into a dilute solution of zinc chloride, heated to 100°, and then wetted with sodium carbonate, washed with water and dried, the colour becomes fine purple, whereas with pure wine the tint would remain sombre grey-lilac.

Cochineal may be discovered by the spectroscope if present in large quantity, but if it amounts to only about 12 per cent. of the total coloration, it cannot be so detected. It rapidly separates from wines, being precipitated in the lees.

Fuchsine.—This should be sought for in all wines found to be adulterated with other substances. The reaction J of Table B. is very sensitive. Great care must be taken to avoid loss of rosaniline from imperfect decomposition of its salts in solution; moreover, arsenic should always be sought for where the wine is found to contain any aniline. Fuchsine rapidly separates from the wines to which it has been added. A skein of silk becomes dyed rose by soaking in a wine adulterated with fuchsine, and its colour passes to yellow on treatment with hydrochloric acid, but to bright red if the wine was pure. The dyed skein treated with dilute cupric acetate, and dried at 100°, becomes fine deep rose-violet if fuchsine is present, and of a lilac tinged with ash-grey if the wine is pure. This reaction is very sensitive.

Phytolacca.—(Portugal berries). The rose or lilac colorations of the re-actions A G, and especially C of Table A., are very sensitive.

Hollyhock—(*Althea rosea*), much used. This substance imparts a peculiar flavour, which in a few months becomes actually disagreeable, while the colouring matter itself rapidly precipitates.

Beetroot.—This is generally employed only to mask other adulterants. The lilac tint of reaction C of Table A., if the beetroot is fresh, and the yellowish colours due to alkalies (reactions D E and F of Table A.) are very sensitive, even with old decoctions.

Black Elder, *Dwarf Elder.*—The dwarf elder imparts a faintly terebinthinate odour to the wines. The berries of both varieties are particularly used to communicate a special colour and flavour to port wine. The *teinte de Fismes,* which is largely used at Fismes, Paris, and elsewhere, is made by digesting 250 to 500 parts of elder-berries, and 30 to 60 parts of alum, with 800 to 600 parts of water, and then submitting the mixture to pressure.

M. Maumené reports having discovered as much as 4 to 7 grms. of alum per litre in wines adulterated with this substance. Sometimes (though rarely) the alum is replaced by tartaric acid. Wines adulterated with elder yield a violet-blue lake (reaction H, Table A). By comparison with pure wine the difference is very marked.

A piece of flannel, or skein of silk, mordanted with aluminium acetate, heated for some time in the suspected wine, then washed, and immersed in water made faintly alkaline with ammonia, becomes green if the wine is pure, but dark brown if black elder is present. Probably the same reaction occurs with dwarf elder.

Privet.—This is very seldom used. The general reactions, particularly N and P of Table A., must be relied on.

Myrtille — (Whortleberries). Very seldom used, and only for the commonest wines. The principal characteristics are given in L (*c*), Table B. In wines suspected to be adulterated with this substance, citric acid should be sought for, its presence being one of the best indications of the adulteration.

Indigo.—The reactions A (*b*) and B (*b*) of Table B. are so sensitive that they are alone sufficient to characterise indigo. Wool or silk mordanted with aluminium acetate, heated with 20 to 40 cc. of the suspected wine nearly to dryness, washed and then dipped into very dilute ammonia, becomes dirty green if the wine be pure, but blue if indigo be present.

Indigo being often used to mask the too bright colours of cochineal and fuchsine, they should always be sought for after the removal of the indigo by clarification with albumen.

Indigo very rapidly separates from wines, and it may frequently be found in the lees, even when the wine itself gives no indication of its presence.

Substances other than those mentioned are occasionally employed for the adulteration of wines; among them are archil residues, sulpho-purpuric, and sulpho-alizaric acids, and their salts; but these have only recently been introduced, and are not yet seriously employed. Except in such cases as indigo and cochineal, it is only upon a series of concordant reactions that the presence of an artificial colouring matter should be affirmed.

10. *Mineral Substances, or Ash.*—The ash of a great many wines, and especially of sherries, imported into this country, consists nearly entirely of sulphates.* This is due either to sulphuring or plastering. It is sometimes found absolutely necessary to charge a wine slightly with sulphurous acid, which in course of time becomes sulphuric acid, and in such a case the chlorides and

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* The sulphuric acid in sherries ranges from 1·5 to 8 grms. per litre (equal to 17·5 to 93·5 grains per bottle of $\frac{1}{6}$ gallon.

carbonic acids are diminished in the ash, the sulphuric increased, but the total weight of the ash itself is not materially increased. On the other hand, plastering (by which is meant the addition of plaster of Paris to the grapes before they are crushed) has the effect, by its reaction in the cream of tartar, of producing a soluble sulphate of potassium, which may very materially increase the ash of the wine.

Under absolutely normal conditions, the ash consists of carbonate, sulphate, phosphate, chloride of potassium, chloride of sodium, phosphate and carbonate of calcium, with very small quantities of magnesia, iron, silica, and frequently lithium and manganese.

The ash from a litre of wine examined by Boussingault contained—

	Grms.
Potash,	0·842
Lime,	0·092
Magnesia,	0·172
Phosphoric Acid,	0·412
Sulphuric Acid,	0·096
Chlorine,	a trace.
Carbonic Acid,	0·250
Sand and Silica,	0·006
	1·870

With regard to the analysis of the ash, &c., see p. 5.

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V.—BRANDY.

§ 96. Brandy, in its present form (Cognac), is a spirit derived from the distillation of wine; inferior varieties are made from the refuse of grapes, with admixture of other materials.* The constituents of brandy are—alcohol, water, acetic, œnanthic (ethyl pelargonate), butyric, and valerianic ethers, small quantities of grape sugar, minute quantities of a volatile oil, colouring matter, a trace of tannin, acetic acid, and a little fixed acid. The specific gravity of genuine brandies varies from ·929 to ·934; the solids from 1 to 1·5; ash, ·04 to ·2; acidity, ·01 to ·05 (reckoned as tartaric acid); and the sugar from 0 to ·4 per cent.

The adulterants to be looked for are—methyl and amylic alcohols, tannin in excess, sulphuric acid, lead, copper, zinc, and hot principles, such as cayenne. The estimation of alcohol and the examination of the distillate are elsewhere described (see p.129). Any acetic acid will be found in the distillate, and can be estimated by volumetric solution of soda. Fixed free acids will remain in the residue, and (if no free mineral acid is detected) may be estimated volumetrically, and returned as tartaric acid (1 cc. of d.n. soda = ·0075 tartaric acid).

If the residue taste hot and pungent, some sophistication, such as capsicum, must be present; an attempt should be made to separate such hot substances in a comparative state of purity by benzole, ether, &c.

If the brandy is coloured by caramel alone, on the addition of a persalt of iron there will be no deepening of tint; if, on the contrary, the colouring be derived from the cask, and the brandy contain tannin, it will deepen very decidedly in colour.

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* The brandy made in England is for the most part artificial. A very usual process is to add to every 100 parts of proof spirit from half-a-pound to a pound of argol, some bruised French plums, and a quart of good Cognac; the mixture is then distilled, and a little acetic ether, tannin, and burnt sugar added afterwards.

Artificial Cognac is sometimes made by oxidising palm-oil by potassic dichromate and sulphuric acid, and then distilling it with 70 per cent. of alcohol and concentrated sulphuric acid. Œnanthic ether is among the products.

Since it appears that in some of the receipts of the trade, tincture of oak bark is used,* should the precipitate by a persalt of iron be very evident, the amount of tannin must be estimated.

The direct addition of SH_2 to acidified spirits produces a sufficiently perceptible dark colour, should lead or copper be present in any quantity; for this the reader is also referred to the special tests (described in the second part of this work). If zinc be sought, the spirit should be evaporated to dryness (adding first a little carbonate of soda), the residue burnt, and the process completed, as described in the article on *Zinc*.

VI.—RUM.

§ 97. The best rum is distilled from fermented molasses, inferior kinds from the *débris* of the sugar-cane. In France a considerable amount of spirit is also derived from the molasses of the beetroot-sugar factories. The specific gravity of rum varies from ·874 to ·926; it is usually a strong spirit, genuine rum never falling below 50 per cent. of alcohol, and often reaching as high as 70 per cent. It is always slightly acid (about ·5 per cent.) The solid residue varies from ·7 to 1·5 per cent. It may contain sugar; the proportion of ash is very small, seldom more than ·1 per cent. The analysis is carried out strictly on the principles before described.

VII.—WHISKY.

§ 98. *Whisky* is one of the corn spirits, and is usually manufactured from malted grain. The Scotch distillers, for the most part, make it entirely from a malt mash, the Irish use malt and raw grain; but in both countries there are considerable differences in its manufacture. The new whisky, impregnated with fousel oil, is called "pot-still whisky." This liquor is often blended with so-called improvers, "Hambro" sherry, prime wine, &c. The specific gravity of whiskies is usually from ·915 to ·920; alcoholic strength from 50 to 60 per cent.; total extract

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* Mr. Griffin found a large quantity of tannin in a sample of brandy. He explains the circumstance by the following receipt for the manufacture of Cognac:—Take of acetic ether three quarters of a pound, French wine eight quarts, oakbark tincture (made with a quarter pound of oak bark and half a quart of spirit) half a quart, purified spirits so much as to bring the whole to 150 quarts of 54 per cent by Tralles.—"Chemical Testing of Wines and Spirits." By John J. Griffin, F.C.S., London, 1872.

under 1 per cent.; it has a minute quantity of volatile acid (seldom, perhaps never, so high as ·1 per cent.), reckoned as acetic, and a trace of ash. If sugar is found, it must have been added.

§ 99. *Adulterations of Whisky.*—The chief adulterant popularly supposed to be mixed with whisky, is potato spirit, or fousel oil; but besides this, methyl alcohol, creosote, fixed acids, and, generally speaking, the sophistications used for the other spirits, have either been proved, or their presence suspected, as fraudulent additions. With regard to fousel oil, small quantities in ordinary whisky are incidental to its manufacture, and not an adulteration. The only estimations of the exact quantity of fousel oil in whisky that we have, are probably those contained in Dr. Dupré's paper before quoted.[*] Dr. Dupré found in a sample of Scotch whisky—

For 100 of Ethylic Alcohol,	0·19	per cent. Amylic.
Cape Smoke,	0·24	,, ,,
Common Samshoe,	0·18	,, ,,
Fine ,,	0·13	,, ,,

Since these appear to be the only determinations worthy of ny credit, it is difficult to say what quantity of amylic alcohol lenotes adulteration, and the question becomes a medical one—iz., Whether fousel oil is injurious or not; if it is, how much is njurious?

§ 100. *Action of Fousel Oil.*—That fousel oil *is* injurious (we nay say, indeed, poisonous) is evident enough from experinents on animals and men, *e.g.*, Eulenberg[†] allowed 30 rms. of amyl alcohol to evaporate in hot sand in a zinc ox in which a kitten was confined. After half the uantity had been put in, the symptoms immediately ommenced, and in an hour the animal lay partly insenible, breathing with difficulty, and shivering. There was, owever, no full narcosis, and it recovered in four days. In nother experiment, in which 40 drops of amyl alcohol had been dministered to a kitten, after seventeen minutes there was alpitation of the heart, irregular breathing, and relaxation of he limbs, and in twenty-two minutes there was full anæsthesia. he animal recovered after a short time, the heart's action emaining more frequent than usual until the next day. Cross[‡] bserved similar symptoms in pigeons and kittens, in the latter he respiration was stertorous. Rabuteau[§] states that 1 of amyl

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[*] *Analyst*, i., 1876, p. 6.

[†] *Gewerbe Hygiène*, 1876, p. 440.

[‡] Cross: de l'Alcohol Amylique et Methyl sur l'Organisme. Thèse. trasburg, 1863.

[§] Rabuteau: Ueber die Wirking des Æthyl, Butyl, und Amyl Alkohols. *'Union*, Nos. 90, 91, 1870. *Schmidt's Jahrb.*, Bd. 149, p. 263.

alcohol in 500 of water causes anæsthesia in frogs in twenty minutes; the heart's action becomes slower, and the skin dark, and in about two hours death occurs, the cardiac pulsations gradually ceasing. Dr. Furst of Berlin killed a rabbit with about 7·6 grms. (2 drachms), injected into the stomach; another, however, recovered from the same dose.

Action on Man.—Men engaged in the manufacture of potato-spirit suffer from headache and general nervous indisposition, unless the vapours are conducted away from them. An experiment by Cross on himself showed that the vapour caused intense aching and heaviness of the head, and other unpleasant symptoms. It has also been shown that 20 cgms. (3·0 grains) of amyl alcohol taken internally produce slight symptoms, the action being first stimulating, then depressing.

From the foregoing we are now in some degree able to judge what amount of amylic alcohol would probably have immediate injurious effects; as to the chronic effects of small doses nothing definite is known. Turning to Dr. Dupré's first sample (a Scotch whisky containing ·19 of amylic to every 100 of ethylic alcohol, the whisky itself containing 54·5 per cent. of alcohol), it would appear that such a whisky has about ·49 of amylic alcohol to the ounce. A person taking 2 ounces of such a liquid would thus swallow nearly a grain of amylic alcohol, and if it contained three times the quantity, the active properties of the amylic would be added to that of the ethylic; for it would then be equal to about 3 grains, the lowest amount at which distinct effects can be obtained. Anything, therefore, like 1½ grains of amylic alcohol per ounce (irrespective of the question whether such a whisky may be pronounced *adulterated* or not), may certainly be considered injurious to health. The analysis of whisky is carried out precisely upon the principles already detailed.

§ 101. *Legal Case relative to Whisky.*—The prosecutions for mere dilution of whisky have been rather frequent, especially in the north of England; but very few *convictions* for other adulterations appear to have been obtained. The following case presents sufficient points of interest to deserve quotation:—

> At the Greenock Police Court, W. D. was accused of selling to two women four gills of whisky adulterated with fixed acid in a free state. . . The analyst stated that the liquor contained—
>
> By Weight per cent.
> 34·5 Alcohol = 74·26 Proof Spirit.
> 6·42 Fixed Acid.
> 9·87 Volatile Acid.
> 32·20 Ash.

The adulteration did not materially increase the weight of the whisky, and it was not hurtful, but the liquor was of inferior quality. Although volatile acid was sometimes found in whisky from natural causes, it did not occur in so large a quantity. He was of opinion that it had been added in the present case in the form of sherry wine. Volatile acid had the quality of changing the tone, and giving it a little flavour. The fixed acid could not be present in pure whisky unless it had been added. A penalty was imposed by the court.—*San. Record*, i., 1874, 442.

VIII.—GIN.

§ 102. Gin is a spirit flavoured with various substances. The different receipts used in the trade include—

Juniper berries.
Coriander seeds.
Orris root.
Angelica root.
Cardamom seeds.
Liquorice powder.
Grains of Paradise.
Cassia buds.
Calamus root.

These generally impart their essential oils to the spirit. A few of the more important will be described here, others are mentioned elsewhere. (See *Index.*)

§ 103. *Oil of Calamus.*—The oil distilled from the root of the calamus, is somewhat thick, yellow, or brownish-yellow neutral, specific gravity 0·950 to 0·952; after rectification, 0·950; boiling point, 196°C. It contains oxygen, is but slowly changed by sodium, and does not fulminate with iodine. It dissolves in all proportions in alcohol and bisulphide of carbon. The spirituous solution of the oil takes a brown colour on the addition of a little chloride of iron.

§ 104. *Oil of Cardamoms* is a pale yellow oil, with a strong smell of cardamoms, of neutral reaction, of specific gravity 0·92 to 0·94. It contains a stearoptene of the formula $C_{10}H_{16}3H_2O$.[*]

§ 105. *Angelica root* contains a volatile acid—*Angelic acid*—a bitter principle, a crystalline substance—*Angelicine*—a resinous substance, an essential oil, and other constituents.

Angelic Acid, $C_5H_8O_2$, forms transparent glittering prisms and needles, melting at 44° to 45°C. into an oil, which may be solidified at 0°C. into a crystalline solid. If the heat be raised up to 190°C. it boils and distils unchanged; it is inflammable, burning with a luminous flame. The acid reddens litmus, and has the odour of the root. It scarcely dissolves in cold water, but is soluble in hot, in alcohol, ether, turpentine, and the fatty oils.

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[*] HUSEMANN.—Die Pflanzenstoffe.
DUMAS and PÉLIGOT.—*Ann. Chim. Phys.* [2], lvii. 334.

It forms salts with bases, which lose a part of the acid on evaporation. It precipitates lead and silver salts white; iron salts, dark yellow; and copper, bluish. By the aid of hydric iodide and red phosphorus, acting at 180° to 200°, angelic acid is changed into valerianic. Melting the acid with KHO decomposes it into propionate and acetate of potash.

Angelicine is, according to Brunner, probably identical with *hydrocarotin*, a principle described by Husemann, found in the *Daucus carota*, L., and to which the following formula is ascribed, $C_{18}H_{30}O$. Hydrocarotin, or angelicine, forms colourless, large, thin plates, without smell or taste, swimming in water, and becoming at 100° hard and brittle. At higher temperatures (120·5) it melts without loss of weight to a yellow fluid, which solidifies as a resinous mass, and cannot be again crystallised. It is readily soluble in ether, chloroform, carbon bisulphide, benzine, oil of turpentine, and warm olive oil. It is not changed in colour by concentrated hydrochloric acid; fuming nitric acid dissolves it with the evolution of gas. Concentrated sulphuric acid dissolves it to a red fluid, depositing brownish-white flakes on dilution with water.

Angelica Oil is colourless, and lighter than water; it has a penetrating odour and camphor-like taste, and resinifies on exposure to the air.*

§ 106. *Oil of Coriander* is a pale yellow oil, smelling like the fruit; of specific gravity ·871 at 14°C., and a portion distilling over at 150°C. The volatile part corresponds to the formula, $C_{16}H_{16}H_2O$; the portion of a higher boiling point to $4C_{10}H_{16}H_2O$. If both portions are distilled with phosphoric anhydride, a powerfully odorous camphor, $C_{10}H_{16}$, is produced.†

§ 107. *Oil of Juniper* is contained in the unripe berries of the common juniper, in the proportion of from ·4 to ·75 per cent. It is colourless, or of a pale yellow, dissolving with turbidity in twelve parts of alcohol of 0·83 per cent., and miscible in all proportions with ether and bisulphide of carbon. Smell and taste mildly aromatic. Specific gravity 0·862 to 0·874, but the poorer

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† HUSEMANN.—Die Pflanzenstoffe. Berlin, 1871.
KAWALIER.—*Journ. Pract. Chem.*, lviii. 226.

commercial samples often have a specific gravity of 0·860. The perfectly colourless oil does not fulminate with iodine, but the commoner kinds explode powerfully.* If 5 to 6 drops of the oil be placed in a test tube, and five times its bulk of sulphuric acid be added, much heat is developed with the evolution of vapour, and the fluid becomes dark yellow-red and turbid; on now diluting with 10 cc. of 90 per cent. alcohol, the colour changes to a somewhat dirty rose tint. The pure oil boils between 140° and 150°; it polarises to the left. On exposure to the air, oxygen is absorbed; and on long standing, colourless tables of juniper camphor are separated. This camphor melts and sublimes without decomposition, is easily soluble in ether and alcohol, and may be obtained in feathery crystals.

The action of warm water in juniper oil, if kept up for some considerable time, results in the formation of a crystalline hydrate. Oil of juniper is officinal in all the Continental pharmacopeias, as well as our own. In such large doses as 15 to 30 grms., it is fatal to kittens, apparently acting in the same way as turpentine.†

§ 108. *Analysis of Gin.*—The analyst should find in good gin at least 80 per cent. of proof spirit, and a variable amount of sugar and flavouring matters, seldom much over 5 or 6 per cent. Sulphuric acid, sulphate of zinc, alum, and lead should always be looked for. Many writers seem to imagine that grains of paradise is an *adulterant.* It is, however, merely a pepper, and much nonsense has been talked about it. It is very doubtful whether any just conviction would be obtained for the addition of any harmless flavouring to the spirit; nearly all prosecutions hitherto have been for dilution, and for dilution only. It appears that no genuine gin‡ is sold to the retailer 22 under proof, and

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* It is said that the oil from the unripe fruit explodes, that from the fully ripe berries losing this property.

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‡ In an appeal case, before Baron Cleasby and Mr. Justice Grove (*Fashler* v. *Stevenilt*), the analyst proved that the gin was 44 degrees below proof. The judges affirmed the conviction. Baron Cleasby thought the conviction was right. When the respondent asked for gin, he meant such gin as is ordinarily sold; and to sell him such gin as that in question was to sell, to the prejudice of the purchaser, gin which was not of the quality demanded. The amount of water proved to have been discovered with the gin, afforded evidence that it had been added for the purpose of fraudulently increasing its measure. Mr.

anything below this may be returned by the analyst as adulterated.

The alcohol should be determined by distillation, as before described (p. 129), and the percentage in the distillate estimated by specific gravity, and, if necessary, in other ways. Neither methyl alcohol nor fousel oil appears to have been found in gin.

The residue after the distillation may be treated with petroleum ether, benzine, &c., as in Dragendorff's process for the testing of beers. The essential oils will be taken up by the petroleum ether, and may be identified by their odour and taste, and (if enough is obtained) by their physical properties. Sulphuric acid, if in a free state, may be separated by quinine, as recommended under article *Vinegar*. The detection of alum, lead, and zinc is elsewhere described.

Justice Grove concurred ; in his opinion, when it was proved that the gin contained so much more water than gin as ordinarily sold, the onus was thrown on the seller of proving that he was not aware of the state in which it was.

PART VI.

VINEGAR.

§ 109. *Constituents of Commercial Vinegar.*—Commercial vinegar is a more or less impure acetic acid, containing usually acetic acid, acetic ether, alcohol, sugar, gum, extractive matter, alkaline acetates and tartrates, a variable amount of salts (depending on the substances from which it has been produced), and legally not more than one-thousandth of its weight of pure sulphuric acid.

§ 110. *Varieties of Vinegar.*—The chief varieties of vinegar are as follows:—

(1.) *Malt-Vinegar.*—The great majority of commercial vinegar in this country is derived from the acetous fermentation of a wort, made from mixtures of malt and barley. Malt-vinegar is of a decided brown colour, in specific gravity varying from 1·017 to 1·019; it is of various degrees of strength, the manufacturers distinguishing different kinds as No. 18, 20, 22, and 24 respectively, the last being the strongest, and containing about 4·6 per cent. of acetic acid. That made by one of the largest firms in this country will be found to contain from ·1 to ·16 per cent. of combined sulphuric acid, and from ·04 to ·08 per cent. of chlorine, as chlorides.

(2.) *Wine-Vinegar* is the chief vinegar in Continental commerce. It is prepared from grape-juice and inferior new wines; that made from white wine is most esteemed. The wine-vinegars vary in colour from pale yellow to red; they have nearly always an alcoholic odour; specific gravity from 1·014 to 1·022. A litre of Orleans vinegar (according to Chevallier's* recent analyses of

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* *Journ. d'Hyg.*, 1877, No. 45.

actual samples) saturates from 6 to 7 grms. of dry carbonate of soda. The extract from pure wine-vinegar varies from 1·7 to 2·4 per cent., the average being 2·05 per cent., and usually contains ·25 grm. of tartrate of potash.

Vinegars of limited use are—*Glucose-vinegar*, recognised chiefly by the presence of dextrine, which may be precipitated by alcohol; *beer-vinegar*, from sour ale; *cider-vinegar*, made both from apples and pears; *crab-vinegar*, made from the crab apple, and used nearly all over Wales and Monmouthshire; and various artificial vinegars.

§ 111. *Adulterations.*—The adulterations of vinegar are—

(1.) Water.

(2.) Mineral acids, especially sulphuric, more rarely hydrochloric, and still more rarely nitric acids.

(3.) Metallic adulterations, or rather impurities; such as arsenic,* derived from sulphuric acid, copper,† lead, zinc, and tin, from the solvent action of the acid on any metallic surfaces with which it may have come in contact.

(4.) Pyroligneous acid.

(5.) Various organic substances, such as colouring agents, and capsicum.

§ 112. *Analysis of Vinegar.*

(1.) *Water.*—Vinegar should contain at least 3 per cent. of acetic acid, and if it does not do so, it may be safely returned as adulterated with water; for it then is so dilute as certainly not to be of the nature and quality of the substance usually sold as vinegar. The strength of vinegar may be accurately estimated by distilling 110 cc., until 100 cc. have been drawn over, that is, ten-elevenths. The 100 cc. will contain 80 per cent. of the whole acetic acid present in the 110 cc., and may be titrated; or the specific gravity of the distillate may be taken, and the strength found from the following table:—

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* "The observation of M. Deschamps induced us to analyse a vinegar sold by a certain Sieur C. . . . The presence of arsenic in this vinegar was ascertained, and the Sieur C. was compelled to confess that the vinegar had been mixed with wood-vinegar. On resorting to the person who furnished the latter product, the whole of the wood-vinegar in his possession was found arsenical, and seized, in order to be employed only for industrial use."—Le Vinaigre, Chevallier, *Journ. d'Hyg.*, No. 46, June, 1877.

† Seven out of twelve samples of vinegar sold in Paris, and analysed by Alfred Riche, contained copper varying from 5 to 15 mgms. per litre. *Journ. Pharm. Chim.* [4], xxvj., 23–28.

Per cent.	Specific Gravity
1	1·001
2	1·002
3	1·004
4	1·005
5	1·007
6	1·008
7	1·010
8	1·012
9	1.013
10	1·015
11	1·016
12	1·017
13	1·018
14	1·020
15	1·022
16	1·023
17	1·024
18	1·025
19	1·026
20	1·027

It will be necessary to test the distillate for the presence of hydrochloric acid, and also to take the acidity of the vinegar without distillation, so as to control the results.

The titration of vinegar may be made with ordinary soda solution, and approximate results obtained.* If absolutely accurate determinations are required, it is best to add an excess of carefully weighed pure carbonate of lime to a known weight of the vinegar; the liquid is boiled, filtered, and the residual carbonate of lime filtered off, dissolved in slight excess of normal hydrochloric acid, and titrated back with caustic soda and cochineal solution. From the amount of carbonate thus found to have been unacted on by the vinegar, the total acidity is calculated.

(2.) *Mineral Acids.*—A great many commercial vinegars contain no trace of free mineral acid; and it has been amply shown that although one-thousandth of free sulphuric acid is allowed by law, such addition is not by any means necessary for the preservation of the vinegar. The mineral acid, if present, is nearly always sulphuric, occasionally hydrochloric, and still more rarely nitric acid.

Hydrochloric Acid is detected by the distillation already described, and the testing of the distillate with nitrate of silver.

Nitric Acid may (in the absence of other reducing agents) be detected by the rapid decoloration of a solution of Indigo carmine added to the boiling vinegar.

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* The results are only approximate, because sodic acetate has itself a feeble alkaline reaction.

Sulphuric Acid cannot be detected by the usual chloride of barium test, for it fails to distinguish between free and combined sulphuric acid. The charring effect of the acid on paper, on sugar, or its action on starch (formerly taken as the basis of the older tests), is now replaced by more scientific methods, and need not be described here.

One of the most speedy tests for the presence of mineral acids is that proposed by A. Hilger*:—Two or three drops of a solution of methyl aniline violet (·01 : 100) are added to 25 cc. of vinegar; if pure, no colour is produced; but if ·2 per cent. of any mineral acid is present, the colour is blue; or if ·5 per cent., blue-green; and if 1 per cent., green.

Another useful test is that of M. Strohl;† it is based on the well-known fact, that oxalate of lime is insoluble in acetic, but soluble in mineral acids.‡ The solutions requisite are—a solution of calcic chloride (15·1 grms. to the litre) and a solution of crystallised ammonic oxalate (28·4 grms. to the litre); $\frac{1}{2}$ cc. of each of these liquids is added to 50 cc. of the vinegar under examination, and if the turbidity which is at first produced does not disappear, the liquid contains less than—

1·70	grm. per cent.	sulphuric acid	(specific gravity 1·843)	per litre.
2·85	,,	hydrochloric acid	(,, ,, 1·174)	,,
4·40	,,	nitric acid	(,, ,, 1·174)	,,

The test, without claim to great accuracy, is extremely useful; for if any suspicious indication be observed, the vinegar may be then submitted to a more elaborate examination for free acids.

As speedy as any of the foregoing, and at once more scientific and accurate, is the process introduced by Mr. Hehner. Its principle is based upon the fact that vinegar always contains potash and soda salts of the organic acid; hence, it is obvious that sulphuric or hydrochloric acids, if added in small quantity, merely decompose an equivalent quantity of acetate or tartrate, as the case may be, and *as free acids* immediately disappear; but if added in excess of the amount of acetates and tartrates, the excess remains as free acid. It thus follows, that if any undecomposed acetate or tartrate exists in the vinegar, it is impossible for a free mineral acid to be present; and since the acetates and tartrates are decomposed by ignition into carbonates, the readiest way to ascertain their existence is to examine the ash of the

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* *Archiv. der Pharmacie*, 1876, 193.

† *Arch. Pharm.* [5], 4, 342-346.

‡ *Ibid.*

vinegar for carbonates. If that ash is *neutral*, free mineral acid is probably present; if *alkaline*, no free acid can be present, although, of course, a small quantity may originally have been added.

The qualitative test devised by Mr. Hehner is also made quantitative. If an accurately-estimated volume of d. n. soda solution is added to a known quantity of the vinegar, so as to neutralise slightly in excess the total amount of free mineral acid present, on ignition the alkalinity of the ash gives the measure of the quantity of free sulphuric or hydrochloric acid. The exact details of this operation, as practised by Mr. Hehner, are as follows:—50 cc. of the vinegar are mixed with 25 cc. of d. n. soda; the liquid is evaporated on the water-bath in a platinum basin, the residue dried at about 110°C., and carefully incinerated at the lowest possible temperature—the ash need not be burned white. 25 cc. of a d. n. sulphuric acid solution are now added to the ash, the liquid heated to expel free CO_2, and filtered. The filter is washed with hot water, litmus added,* and the acidity ascertained by d. n. soda. The volume of soda necessary for neutralisation directly gives the proportion of free mineral acid present in the vinegar, 100 cc. of d. n. corresponding to ·49 grm. of H_2SO_4. If the amount of alkali originally added should have been insufficient, it is necessary to recommence the experiment. For this reason Messrs. Allen and Bodmer made some experiments, in which the preceding manipulation was modified by neutralising the *whole* of the acid, organic and inorganic, by soda solution. The results were satisfactory, but great care must be taken to titrate accurately.

Another very satisfactory way of separating and identifying the free mineral acids in vinegar is the following:—Saturate a known quantity with quinine, evaporate to dryness, take up the quinine salts with spirit, recover the spirit by distillation, dissolve the quinine salt in water, and precipitate by ammonia. The aqueous liquid will now contain the acetate of ammonia, together with the sulphate chloride or nitrate; if any one, or all three, of the free acids were present, the acids may be determined in the usual way.

A method of separating free sulphuric acid from sulphates is to evaporate the vinegar to a syrup, precipitate the sulphates by alcohol, filter, wash the precipitated salts with alcohol, and determine the free sulphuric acid in the alcoholic solution. Provided sufficient alcohol be added, the separation of free from combined sulphuric acid is exact.

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* Instead of litmus, cochineal may be used; the latter is unaffected by CO_2, and therefore preferable.

Another method, the principle of which was proposed by Mr. Thresh, and which has been improved upon by Mr. W. C. Young, is, to add to a known measure of vinegar an excess of $BaCl_2$; the chlorine in a portion of the liquid is now determined with great care, the rest is evaporated, ignited, and the chlorine of the ash determined. The difference represents the free mineral acid in terms of chlorine. The presence of free tartaric or citric acids quite invalidates the accuracy of the process, but, with these exceptions, it is generally applicable.

(3.) *Metallic Adulterations.*—Metals in vinegar are detected by saturating the liquid with hydric sulphide, or by specially testing for arsenic, copper, zinc, tin, and lead, by the methods detailed in the second part of this work. Metals of the first group may, however, be presumed absent, if there is no deepening of colour on saturation with hydric sulphide; arsenic, if Reinsch's test gives negative results; and zinc, if the nearly neutralised vinegar gives no precipitate with hydric sulphide.

(4.) *Pyroligneous Acid.*—The addition of pyroligneous acid to vinegar is said to be revealed by the presence of an excess of sulphate and acetate of soda.

(5.) *Organic Adulterations.*—The other organic adulterations—such as capsicum—must be looked for in the extract; Chevallier has found fuchsine in French vinegars. Methods for the detection of this in wine, given at pp. 191 and 198, are also applicable to vinegar.

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PART VII.

CONDIMENTS—MUSTARD, PEPPER, &c.

I.—MUSTARD.

§ 113. Mustard is made from the seeds, finely ground, of the *Sinapis nigra,* or black mustard, or from those of the *Sinapis alba,* or white mustard, or again, from a mixture of both varieties. The manufacturer reduces the seeds to powder, and passes the product through a series of sieves. The portion in the first sieve is called the *dressings,* that which passes through is an impure *mustard flour.* The impure flour, on being passed through a second sieve, yields the pure flour of mustard and a second quantity of dressings. The dressings are utilised, by being submitted to pressure, for the sake of the fixed oil they contain.

§ 114. *Microscopical Structure of the Seed.*—The white mustard seed is made up of the husk and the seed proper. The *seed proper* is simple in structure, consisting entirely of minute oil-bearing cells; their size averages ·00041 inch in the finely powdered seed; and they look extremely like starch corpuscles, but neither polarise light nor strike a blue colour with iodine.

The *husk* is more complex, and consists of three membranes:—

1. An outer membrane, composed of two kinds of large transparent cells, which are described by Dr. Hassall thus:—Those of the first kind are of an hexagonal figure, and united by their edges so as to form a distinct membrane, the centre of each cell being perforated; the cells of the second kind occupy the apertures which exist in the previously-described cells, and they are themselves traversed by a somewhat funnel-shaped tube, which appears to terminate on the surface of the seed. Immersed in water, these cells swell up to several times their original volume, occasion the rupture of the hexagonal cells, and become themselves much wrinkled or corrugated, the extremity of the tubes in some cases being seen protruding from the proximate termination of the cells. It is possible, however, that what are here

described as two different kinds of cells really form distinct parts of the same cells. It is from these cells that the thick mucilage obtained by digesting mustard seeds in water is derived.

2. The second layer, or *middle tissue*, consists of very minute, angular, coloured cells.

3. The inner or third layer of the husk consists of a single layer of angular cells.

The black mustard in its structural composition differs from the white only in not containing the large perforated cells of the husk, the outer membranes consisting of two or three layers of large, transparent, hexagonal cells, the other structures being similar to those already described.

§ 115. *The Chemistry of Mustard* is extremely interesting; both seeds, white and black, contain a fixed oil (from about 36 per cent.), and a sulphocyanate of sinapin and myrosin. Black mustard seeds contain, in addition to the foregoing, myronate of potash (about ·5 to ·6 per cent.) When the powdered black mustard seeds (or the mixed black and white) are moistened with water, the myronate of potash acts upon the myrosin, and produces *the volatile oil of mustard.* White mustard seeds, on the other hand, contain also a sulphur principle, *sinalbin,* not found in black.

§ 116. *Sinapin*, $C_{16}H_{23}NO_5$.—Sinapin exists as a sulphocyanate, both in black and white mustard seeds, as well as in the seeds of *Turritis glabra*, L. It was first prepared by Henry and Garot in 1825. The best process for extraction of the sulphocyanate on a small scale is (according to Von Babo) to exhaust the oil from the seeds by ether, then to treat with cold absolute alcohol, which only takes up a little of the sulphur compound, and lastly, to dissolve the sulphocyanate of sulphur out with alcohol of 90 per cent. The excess of alcohol is then separated by distillation, and the substance crystallises out, yielding about 1·1 per cent.

Sinapin itself cannot be obtained pure, but a watery solution may readily be prepared by decomposing a solution of the bisulphate with a proper quantity of baryta. After filtering away the sulphate of baryta, the filtrate is of a yellow colour and intensely alkaline reaction; it precipitates many metals from their solution, but on evaporation its colour changes through green and red into brown, and at last it leaves behind an uncrystallisable brown residue. On boiling a solution of sinapin with the alkalies or alkaline earths, the sinapin splits up into sinkalin and sinapric acid,

$$C_{16}H_{23}NO_5 + H_2O = C_5H_{13}NO + C_{11}H_{12}O_5,$$

and similar treatment of the sulphocyanate of sinapin produces the same decomposition. To sulphocyanate of sinapin is ascribed the formula, $C_{16}H_{23}NO_5CNHS$. It forms colourless, transparent, truncated prisms, in warty or starlike groups, without odour, but of a bitter taste, of neutral reaction, melting at 130°C. to a yellow fluid, solidifying again in an amorphous mass. Sulphocyanate is readily soluble in water; but ether, turpentine, and bisulphide of carbon do not dissolve it. If to a hot solution in alcohol, concentrated sulphuric acid be added, bisulphate of sinapin, $C_{16}H_{23}NO_5, SH_2O_4 + 2OH_2$, separates on cooling in rectangular plates. From this salt the neutral sulphate may be obtained by solution in water, and precipitating half the sulphuric acid by baryta.

§ 117. *Sinalbin*, $C_{30}H_{44}N_2S_2O_{16}$, a substance which exists only in white mustard, and may be supposed to take the place of myronate of potash. It splits up into sugar, bisulphate of sinapin, and sulphocyanide of acrinyl, C_8H_7NSO. The last, on treatment with alkalies, yields ammonia and the salt of an acid melting at 136°C., to which the formula $C_8H_8O_3$ is ascribed.

§ 118. *Myrosin*, a substance analagous to emulsin, has not yet been obtained albumen- or lime-free; its solution froths on being shaken; it is coagulated by warming to 60°C., as well as by acids and alcohol.

§ 119. *Myronate of Potash* ($C_{10}H_{18}KNS_2O_{10}$) crystallises out of spirit, in needles; out of water, in rhombic prisms. It is destitute of water of crystallisation, is of neutral reaction, and has no odour, but is of a bitter taste. It is easily soluble in water, with difficulty in diluted spirit, and scarcely at all in absolute alcohol, whilst it is quite insoluble in ether, chloroform, and benzole. If the concentrated aqueous solution of the salt be digested with tartaric acid and absolute alcohol, the tartrate of potash separated, and the filtered fluid evaporated with carbonate of baryta, the filtrate from the latter will yield easily soluble crystals of myronate of baryta ($C_{10}H_{18}BaNS_2O_{10}$), which soon become opaque on exposure to the air; if heated, it develops ethereal oil of mustard, leaving behind sulphate of baryta. A solution of myronate of potash gives with zinc and hydrochloric acid sulphuretted hydrogen, and then contains a salt of ammonia, sugar, and half of the sulphur as sulphuric acid. Boiling hydrochloric acid decomposes similarly. Concentrated potash-lye digested on the dry salt, and heated, develops volatile oil of mustard, cyanide of allyl, and ammonia. If to a watery solution of myronate of potash, myrosin is added, volatile oil of mustard, sugar, and bisulphate of potash are formed; thus,

$$C_{10}H_{18}K.NS_2O_{10} = C_4H_5NS + C_6H_{12}O_6 + SHKO_4,$$

the same reaction takes place if the freshly-prepared watery extract of the white or black mustard seeds be added.

§ 120. *The Fixed Oil of both Black and White Mustard appears to be identical.*—It is a yellow, non-drying oil of 0·915 to 0·920 specific gravity at 15°C., solidifying from −12° to −16°C., and of a mild taste. It contains the glycerides of erucic acid, of stearic acid, and of oleic acid, which last Darby considers different from ordinary oleic acid.

Erucic Acid, $C_{22}H_{42}O_2$, was discovered by Darby in the fatty oil of the seeds of the white and black mustard in 1849, and the same acid has also been found in rape oil. It is easily obtained by saponifying the oil with litharge, treating the soap with ether, which dissolves out the erucate of lead, and decomposing the salt with hydrochloric acid. The erucic acid in solution is filtered from the chloride of lead, the filtrate evaporated in the water-bath, and the residue recrystallised from ether. Erucic acid forms slender, long, white, glittering needles, without odour or taste, melting at from 33° to 34°, and coagulating again at 33°C.; it is insoluble in water, but dissolves easily in alcohol and ether. The acid, exposed to the air, gradually becomes coloured and rancid. If to water saturated with erucic acid bromine be added gradually, a crystalline compound can be obtained, $C_{22}H_{42}B_2O_2$, which crystallises out of alcohol in small, white, warty masses, melting at 42° to 43°. Again, if the solution be decomposed with hydrochloric acid and sodium amalgam, it can again be changed back to erucic acid. Erucic acid forms definite salts, of the formula $C_{22}H_{41}NO_2$.

§ 121. *The Volatile Oil of Mustard*, C_4H_5NS, is mixed with cyanide of allyl, which may be separated by fractional distillation. Ordinary distillation of black mustard seeds yields it in the proportion of 0·5 to 0·7 per cent. It is colourless or slightly yellow; has a boiling point of 148°C., and specific gravity 1009 to 1010; is somewhat soluble in water, dissolving easily in alcohol, ether, and petroleum ether. According to Hager (*Pharm. Centralb.*, x. 65), the commercial oil is much adulterated; he enumerates as fraudulent additions, alcohol, bisulphide of carbon, oil of gilliflowers, and castor oil. The volatile oil of mustard prevents the coagulation of serum albumen, as well as alcoholic fermentation. According to Mitscherlich, this is the most deadly of all the ethereal oils, 4 grms. killing a kitten in two hours, 15 grms. in a quarter of an hour. The post-mortem appearances were those of acute gastroenteritis, and the smell of the oil pervaded the blood, urine, and lungs. It has been used in medicine, chiefly externally, for its powerful rubefacient properties, blistering the skin when applied to it.

§ 122. *Adulterations.*—The adulteration most commonly met with is a dilution of ground mustard with turmeric and wheat flour. Other substances usually enumerated as having been fraudulently mixed with mustard are—cayenne pepper, ginger, gamboge, potato starch, pea flour, radish and rape seed, linseed meal, yellow ochre, chromate of potash, plaster of Paris, and clay, besides the ground seeds of the *Sinapis arvensis.*

A careful microscopical examination by both ordinary and polarised light will detect most organic adulterations. If on the addition of iodine to an infusion of the mustard in hot water, no blue colour is produced, it is certain that neither wheat nor any other starch is present.

The chemical examination of mustard, for the purposes of the food analyst, mainly resolves itself into—

1. Testing for turmeric.
2. Estimation of the total sulphur.
3. Estimation of the fat or oil.
4. Estimation of the ash.
5. Testing for gamboge.

1. *Testing for Turmeric.*—The detection of turmeric by its microscopical appearance is usually satisfactory; there are, however, some good chemical tests.

A. Extract the mustard with two or three times its volume of methylic alcohol, filter, and evaporate to dryness. If turmeric be present, the addition of hydrochloric acid to the extract will produce a red-orange-green colour, turned by excess of an alkali to green and blue; or the extract may be dissolved in the least possible quantity of methyl alcohol, and evaporated to dryness in a porcelain capsule, in which there has been placed a small piece of filter paper. When the evaporation is complete, the paper is moistened with a strong solution of boric acid, and then dried; if turmeric be present, the paper will take a reddish colour; if it be then treated by an alkali, there is a play of colours, among which green and purple predominate.

B. Advantage may be taken of the fact, that the colouring matter of turmeric is strongly fluorescent; that of mustard, on the other hand, is devoid of fluorescence. The simplest method to detect the fluorescence of the yellow colouring matter of turmeric, when mixed with mustard, is to pass a little castor oil through the suspected sample on a filter; the oil, if turmeric be present, shows a very distinct green colour; this is a test of considerable delicacy. Or an alcoholic solution may be placed in a test-tube, and held vertically in water contained in a glass blackened internally; if the observer now slightly incline the top from the window, and look from above *outside* the test-tube, the green fluorescence, if present, will be readily observed.

2. *Estimation of the Total Sulphur.*—Most of the adulterants of mustard contain no sulphur, or at least no very appreciable amount, in the unoxidised state. Mustard, on the other hand, in common with a large number of cruciferous plants, contains sulphur-organic compounds; hence a great deficiency or excess of sulphur is indicative of adulteration, a normal amount no conclusive sign of purity.

The writer found that white mustard seeds, ground by himself, gave as the mean of sixteen experiments 1·8631 per cent. of total sulphur—the lowest determination being 1·2 per cent., the highest 2·5 per cent.; the mean quantity of sulphur in the ash being ·3483 per cent.

Black mustard, oxidised in a similar manner, gave 1 per cent. of total sulphur, while the ash gave ·22 per cent. Thus black mustard contains less sulphur than white mustard.

The best method to oxidise the sulphur compounds the writer has found to be as follows:—About 1 grm. of the substance is placed in a flask adapted to an upright Liebig's condenser, and digested for some time at a gentle heat with fuming nitric acid. The resulting liquid filters with ease, and the sulphates are precipitated in the usual way with a solution of chloride of barium, the precipitate thoroughly washed, dried, ignited, and weighed; sulphate of baryta multiplied by ·13734 = sulphur. On now making a determination of the sulphates contained in the ash, and subtracting the latter from the former, the amount of *organic sulphur* is obtained.

3. *Estimation of the Fat or Oil.*—This is particularly useful when wheat starch is the adulterating agent. Wheat flour does not contain more than 1·2 to 2·1 per cent. of oil; mustard, on the other hand, from 33·9 to 36·7 per cent. A weighed portion of the previously dried sample may be placed in the little apparatus figured at p. 109. As a rough guide the following formulæ may be used:—

x Amount of mustard, y of oil found.

$$\frac{33{\cdot}9x}{100} + \frac{1{\cdot}2(100 - x)}{100} = y$$

$$\frac{36{\cdot}7}{100} + \frac{2(100 - x)}{100} = y$$

4. *Estimation of the Ash.*—The ash is taken in the way already described (see p. 4). The total ash of dried mustard averages

5 per cent. The highest number the writer has obtained is 5·3 per cent., the lowest 5·088 per cent. Of this ash 1·2 at least is soluble in water; in other words, the ash of mustard consists of 30 parts per cent. soluble, 70 parts per cent. insoluble in water. It hence follows, that if found above 5·5 per cent., mineral matters of foreign origin are present; if below 4 per cent., it is an indication of some organic adulterant.

5. *Gamboge.*—Gamboge as an adulterant of mustard, is somewhat apocryphal; if suspected of being present, an alcoholic extract of the mustard must be prepared; such an extract when treated with caustic soda becomes of a bright red colour, hydrochloric acid produces a yellow colour.

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II.—PEPPER.

§ 123. Black pepper is the dried *immature* fruit of *Piper nigrum*, one of the *Piperaceæ*, or pepperworts.

White pepper is the same berry decorticated, or deprived of ts outer and black husk or covering.

The pepperworts are a well-defined natural order, confined to he hottest parts of the world, and delighting in low places, alleys, and the banks of rivers. Although neither the number f its genera nor of its species is great, yet the whole order is emarkable for a variety of active and useful plants—*e.g.*, the romatic black and long peppers, the astringent matico, the ntoxicating *Macropiper methysticum*, the different varieties of ubebs useful in the treatment of inflamed mucous membranes, and several other plants possessing medicinal properties,* belong to the natural order of *Piperaceæ.*

Black pepper itself is a climbing plant, attaining the height of from 8 to 12 feet; the berries—or, botanically speaking, "drupes"—are at first green, then red, and if left still longer ungathered, turn to black; but before this latter change takes place the berries are gathered by hand and dried in the sun, the result being an entire change of appearance; instead of a red, smooth berry, a black or reddish-black peppercorn, with the cortex contracted and shrivelled in such a manner as to form a veined network, is obtained. The plant is cultivated in various portions of the equatorial regions of the earth, the zone of cultivation being confined to the isotherms of 82°. It would not, however, be strictly correct to say that this high mean annual temperature is essential, or even necessary; for the fact is, that it is produced principally in the cooler valleys, where the mean annual temperature does not perhaps exceed 70°F.

The black pepper imported into this country principally comes from the islands of Malacca, Java, Borneo, and Sumatra. The commercial varieties are at least five—viz., Malabar, Penang, Sumatra, Trang, and Tellicherry, names indicating the localities whence they are derived. The differences which these different varieties of pepper present *to the eye* are evident enough when the several samples are at hand for comparison; but it takes a very practised observer to identify a solitary sample; and if samples of each of the kinds named were mixed together, it is doubtful whether an adept even could separate the berries again, identifying each sort with any correctness. The merchant, indeed, relies more upon the weight than the appearance; he takes a handful of peppercorns, and by long practice can tell in a moment whether it is a light or a heavy sample. Chevallier has determined the weight of what is technically called heavy, half-heavy, and light pepper. A litre of the first weighed 530 grms.; of the second, 512 grms.; of the third, 470 grms. That there is considerable difference in weight in the different berries is certain, for the writer carefully weighed 100 berries of each kind, with the following result:—

	Grammes.
100 peppercorns of Penang weighed . .	6·2496
100 ,, Malabar ,, . .	6·0536
100 ,, Sumatra ,, . .	5·1476
100 ,, Trang ,, . .	4·5736
100 ,, Tellicherry ,, . .	4·5076

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* The *Artanthe eucalyptifolia* is used in Brazil in case of colic; *Piper parthenium,* used in menstrual disturbances; *Chapica betle* and *Siriboa* cause

If, then, quality is to be judged of by weight, Penang and Malabar may be bracketed together as standing first, Sumatra holding the second place, and Trang and Tellicherry bracketed together in the third. The general opinion of the trade is, that Malabar is really the heaviest, and possibly the samples of Penang which the writer possesses are unusually fine. The whole of the ground peppers of commerce are mixtures of different kinds of pepper; there is no such thing to be found in the shops as a pure ground Malabar or a pure ground Penang. The principal varieties mixed for household purposes and retailed are Malabar, Penang, and Sumatra; the first of these is the dearest.

The usual mixture, according to Chevallier is—

33 per cent. of Malabar to give weight,
33 ,, Penang ,, strength, and
33 ,, Sumatra ,, colour.

The pepper thus mixed is either ground by the aid of large millstones, or in an apparatus perfectly analogous to a coffee-mill. The latter mode is far preferable to the former, as the friction of the stones develops considerable heat, and dissipates some of the aromatic principles. Pepper thus damaged by the heat of the mechanical operations is technically known as "burnt."*

§ 124. *Structure of Pepper.*—A thin section of the pepper berry shows, from without inwards (1.) a layer of elongated cells, large and distinct, having a central cavity from which numerous lines radiate towards the circumference; (2.) a layer of small, angular, dark-coloured cells; (3.) a thin stratum of woody fibre and spiral vessels; (4.) a layer of large round cells; (5.) a tissue divisible into two layers, the outer consisting of coloured cells, the inner colourless, and really constituting a membrane.

Pepper contains an alkaloid (*Piperin*), a volatile oil, and an acrid resin, besides gum, starch, vegetable albumen, salts, and other substances.

§ 125. *Oil of Pepper* has a specific gravity of from 0·86 to 0·99, and a boiling point 167° to 170°C. It is a clear fluid, possessing a mild taste, and corresponds to the formula $C_{10}H_{16}$. Both white and black pepper contain a little more than 1 per cent. of this oil.†

§ 126. *Piperin*—($C_{17}H_{19}NO_3$)—was discovered by Oerstedt in 1819; it is found in white, long, and black pepper, in *Chavica*

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salivation and decrease the function of the skin. Besides these, *Acrocarpidium hispidulum*, *Coccobryon capense*, *Artanthe adunca*, *Chavica adunca*, and others, possess active and useful properties.

* From Art. Pepper in the Author's "Dict. of Hygiène."

† Dumas.—*Journ. Chim. Med.*, xi. 308.

officinarum, in cubebs, in the berries of *Schinus. mollis*, and in the bark of *Liriodendron tulipifera*. When pure piperin crystallises, in colourless, brilliant, four-sided prisms, it is almost tasteless, and presents no alkaline reaction. It melts to an oily mass at about 100°C., solidifying in a resinous form; is soluble in petroleum ether, alcohol, ether, the volatile oils, benzole, chloroform, and creosote. Concentrated nitric acid changes it into an orange-red resin; if this be treated with a solution of caustic potash, a blood-red colour is produced, and on boiling piperidin developed. Long heating with alcoholic potash decomposes piperin into piperidin and piperinate of potash, and the same substance is quickly developed by heating with soda lime.

§ 127. *Piperidin*—$C_5H_{11}N$ (best obtained by dry distillation of piperin with three times its weight of soda lime)—is a clear, colourless, bitter, strongly alkaline fluid, which boils at 106°, and has an odour both of pepper and ammonia. It dissolves in water and alcohol in all proportions, and forms good crystalline salts with acids.

§ 128. *Piperic Acid*—$C_{10}H_{12}O_4$—is obtained by boiling piperin with alcoholic potash, decomposing the piperate of potash by the addition of HCl, and subsequent purification of the acid by crystallisation from alcohol. The acid is in the form of yellow hair-like needles, some of which may be sublimed undecomposed; they dissolve easily in boiling alcohol, but are scarcely soluble in water.

§ 129. *The Ash of Pepper.*—The following is an analysis of the ash of Tellicherry pepper:—

	100 Grms. of Ash.
Potash,	24·380
Soda,	3·226
Magnesia,	13·000
Lime,	11·600
Iron,	0·300
Phosphoric Acid,	8·470
Sulphuric Acid,	9·613
Chlorine,	7·570
Carbonic Acid,	14·000
Sand,	6·530

Of all of these constituents the sand is the most variable. The highest determination of sand which the writer has as yet met with, occurred in a sample of Penang pepper, which gave 9 parts of sand in every 100 of ash; but if we allow that a pepper ash may contain 10 parts in every 100 of sand, how on any theory, except that of wilful adulteration, can we account for the fact of the ground pepper of commerce yielding to the analyst an ash one-third or one-half of which is very commonly found to consist of sand? The iron, part of which is magnetic, the alkaline earths, the chlorine, the alkalies, all vary somewhat; but there is one constituent which is extremely constant, and may be of technical utility, and that is the phosphoric acid. The phosphoric acid averages 8·5 per cent. of the ash. Pepper also has very minute quantities of carbonate; a sample of finely powdered Malabar pepper, treated with acid, and placed in an absorption apparatus connected with an aspirator, which drew through the solution perfectly dried carbonic acid free air, yielded ·657 milligramme of CO_2, or about ·143 per cent. of the ash; hence the 10 or 11 per cent. of CO_2 in the ash must be produced from the organic salts, &c.

Nitrates and Nitrites in Pepper.—Comparatively few observations of the amount of nitrates and nitrites in organic substances are on record: it is a subject of some scientific interest, especially since it has been observed that nitrates and nitrites are decomposed in the presence of free oxalic acid. Whether the determination of nitric acid will be of service to the food analyst or not is unknown: it certainly may be so, if it be found that a substance rich in nitrates is fraudulently mixed with one poor in nitrates.

				Calculated as Nitric Acid. Grms.
100 grms.	undried	Penang	pepper yield	0·04470
,,	,,	Malabar	,,	0·03858
,,	,,	Tellicherry	,,	0·08860
,,	,,	Sumatra	,,	0·06560
,,	,,	Trang	,,	0·11870

§ 130. *General Composition of Pepper.*—In a sample of Penang pepper analysed by the writer:—

	Per cent.
Volatile Oil, ...	1·04
Acrid Resin, ...	1·77
Piperin, ...	5·17
Substances soluble in water, gum, starch, and other matters, subtracting ash,	14·74
Substances insoluble in alcohol and water,	67·75
Water, ...	9·53
	100·00

The following table exhibits some analyses made by the writer n 1876 of genuine black peppers, and may be compared with imilar determinations of white and long peppers:—

General Composition of Commercial Peppers.

	Hygroscopic Moisture.	Piperin in Pepper dried at 100° C.	Resin in Pepper dried at 100° C.	Aqueous Extract in Pepper dried at 100° C.	Ash in Pepper dried at 100° C.	
					Soluble in water.	Total.
	Per cent.	Per cent.	Per cent.	Per cent.		
Penang,	9·53	5·57	2·08	18·33	2·21	4·18
Tellicherry,	12·90	4·675	1·70	16·5	3·38	5·77
Sumatra,	10·10	4·702	1·74	17·59	2·62	4·31
Malabar,	10·54	4·632	1·74	20·37	3·45	5·19
Trang,	11·66	4·600	1·70	18·17	2·53	4·77
White Pepper, Commercial,	10·30	5·600	2·05	...	0·56	1·12
Long Pepper,	...	1·800	0·80	16·82	4·47	8·30

§ 131. *Analysis of Pepper.*—The ash and hygroscopic moisture are estimated in the usual manner. The commercial value of a pepper ought to bear a definite relation to the piperin and acrid resin, so that the latter constituents are the most important to determine.

There are two methods of estimating the piperin and resin :—The one is to exhaust thoroughly the finely powdered pepper with strong alcohol, evaporate, and weigh the extract, which practically consists of nothing but resin and piperin. The latter is now separated by digestion with soda-lye, which dissolves the resin, leaving insoluble the piperin, which may be redissolved in strong alcohol, filtered, evaporated, and weighed as piperin. The other process which, on the whole, is preferable, is to dissolve the piperin out by petroleum ether, and purify the extract thus obtained as before. Some chemists, again, first extract with alcohol, and then treat the alcoholic extract with petroleum ether, a method which is equally valid, but not, perhaps, so convenient as the second given.

§ 132. *Adulterations of Pepper.*—Pepper has been adulterated for at least two centuries and a half; for Pierre Pomet,* writing in 1614, says, "As the greatest part of pepper, white as well as black, is sold '*battu*' (that is to say, powdered), it should only be bought of honest merchants; because all the pepper the retailers sell is no other thing for the white than '*épices d'Auvergne blanchées*,' or rather black pepper whitened with ground rice ; the

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* Pomet, "Hist. Gén. des Drogues," 1735.

black is only the dust either of the crust of bread, grey Auvergne spices, or manignette."

The list of the adulterations enumerated by authors is an extraordinary one. Linseed meal, rice, pepper leaves, mustard, wheat flour, sago, woody fibre, chillies, rape-seed, potato, spices, capsicum, manignette (otherwise known as Guinea pepper), chicory, rye, powdered leaves of the laurel, which had been previously used to wrap round extract of liquorice, the stones from olives, bone-dust, marine salt, and various mineral adulterations, are all said to have been detected.

However various may be the adulterations in France (where, Chevallier tells us, in Paris alone he is acquainted with a manufactory producing 1,200 to 1,500 kilogrammes annually of a mixture sold solely for the purpose of adulterating pepper), the only common adulterations of this country are what are known in the trade as P.D., H.P.D., and W.P.D., abbreviations for pepper-dust, hot pepper-dust, and white pepper-dust; the first, or P.D., used to be principally composed of faded leaves, but linseed meal is now preferred; H.P.D. is chiefly the husks of mustard; and W.P.D. is ground rice. To all these we must add sand, which is most certainly used, though whether derived from the sweepings of the shops, or added as sand, is by no means clear. The sand, of course, influences the weight of the ash, which should never exceed 7 per cent.

Dr. Hassall made some determinations of the ash of some fifteen or sixteen commercial samples of black pepper; of these only one was under 5 per cent., the percentages of the other fifteen being distributed as follows:—

One	gave between	5 and 6	per cent.	of ash.
Three	,,	6 and 7	,,	,,
Three	,,	7 and 8	,,	,,
Seven	,,	9 and 10	,,	,,
One	,,	11 and 12	,,	,,

It is difficult to believe that more than 2 per cent. of unavoidable mineral dust can get into the pepper by grinding, &c., and the inference naturally is that most of the above samples were adulterated. The maximum percentage of ash from genuine pepper which the writer has obtained is 5·3 per cent.

Besides the formidable list of adulterations already mentioned, the berry itself is not free from manipulation; for, as the merchant judges by the weight of the sample, means are taken to render the lighter sorts equal in weight to the heavy Malabar and Penang, and in order to do this they are macerated in tubs of brine for twenty-four hours, and thus impregnated with salt and water, find their way into the market as Malabar; but such samples are quickly recognised by the astute merchant; and the high chlorides, the high ash, the great amount of humidity, could hardly fail to reveal their nature to the analyst.

As coffee has been cleverly imitated by chicory pressed into the shape of the coffee-berry, so by pressing various pastes into the shape of the pepper-berry has pepper been imitated. Of this adulteration there is the most undoubted evidence. Accum noticed artificial peppercorns made of oilcake, common clay, and Cayenne pepper, and Chevallier, in a recent paper, states that in 1843 he was requested to examine a sample taken from forty bales, in which he found from 15 to 20 per cent. of artificial pepper, composed of pepper-dust, bran, and other matters.*

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III.—CAYENNE PEPPER.

§. 133. Cayenne pepper consists of the powdered pods or see vessels of the *Capsicum annuum*, a plant belonging to the natur order *Solanaceæ*. It is a native of America, but is also cultivate

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* Art. Pepper in author's "Dict. of Hygiène."

to a slight extent in the greenhouses of England and other European countries. It is sold entire under the name of *Chillies.* The microscopical structure of the capsules is somewhat peculiar: the epidermis is formed of cells the walls of which are thick, flattened, tortuous, well defined, and punctuated here and there; frequent drops of a reddish-orange oil occur, especially in the parenchyma, which is formed of thin-walled, rounded cells. The envelope of the grain itself, when cut in thin vertical sections, presents a very singular appearance, that of radiating dentiform processes, the apex of each being apparently fixed in the outer membrane. The substance of the seed proper is composed of small angular cells, with thick colourless walls, filled with granules and a yellow-orange oil, but without starch.

Cayenne pepper, as met with in commerce, is in the form of a somewhat coarse, brick-dust like powder, the least particle of which, if heated strongly, volatilises a very acrid vapour, causing intense irritation of the throat. This sensation can be produced by so minute a portion of cayenne, that any foreign substance mixed with it could in this way be detected; it would be only necessary to separate carefully, by the aid of the microscope and a camel's-hair brush, all particles of cayenne, and heat the portion suspected; if no acrid vapours were given off, the substance could not be cayenne. This intense acridity appears to be due to a body recently discovered by Mr. Thresh, and named by him Capsaicin.

§ 134. *Capsaicin*—($C_9H_{14}O_5$), specific gravity 1060—is in the form of minute crystals, which melt at 55·5°C. (138°F.), volatilise unchanged at 115·5°C. (240°F.), and at 120°C. (248°F.), become brownish-black. It may be obtained by exhausting cayenne by petroleum, evaporating the petroleum, and treating the extract thus obtained by dilute solution of potash; on now saturating the solution with carbonic anhydride, it is precipitated in very small crystals. It dissolves slightly in cold, and more readily in boiling, water; is easily soluble in alcohol, proof spirit, ether, amylic alcohol, acetic ether, acetic acid, benzine, the fixed oils, and solutions of the alkalies. It dissolves slowly in turpentine and carbonic disulphide; when pure, petroleum does not dissolve it readily, but the presence of the red oil in the pepper increases its solvent powers; it is totally insoluble in solutions of the carbonates of the fixed alkalies, and in ammonia. Silver nitrate gives a precipitate with alcoholic solutions of capsaicin; it also yields white precipitates with barium and calcium chlorides. It is powerfully pungent, causing, if volatilised, severe fits of coughing.

It would appear that capsaicin is not contained in the substance of the seed; for if the pericarp be carefully separated, the seeds are entirely devoid of acrid taste.

Mr. Thresh has also described a conium-like alkaloid, obtained by exhausting the pericarp with benzine, evaporating, dissolving in ether, shaking the solution with dilute sulphuric acid, partially neutralising with barium carbonate, and evaporating to a small bulk. Some red fat now separates, and after the removal of this (upon adding an excess of alkali, shaking with ether, and evaporating) a brown residue is obtained, smelling like conium, and giving precipitates with Nessler reagent, iodine, and iodides of potassium and cadmium.

The acrid oil *Capsicol*, *Capsicin*, and other substances described by Bucholz, Bracannot, Buchheim, &c., are undoubtedly mixtures. The general composition of cayenne pepper may, however, be gathered from the following analyses, one made in 1816 by Bucholz, the second in 1817 by Bracannot, of course neither taking cognisance of capsaicin :—

Bucholz's Analysis.

Acrid soft resin (capsicum), . . .	4·0
Wax, ...	7·6
Bitter aromatic extractive, . . .	8·6
Extractive, with some gum, . . .	21·0
Gum, ...	9·2
Albuminous matter, ...	3·2
Woody fibre, ...	28·0
Water, ...	12·0
Loss, ...	6·4
Fruit of *Capsicum annuum*, without seeds, ...	100·0

Bracannot's Analysis.

Acrid oil, ...	1·9
Wax and red colouring-matter, . .	0·9
Brownish starchy matter, . . .	9·0
Peculiar gum, ...	6·0
Animalised matter, ...	5·0
Woody fibre, ...	67·8
Salts: extract of potash, 6·0; phosphate of potash, and chloride of potassium, 3·4,	9·4
Fruit of *Capsicum annuum*, . . .	100·0

The hygroscopic moisture ranges in different samples from 10 to 13 per cent. The writer analysed several samples of genuine cayenne, and the mean of these analyses was as follows :—

Aqueous extract of dried cayenne,	32·1	per cent.
Alcoholic extract,	25·79	„
Benzole extract,	20·00	„
Ethereal extract,	10·43	„
Ash,	5·693 (soluble, 3·32)	„
Total nitrogen in 100 grms.,	2·04	„

Hence the ash of cayenne should not exceed 6 per cent.; it should yield at least one quarter of its weight to alcohol, and from 9 to 10 per cent. to ether.

§ 135. *The Adulterations of Cayenne* usually enumerated are: all kinds of red mineral powders, from brick-dust to cinnabar, and a few starches. There does not appear, however, to have been any conviction recently for the adulteration of cayenne, and the numerous samples the writer has examined were all genuine. Most of these additions would be easily detected in the ash, or by the microscope. Cinnabar is highly improbable; for its detection, see *Mercury*, in the second portion of this work.

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IV.—THE SWEET AND BITTER ALMOND.

§ 136. The sweet almond, the seed of *Amygdala communis*, and the bitter almond, the seed of *Amygdalus communis*, var. *Amara*, enters either in whole or in part into so many articles of food (such as sweetmeats and pastry, and as a flavouring ingredient into certain drinks), that it is absolutely necessary to be acquainted with its chemical composition. Both varieties of almond agree in containing about 50 per cent. of a bland fixed oil (consisting chiefly of olein, and liable to become rancid), as well as an albuminous principle, emulsin, sugar, gum, and woody fibre; but only in the bitter almond is found, in addition to the foregoing, *amygdaline*.

§ 137. *The Oil of Almonds* is a thin fluid oil, of a clear yellow colour, specific gravity 0·914 to ·920, not coagulated by cold if − 10° −; at − 16° it becomes cloudy, and at − 22° it solidifies to a white butter. Oil of almonds appears to be rather frequently adulterated with other oils.

2·5 drops of the oil, shaken with an equal bulk of nitric acid (specific gravity 1·20) and bisulphide of carbon, should not show any colour after standing a few minutes; if it becomes within half an hour yellow, or reddish-yellow, the change indicates oil from *cherry* or *apricot kernels.*

The following test will detect drying oils:—Dissolve 1 part of starch in 3 parts of warm nitric acid, of 1·20 specific gravity, and warm in a capacious vessel over the water-bath with 10 parts of almond oil, until all evolution of gas ceases. The oil after cooling is within two days changed into a warty, crystalline, greasy mass of elaidin. Should it, however, contain a drying oil (*poppy*, for example), it either remains quite fluid or semi-fluid, according to the proportion of the adulterant present. The colour of the elaidin is also a guide; that produced by the sweet almond is pure white, by the bitter, yellowish-white, and by the small or inferior kinds of almonds, brownish-yellow; if the elaidin should be red, it denotes adulteration of some foreign oil, especially of *sesame.*

Pure almond oil dissolves in 25 parts of cold and 6 of hot alcohol. The above tests, and in addition the low temperature required for congelation, should detect all ordinary adulterations.

§ 138. *Amygdaline* ($C_{20}H_{27}NO_{11}$) is a glucoside, discovered in 1830 by Robiquet and Boutron-Charlard. It may be extracted from almond-cake by boiling alcohol of 95 per cent., and then precipitated from the somewhat concentrated alcoholic solution by ether. Amygdaline[*] crystallises from 80 per cent. alcohol in colourless, glittering scales, containing 2 atoms of water; it can also be obtained in crystals. Amorphous amygdaline of the

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[*] Lehmann, in his recent elaborate researches, found the method of Liebig and Wohler the best for obtaining *crystalline* amygdaline. The process consists in boiling the substance with strong alcohol (of 94 to 95 per cent.) twice successively, after having first removed the fixed oil by petroleum benzine, concentrating to about one-half or one-sixth of its volume; and then adding ether, which precipitates the amygdaline, and removes any of the remaining fixed oil. Lehmann obtained from

Bitter almonds, . .	2·5	per cent. crystallised amygdaline.
Cherry-kernels, . .	0·82	,, ,, ,,
Plum-kernels, . .	0·96	,, ,, ,,
Apple-seeds, ...	0·60	,, ,, ,,
Peach-kernels, . .	2·35	,, ,, ,,
Cherry-laurel leaves, .	1·38	per cent. amorphous amygdaline.
Bark of *Rhamnus frangala,*	0·7	,, ,, ,,

Both of these latter substances contain hydrocyanic acid ready formed.

before-mentioned cherry-laurel leaves and buckthorn bark is best obtained by the following method :—The dried buckthorn bark is boiled with absolute alcohol, agitated with lead oxide, and evaporated to dryness. Dried in a vacuum over SO_4H_2 it forms a brittle, yellow, transparent, resin-like mass, which, when heated to 100°C., becomes dark-brown ; it can be dissolved by boiling alcohol and by water, but is insoluble in ether. Although amorphous, it is a crystalloid with 3 atoms of water, as proved by dialysis from water or weak spirit, but in such a case it loses 1 atom if dried over sulphuric acid. At 100° to 120° it may be obtained anhydrous.

Amygdaline possesses no smell ; it has a slightly bitter taste ; its reaction is neutral, and it polarises to the left $[a]\ r = -35{\cdot}57°$. It dissolves in all proportions in boiling water, and in 12 parts of cold of 10°C. ; requires 148 parts of alcohol, specific gravity 148, 904 parts of alcohol, specific gravity 0·819, if cold—but if boiling, 11 parts of the first and 12 of the last ; it is insoluble in ether. It melts at 120° and begins to carbonise at 160°, when it develops a caramel smell, and is at length fully destroyed.

Amygdaline, by the action of dilute acids, splits up into sugar, volatile oil of almonds, and formic acid. If boiled with solutions of potash or baryta it forms ammonia and amygdalic acid. The most interesting decomposition is, however, that which takes place by the action of emulsin ; it then breaks up into volatile oil of almonds, hydrocyanic acid, and formic acid. (See *Prussic Acid,* in the second part of this work.)

Volatile Oil or Essence of Almonds does not exist as such in the bitter almond ; it is, as above explained, the result of a decomposition of the amygdaline. The oil of almonds, when properly purified from prussic acid, is identical with the hydride of benzole, C_7H_5OH. It is colourless, thin, turning a ray of polarised light to the right, of a peculiar, pleasant odour, and a burning aromatic taste. Its specific gravity is 1·043 to 1·07, usually 1·06 (*Hirsch*). Its boiling point is 180°. By the action of light and air it is gradually oxidised into benzoic acid. It is soluble in equal parts of alcohol, ·083 specific gravity, and in about 30 parts of water. The ethereal or volatile oil is officinal in the French, Swiss, and Norwegian pharmacopeias. The ethereal oil is much adulterated. The analyst will specially look for alcohol, prussic acid, nitrobenzine, and ethereal oils.

If *alcohol-free,* the addition of an equal weight of fuming nitric acid produces no effervescence, and after two or three days the mass becomes emerald green, and crystals of benzoic acid appear. On the other hand, if it contain alcohol from 0·08 per cent. upwards, there is immediately a strong effervescence. Some of the tests given for alcohol at p. 127 may also be of service.

The detection and estimation of *prussic acid* in the essence is carried out on the principles detailed in the article on *Prussic Acid.*

Nitrobenzine is indicated when the essence is not entirely soluble in a solution of bisulphate of potash, and the specific gravity is higher than 1·07, the specific gravity of nitrobenzine being 1·20 to 1·29; the boiling point will also be raised. In such a case nitrobenzine should be specially tested for, by changing it into aniline by reducing agents. For this purpose 10 parts of dilute sulphuric acid (specific gravity 1·117) may be added to 10 of granulated zinc and 1 part of the essence. At the end of two hours (after frequent agitation) the fluid is passed through a moistened filter, and a crystal of chlorate of potash added to the filtrate with a drop of concentrated sulphuric acid. If a violet or red colour is produced, it is due to the presence of an aniline salt, produced from nitrobenzine; but if there is no coloration, nitrobenzine must have been absent.

Another special method used for the detection of nitrobenzine was proposed by Maisch:—1 grm. of the essence is dissolved in twelve times its volume of alcohol, ·75 of caustic melted potash is added, and the whole heated until the liquid is diminished to about one-third. The pure essence, on cooling, is of a light brown colour, and dissolves entirely in water; but if nitrobenzine is present, the residue is brown, crystalline, and insoluble in water.

The action of sodium on the essence may also be utilised as a test:—Pure almond essence, when treated with sodium, gives white flocks; if nitrobenzine should be present, the sodium is immediately covered with yellow or brown flakes, according to the amount of adulteration; if the percentage rises as high as 0·30 to 0·50, the whole liquid after a minute becomes thick and opaque.—(*Dragendorff.*)

However, the action of potash alone on a sample adulterated with nitrobenzine is tolerably conclusive. If 1 grm. of the essence is treated in a test-tube with half its weight of pure caustic potash, a yellow coloration is produced, should the essence be pure; but if nitrobenzine be present, the tint soon becomes yellowish-red, and at the end of a minute green. On the addition of a little water, the mixture separates into two layers, of which the lower is yellow and the upper green, the latter changing in the course of a day into red. Most foreign *ethereal oils* may be detected by the bisulphate of soda test:—If a little of the pure essence be dropped into a warm solution of this salt, of from 1·24 to 1·26 specific gravity, shaken, and then diluted with hot water, it is fully dissolved; other essences, on the contrary, are insoluble.

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V.—ANNATTO.

§ 139. Annatto is a colouring matter obtained from the seeds f the *Bixa orellana*, chiefly prepared in Brazil and Cayenne. Although not used itself as a food, it enters into several articles f consumption, and has been employed to colour milk, butter, nd cheese.

Characters, Microscopical.—When annatto is examined by the icroscope, the outer red portion presents an almost homogeneous ppearance, and the surface of the seed proper consists of narrow r elongated cells or fibres vertically disposed, while the inner hite portion consists of cells filled with starch corpuscles, well efined, of medium size, and resembling in the elongated and ellate hilum the starch granules of the pea and bean.

In manufactured unadulterated annatto, but little structure is et with. Portions of the outer cells may be seen; and in those ecimens, which in the course of their preparation have not been bjected to the action of boiling water, a few starch granules ay be noticed.

Since this is the case with annatto itself, we can the more easily detect the presence of most foreign vegetable substances, such as turmeric powder, the starch of wheat, rye, barley, and sago flours. The salt and alkali present in the annatto generally greatly alter the appearance of the turmeric. Most of the colouring matter of the cells is discharged, so that the starch corpuscles contained within them become visible. Loose starch granules of turmeric may also be frequently seen, and in consequence of the action of the alkali much enlarged.

§ 140. *Chemical Composition of Annatto.*—Dr. John found the pulp surrounding the fresh seed to consist of 28 parts of colouring resinous matter, 26·5 of vegetable gluten, 20 of ligneous fibre, 20 of colouring extractive matter, 4 formed of matters analagous to vegetable extractive, and a trace of spicy and acid matters. The colouring matter consists of a red substance—*bixin*, associated with a yellow *orellin;* the latter has been as yet but little studied.

§ 141. *Bixin*, $C_{15}H_{18}O_4$, when pure, is an amorphous, resinous, cinnabar-red substance. It is scarcely soluble in water and bisulphide of carbon, soluble in about 89 parts of cold, and in 25 of hot, alcohol; in 345 parts of ether, in 93 of chloroform, and also in the caustic and carbonated alkalies. The alcoholic solution is coloured orange-red by lead acetate, brownish-yellow by chloride of mercury and acetate of copper, brown-red by chloride of iron, and it is precipitated yellow by stannous or stannic chloride; concentrated sulphuric acid produces a deep blue. A solution of bixin in an alkaline liquid, on neutralisation with an acid, gives a precipitate of the resin, and in this way it may be purified.

§ 142. *Adulterations.*—Annatto is one of the most adulterated substances met with in commerce, the adulterants being both organic and inorganic. The organic substances used are—turmeric, rye, barley, and wheat flours. The inorganic—sulphate of lime, carbonate of lime, salt, alkali, an oily substance (probably soap), red ferruginous earths (mostly venetian red), red lead, and copper.

When large quantities of flour and lime are used, the colour of the annatto is so reduced that it becomes necessary to use salt, alkalies, and the red earths, to restore it to its original standard. Salt heightens the intensity of vegetable reds, hence its use. Lead is probably introduced into the annatto through the venetian red used. Copper is added to prevent the annatto becoming attacked by fungi.

The following is an analysis by the writer of a fair commercial sample.

No. 1. The sample was in the form of a paste, colour deep red, odour peculiar, but not disagreeable:—

Water,	24·2
Resin,	28·8
Ash,	22·5
Starch and Extractive Matter,	24 5
	100·0

The following is an analysis of an adulterated sample. It was in the form of a hard brown cake, texture hard and leathery, odour disagreeable:—

Water,	13·4
Resin,	11·0
Ash—consisting of Iron, Silica, Chalk, Alumina, and Salt,	48·3
Extractive Matter,	27·3
	100·0

§ 143. The *analysis of annatto*, as may be gathered from the preceding description, principally resolves itself into a determination of the ash, and an estimation of the resin. The former is determined in the usual way, the latter, by exhausting the sample by boiling alcohol, getting rid of the spirit by evaporation, and then redissolving the extract thus obtained in an alkaline solution, and finally precipitating the nearly pure resin by careful neutralisation with an acid.

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SECOND DIVISION.

DETECTION OF POISONS.

PART I.

INTRODUCTORY.

§ 1. In the Toxicological portion of this work, many substances usually discussed in a treatise of the kind have been intentionally omitted, either on account of their properties being well-known, of fatal results from their accidental or premeditated use being rare, or of their detection offering but little difficulty. Such substances are—the strong acids, the caustic alkalies, tartaric acid, nitrate of potash, &c.* A few introductory words, however, on the *general* manner of procedure in investigating for poisons may not be out of place.

In rare instances, the analyst has some good clue (either from the symptoms or the attendant circumstances) to the nature of the poison which has caused death, and can at once pass to the best and most convenient special process for the discovery of the particular substance. In most cases, however, and especially in those where it is doubtful whether death has resulted from disease or from the suspected poison, a very exhaustive and methodical analysis is necessary, and one that will detect the majority of poisons.

§ 2. *Symptoms of Poisoning.*—With regard to symptoms in the investigation of a fatal case of poisoning, the toxicologist will necessarily be guided by the statements of others, for he will rarely have the opportunity of seeing a similar case during life. On this account, therefore, a rough classification of poisons, founded on the principal symptoms they produce, may be found useful :

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* Mohr very correctly observes—"Most toxicological or forensic Manuals re burdened with unnecessary ballast. The history of metals in their netallic state, of the discovery of substances, and the description of all the ompounds of a poisonous metal, do not belong to forensic, but to general hemistry. What relation, for instance, Sal-ammoniac, Saltpetre, Alum, artaric, Citric, and Acetic Acids, the Carbonates of Potash and Ammonia, ave to Toxicology, we cannot conceive."—Dr. F. Mohr, "Chemische oxicologie." Braunschweig, 1874, p. 9.

A. POISONS CAUSING DEATH IMMEDIATELY, OR IN A FEW MINUTES.

There are but few poisons which destroy life in a few minutes. Omitting the strong mineral acids and carbonic anhydride, with the irrespirable gases—*Prussic acid, the cyanides, oxalic acid,* and, occasionally, *strychnine,* are the chief poisons coming under this head.

B. IRRITANT POISONS (symptoms mainly pain, vomiting, and purging).

Arsenic, antimony, phosphorus, cantharides, savin, ergot, digitalis, colchicum, zinc, mercury, lead, copper, silver, iron, baryta, chrome, yew, and *laburnum.*

C. IRRITANT AND NARCOTIC POISONS (symptoms those of an irritant nature, with the addition of more or less pronounced cerebral indications).

To this class more especially belong *oxalic acid,* and *the oxalates;* with several poisons belonging to the purely narcotic class, but which produce occasionally irritant effects.

D. POISONS MORE ESPECIALLY AFFECTING THE NERVOUS SYSTEM.

1. NARCOTICS (chief symptom insensibility, which may be preceded by more or less cerebral excitement): *Opium, chloral chloroform.*

2. DELIRIANTS (delirium for the most part a prominent symptom): *Belladonna, hyoscyamus, stramonium, with others of th Solanaceæ,* to which may be added—*poisonous fungi, Indian hemp, lolium temulentum, œnanthe crocata,* and *camphor.*

3. CONVULSIVES.—Almost every poison has been known to produce convulsive effects, but the only true convulsive poisons ar the *alkaloids of the strychnos class.*

4. COMPLEX NERVOUS PHENOMENA: *Aconite, digitalis, hemlock calabar bean, tobacco, lobelia inflata,* and *curara.*

§ 3. *Method of Procedure.*—Mineral substances, or liquids containing only inorganic matters, can cause no possible difficult to any one who is practised in analytical investigation; but th substances which exercise the skill of the expert are organi fluids or solids.

The first thing to be done is to note accurately the manner which the samples have been packed, whether the seals have been tampered with, whether the vessels or wrappers themselves are likely to have contaminated the articles sent; and then to make a very careful observation of the appearance, smell, colour, and reaction of the matters, not forgetting to take the weight, if solid—the volume, if liquid. All these are obvious precautions, requiring no particular directions.

If the object of research is the stomach and its contents, the latter should be carefully transferred to a tall conical glass; the organ cut open, spread out on a sheet of glass, and examined closely by a lens, picking out any suspicious-looking substance for closer observation. The mucous membrane should now be well cleansed by the aid of a wash-bottle, and if there is any necessity for destroying the stomach, it may be essential in important cases to have it photographed. The washings having been added to the contents of the stomach, the sediment is separated and submitted to a close inspection, for it must be remembered that, irrespective of the discovery of poison, a knowledge of the nature of the food last eaten by the deceased may be of extreme value.

If the death has really taken place from disease, and not from poison, or if it has been caused by poison, and yet no definite hint of the particular poison can be obtained either by the symptoms or by the attendant circumstances, the analyst has the difficult task of endeavouring to initiate a process of analysis which will be likely to discover any poison in the animal, vegetable, or mineral kingdom. This, although theoretically ossible, becomes in practice impossible, and an approximation o it is all that can be aimed at.

Taking one of the most difficult cases that can occur—viz., one n which a small quantity only of an organic solid or fluid is vailable—the best method of procedure is the following:—Place he matters in a retort or flask, and submit them to the gentle eat of a water-bath, condensing any volatile products; if neces-ary, water may be added, and the process continued a reasonable ime; it is then repeated, and should the reaction be alkaline, he substances under examination are first neutralised (or, rather, endered feebly acid) with acetic acid. In this way some indica-on of such poisons as prussic acid and phosphorus can hardly il to be obtained; and in order the more readily to detect the tter substance, it is essential that this preliminary distillation e undertaken in the dark, with the precautions detailed under hosphorus.

The distillation completed, the next step is to dry the sub-ances, which must be effected by the heat of the water-bath. his heat, we may remark, and the distillation mentioned above, may destroy not a few important poisons, but scarcely those of more frequent occurrence. The drying will not be complete unless carried out in open, shallow dishes. The dry residue is now exhausted with hot absolute alcohol, then with alcohol of 90 per cent., and lastly with ether. The ether and alcohol respectively are driven off, and the extracts dissolved in water, and examined, not only for alkaloids and glucosides, but also for organic acids, and those few metallic compounds which, like corrosive sublimate, are soluble in ether or alcohol.

Should this lead to no result, the last step is to reunite all the residues possible, and search for inorganic poison. This is done by distilling the dried substances with pure hydrochloric acid, by means of a sand-bath, and properly condensing the products—an operation which should be repeated twice at least, and each time carried to dryness.

The distillate is saturated with hydric sulphide, and any precipitate collected and examined. The residue in the retort will contain the fixed metals, such as zinc, copper, lead, &c.; it is treated with dilute hydrochloric acid, filtered, the filtrate saturated with SH_2, and any precipitate collected. The filtrate is now treated with sufficient acetate of soda to replace the HCl, again saturated with SH_2, and any precipitate collected and tested for zinc. By this treatment, viz. :—

1. Collecting the volatile products,
2. Searching for alkaloids, glucosides, and organic acids,
3. Destroying organic matter, and searching for metals,

a very fair and complete analysis may be made from a relatively small quantity of material. There is, however, fortunately, in most cases, sufficient material to be obtained in order to admit of division into a convenient number of parts, so that at least one portion may be reserved for the organic and another for the inorganic poisons.

§ 4. *Destruction of Organic Matter*, &c.—The destruction of organic matter through simple distillation by means of pure hydrochloric acid is the most perfect which has been devised, and far superior to that by sulphuric acid, chlorate of potash, and the carbonisation methods. The object of the chemist not being to dissolve every fragment of cellular tissue, muscle, and tendon, but simply all mineral ingredients, the less organic matter which goes into solution the better. That hydrochloric acid would fail to dissolve sulphate of baryta and sulphate of lead, and that sulphide of arsenic is also almost insoluble in the acid, is no objection to the process recommended, for it is always open to the analyst to treat the residue specially for these substances. The sulphides precipitated by hydric sulphide from an acid solution are—arsenic, antimony, tin, cadmium, lead, bismuth, mercury, copper, and silver. Those not precipitated are—iron, manganese, and zinc; of the three last, one alone—viz., zinc—is of any importance.

As a rule, one poison alone is present; so that if there should be a sulphide, it will belong only exceptionally to more than one metal.

The colour of the precipitate from hydric sulphide is either yellowish or black. The yellow and orange precipitates are sulphur, sulphides of arsenic, antimony, tin, and cadmium. In pure solutions they may be almost distinguished by their different hues, but in solutions contaminated by a little organic matter the colours may not be distinctive. The sulphide of arsenic is of a pale yellow colour; and if the very improbable circumstance should happen that arsenic, antimony, and cadmium occur in the same solution, the sulphide of arsenic may be first separated by ammonia, and the sulphide of antimony by sulphide of sodium, leaving cadmic sulphide, which is insoluble in both of these solvents.

The black precipitates are—lead, bismuth, mercury, copper, and silver. The black sulphide is freed from arsenic, if present, by ammonia, and digested with dilute nitric acid, which will dissolve all the sulphides, save those of mercury and tin, so that if a complete solution is obtained (sulphur flocks excepted), it is evident that both these substances are absent. The presence of copper is betrayed by the blue colour of the nitric acid solution, and through its special reactions; lead, by the deep yellow precipitate which falls by the addition of chromate of potash and acetate of soda to the solution; bismuth, through a white precipitate on dilution with water. If the nitric acid leaves a black insoluble residue, this is probably sulphide of mercury, and should be treated with concentrated hydrochloric acid to separate flocks of sulphur, evaporated to dryness, again dissolved, and tested for mercury by iodide of potash, copper foil, &c., as described in the article on *Mercury*. Zinc is likewise tested for in the filtrate as described in the article on *Zinc*.

PART II.

POISONS DETECTED MAINLY BY DISTILLATION-METHODS: HYDROCYANIC ACID—CHLOROFORM—PHOSPHORUS.

I.—HYDROCYANIC ACID.

§ 5. *Hydrocyanic Acid*—Hydric cyanide—specific gravity of liquid 0·7058 at 70°C., boiling point 26·5°C. (80°F.), HCy = 27. The anhydrous acid is not an article of commerce, and is only met with in the laboratory. It is a colourless, transparent liquid, and so extremely volatile that, if a drop fall on a glass plate, a portion of it freezes. It has a very peculiar peach-blossom odour, and is intensely poisonous. It reddens litmus feebly and transiently, dissolves red oxide of mercury freely, forms a white precipitate of argentic cyanide when treated with silver nitrate, and responds to the other tests described hereafter.

§ 6. *Medicinal Preparations of Prussic Acid.*—The B.P. acid is a watery solution of prussic acid; its specific gravity should be 0·997, and it should contain 2 per cent. of the anhydrous acid. 2 per cent. is also the amount specified in the pharmacopeias of Switzerland and Norway, and in that of Borussica (VI. ed.); the latter ordains, however, a spirituous solution, and the Norwegian an addition of ·1 per cent. of concentrated sulphuric acid. The French prussic acid is ordered to be prepared of a strength equalling 10 per cent.

The adulterations or impurities of prussic acid are hydrochloric, sulphuric,* and formic acids. Traces of silver may be found in the French acid, which is prepared from cyanide of silver. Tartaric acid is also occasionally present. Hydrochloric acid is most readily detected by neutralising with ammonia, and evaporating to dryness in a water-bath; the ammonium cyanide decomposes

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* A trace of sulphuric or hydrochloric acid should not be called an *adulteration*, for it greatly assists the preservation, and therefore makes the acid of greater therapeutic efficiency.

and volatilises, leaving as a saline residue chloride of ammonium. This may easily be identified by the precipitate of chloride of silver, which its solution gives on testing with silver nitrate, and by the deep brown precipitate with Nessler solution. Sulphuric acid is, of course, detected by chloride of barium, formic acid by boiling a small quantity with a little mercurous oxide; if present, the oxide will be reduced, and metallic mercury fall as a grey precipitate. Silver, tartaric acid, and any other fixed impurities are detected by evaporating the acid to dryness, and examining any residue which may be left. It may be well to give the various strengths of the acids of commerce in a tabular form:—

	Per cent.
British Pharmacopeia, Switzerland, Norway, and Bor. (vj),	2
France,	10
Vauquelin's Acid,	3·3
Scheeles's ,,	4 to 5*
Riner's ,,	10
Robiquet's ,,	50
Schraeder's ,,	1·5
Duflos's ,,	9
Pfaff's ,,	10
Koller's ,,	25

In English commerce the analyst will scarcely meet with any acid stronger than Scheeles's 5 per cent.

§ 7. *Poisoning by Prussic Acid.*—Irrespective of suicidal or criminal poisoning, accidents from prussic acid may occur—

1. From the use of the cyanides in the arts.
2. From the somewhat extensive distribution of the acid, or rather of prussic-acid-producing substances in the vegetable kingdom.

1. *In the Arts.*—The galvanic silvering† and gilding of metals, photography, the colouring of black silks, the manufacture of Berlin blue, the dyeing of woollen cloth, and in a few other manufacturing processes, the alkaline cyanides are employed, and not unfrequently fumes of prussic acid developed.

2. *In the Vegetable Kingdom.*—A large number of plants contain amygdaline, or bodies formed on the type of amygdaline. In the presence of emulsin (or similar principles) and water, this

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* Strength very uncertain.

† The preparation used for the silvering of copper vessels is a solution of cyanide of silver in potassic cyanide, to which is added finely powdered chalk. Manipulations with this fluid easily develop hydrocyanic acid fumes, which, in one case related by Martin (*Aertzl. Intelligenzbl.*, p. 135, 1872), were powerful enough to produce symptoms of poisoning.

breaks up into prussic acid and other compounds—an interesting reaction usually represented thus—

$$C_{20}H_{27}NO_{11} + 2H_2O = CNH + C_7H_6O + 2C_6H_{12}O_6$$

1 equivalent of amygdaline—*i.e.*, 457 parts—yielding 1 equivalent of CNH or 27 parts; in other words, 100 parts of amygdaline yield theoretically 5·909 parts of prussic acid,[*] so that the amount of either being known, the other can be calculated from it.

The following plants, with many others, all yield, by appropriate treatment, more or less prussic acid:—Bitter almonds (*Amygdalus communis*); the *Amygdalus persice;* the cherry laurel (*Prunus laurocerasus*); the kernels of the plum (*Prunus domestica*); the bark, leaves, flowers, and fruit of the wild service-tree (*Prunus padus*); the kernels of the common cherry and the apple; the leaves of the *Prunus capricida;* the bark of the *Pr. virginiana;* the flowers and kernels of the *Pr. spinosa;* the leaves of the *Cerasus acida;* the bark and almost all parts of the *Sorbus ancuparia, S. hybrida* and *S. torminalis;* the young twigs of the *Cratægus oxycantha;* the leaves and partly also the flowers of the shrubby *Spiræacea*, such as *Spirea aruncus, S. sorbifolia*, and *S. japonica;*[†] together with the roots of the bitter and sweet *Cassava.*

In only a few of these, however, has the exact amount of either prussic acid or amygdaline been determined; 1 grm. of bitter almond pulp is about equal to 2½ mgrms. of anhydrous prussic acid. The kernels from the stones of the cherry, according to Geiseler, yield 3 per cent. of amygdaline; therefore, 1 grm. equals 1·7 mgrm. of HCN. From the kernels of the wild service tree, Hermann separated 1½ per cent. of amygdaline (1 grm. = HCN, ·8 mgrm.); Riegel, from the flower, fruit, and bark, 1 per cent. (1 grm. = HCN, ·6 mgrm.); and Frances,[‡] in a recent research on the prussic acid in cassava root, gives as the mean in the sweet cassava ·0168 per cent., in the bitter ·0275 per cent., the maximum in each being respectively ·0238 per cent. and ·0442 per cent. The bitter fresh cassava root has long been known as a very dangerous poison; but the sweet has hitherto been considered harmless, although it is evident that it also contains a considerable quantity of prussic acid.

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[*] According to Liebig and Wohler, 17 grms. of amygdaline yield 1 of prussic acid (*i.e.*, 5·7 per cent.) and 8 of oil of bitter almonds. 34 parts of amygdaline, mixed with 66 of emulsin of almonds, give a fluid equalling the strength of acid of most pharmacopeias, viz., 2 per cent.

[†] The bark and green parts of the *Prunus avium*, L., *Prunus mahaleb*, L., and herbaceous *Spiræœ* yield no prussic acid.

[‡] On Prussic Acid from Cassava, *Analyst*, April, 1877, p. 5.

In cases of criminal poisoning by prussic acid, the defence not unfrequently insists upon the poison developing internally through fruit previously eaten; and in some cases it may be advisable for the analyst to make, if possible, special quantitative experiments on the fruits the deceased is supposed or known to have eaten.

§ 8. *Action of Prussic Acid on the Blood.*—Hydrocyanic acid combines with the hæmoglobin of the blood, and is slowly excreted; it also more than any other poison prevents the exchange of oxygen. If blood saturated with hydrocyanic acid be treated in an absorption tube with pure oxygen, the gas is not absorbed, nor is the colour of the blood changed; if blood saturated with oxygen be confined over mercury, and a little hydrocyanic acid in solution be added, there is a gradual development of gas, which is found to consist of oxygen and carbonic anhydride.

Hydrocyanic acid appears to form a definite crystalline compound with the blood; and Hoppe Seyler has observed crystals from blood containing HCN, in which the latter was in such powerful combination, that they crystallised out of warm water. By distillation with an acid, prussic acid was obtained.* Ralph† has described blue masses, like Berlin blue, in the blood, which he considers characteristic of hydrocyanic acid poisoning. Dragendorff has specially looked for this appearance, but has failed to find the blue substance.

According to Schönbein, the blood corpuscles possess the power of decomposing peroxide of hydrogen into water and oxygen; they lose this property if the blood contains hydrocyanic acid. In the latter case an addition of peroxide of hydrogen‡ produces a brown colour with the blood, and causes the spectroscopic bands to disappear. As we have stated, this brown colour is not produced by normal blood. Normal blood, again, effervesces (owing to the escape of oxygen) when treated with hydric peroxide; this does not take place with the cyanised blood. Caspar speaks very favourably of these characteristics as confirmatory tests in cases of suspected prussic acid poisoning.§ In performing the test with cyanide of potash, the alkali decomposes hydric peroxide, and it is necessary to neutralise with an acid.‖

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* *Virchow's Archiv. fur Path. Anat.* Bd. 38, p. 435.

† *Journ. of Microscop. Science.* London, new series, Oct. 24, 1866.

‡ Peroxide of hydrogen is an article of commerce; should, however, none be at hand, it may be prepared by heating baryta in a current of air, then by the action of dilute HCl in the peroxide of barium a solution of H_2O_2 is obtained.

§ *Handbuch*, 6th ed., p. 497.

‖ Jüdell, Die Vergiftung mit Blausaure. Erlangen, 1876.

§ 9. *Fatal Dose of Hydrocyanic Acid and Cyanide of Potash, &c.*—Dr. Taylor considers that 1 grain (6·4 centigrms.) of anhydrous prussic acid would commonly suffice to destroy the life of an adult. The smallest dose of cyanide of potassium which has hitherto been known to destroy life, is a little less than 5 grains.

§ 10. *Tests for Hydrocyanic Acid and Cyanide of Potassium.*—(1.) The addition of silver nitrate to a solution containing prussic acid, or a soluble cyanide,* produces a precipitate of argentic cyanide. 100 parts of argentic cyanide are composed of 80·60 Ag and 19·4 CN, equivalent to 21·4 HCN. It is a white anhydrous precipitate, soluble either in ammonia or in a solution of cyanide of potassium, but insoluble in dilute nitric acid and water. Upon ignition it is decomposed into CN and metallic silver, mixed with a little paracyanide of silver.

A very neat process for the identification of cyanide of silver is the following: Place the perfectly dry cyanide in a closed or sealed tube, containing a few crystals of iodine. On heating slightly iodide of cyanogen is sublimed in beautiful needles. These crystals again may be dissolved in a dilute solution of potash, a little ferrous sulphate added, and hydrochloric acid, and in this way Prussian blue produced. If the quantity to be tested is small, the vapour of the acid may be evolved in a very short test tube, the mouth of which is closed by the ordinary thin discs of microscopic glass, the under surface of which is moistened with a solution of nitrate of silver; the resulting crystals of silver cyanide are very characteristic, and readily identified by the microscope.

(2.) If, instead of silver nitrate, the disc be moistened with a solution of sulphate of iron (to which has been added a little potash), and exposed to the vapour a short time, and then some dilute hydrochloric acid added, the moistened surface first becomes yellow, then green, lastly, and permanently, blue. No other blue compound of iron (with the exception of Prussian blue) is insoluble in dilute hydrochloric acid.

(3.) A third and, perhaps, the most delicate of all, is the so-called sulphur test. A yellow sulphide of ammonium containing free sulphur is prepared by saturating ammonia by SH_2, first suspending in the fluid a little finely-precipitated sulphur (or an old, ill-preserved solution of sulphide of ammonium may be used). Two watch-glasses are now taken; in the one the fluid containing prussic acid is put, and the second (previously moistened with the sulphide of ammonium described) is inverted over it. The glasses are conveniently placed for a few minutes in the water-oven; the upper one is then removed, the moist surface evapo-

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* In the case of testing in this way for the alkaline cyanides, the solution must contain a little free nitric acid.

rated to dryness in the water-bath, a little water added, and then a small drop of solution of chloride of iron; if hydrocyanic acid is present, the sulphocyanide of iron will be formed of a striking blood-red colour.

(4.) The reaction usually called Schönbein's, or Pagenstecher and Schönbein's* (but long known,† and used before the publication of their paper), consists of guiacum paper, moistened with a very dilute solution of sulphate of copper (1 : 2000); this becomes blue if exposed to the vapour of hydrocyanic acid. Unfortunately, the same reaction is produced by ammonia, ozone, nitric acid, hypochlorous acid, iodine, bromine, chromate of potash, and other oxidising agents, so that its usefulness is greatly restricted.

(5.) A very delicate test for prussic acid is as follows:—About one-half centigrm. (2 grains) of ammonia, ferrous sulphate (or other pure ferrous salt), and the same quantity of uranic nitrate, are dissolved in 50 cc. of water, and 1 cc. of this test-liquid is placed in a porcelain dish. On now adding a drop of a liquid containing the smallest quantity of prussic acid, a grey-purple colour, or a distinct purple precipitate, is produced.‡

(6.) A hot solution of potassic cyanide, mixed with picric acid, assumes a blood-red colour, due to the formation of picrocyanic acid. Free HCN does not give this reaction, and therefore must first be neutralised by an alkali.

All these tests, where there is sufficient material, can be directly applied either to the solution of prussic acid itself, or to that of cyanide of potash; where necessary, neutralising the one with an alkali, and acidifying the other with an acid—cyanide of potash readily yielding free prussic acid.

§ 11. *Prussic Acid or Cyanide of Potash in Organic Matters* (*such as the contents of the stomach*, &c.).§—The substances, if fluid, are at once placed in a retort or flask, after acidification with sulphuric acid; if solid, they may be finely divided or pulped, and distilled with acidulated water. It has hitherto been the custom to perform this operation by the moderate heat of a

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* *Neues Repert. der Pharm.*, 18, 356.

† "This reaction (with tincture of guiacum and copper) has been long known. I remember a pharmaceutist, who attended my father's laboratory, showing me this test in 1828 or 1829."—Mohr's "Toxicologie," p. 92.

‡ M. Casey Lea.—*Amer. Journ. of Science* [3], ix. 121-123; *J. C. Society*, 1876, vol. i., p. 112.

§ In the search for cyanides, the analyst must not commit the unpardonable error of first producing a cyanide by reagents acting on animal matters, and then detecting as a poison the cyanide thus manufactured. If, for example, a healthy liver is carbonised by nitric acid, saturated with potash, and then burnt up, cyanide of potash is always one of the products; and, indeed, the ashes of a great variety of nitrogenous organic substances may contain cyanides—cyanides not pre-existing, but manufactured by combination.

water-bath, receiving the distillate in a little weak potash water, and not prolonging the process beyond a few hours; and, indeed, for the mere detection of prussic acid this is quite sufficient. The experiments of Sokoloff, however, throw a grave doubt on the suitability of this simple method for quantitative results.

N. Sokoloff* recommends the animal substances to be treated by water strongly acidified with hydric sulphate, and then to be distilled in the water-bath for from two to three days! or to be distilled for twenty-four hours, by the aid of an oil-bath, at a high temperature. He gives the following example of quantitative analysis by the old process of merely distilling for a few hours, and by the new:—

Old Process.—(1.) Body of a hound—age, two years; weight, 5180 grms.; dose administered, 57 mgrms. HCN; death in fifteen minutes. After five days there was found in the saliva 0·6 mgrm., stomach 3·2 mgrms., in the rest of the intestines 2·6 mgrms., in the muscles 4·1—total, 10·5.

(2.) Weight of body, 4000 grms.; dose given, 38 mgrms.; death in eleven minutes. After fifteen days, in the saliva 0·8, in the stomach 7·2, in the rest of the intestines 2·2, in the muscles 3·2—total, 13·4.

New Process.—Weight of body, 5700 grms.; dose, 57 mgrms.; death in twenty-four minutes. After fifteen days, in the saliva 1·1 mgrm., in the stomach 2·6, in the rest of the intestines 9·6, in the muscles 31·9, and in the whole, 45·2 mgrms. Duration of process, thirteen hours.

From a second hound, weighing 6800 grms., dose 57 mgrms., 25·1 mgrms. were separated three days after death.

From a third hound, weighing 5920 grms., dose 98 mgrms.; after forty days, by distillation on a sand-bath, there were separated 2·8 mgrms. from the saliva, 4·8 from the stomach, 16·8 from the intestines, 23·6 from the muscles—total, 48 mgrms.

It would also appear that he has separated 51·2 mgrms. of anhydrous acid from the corpse of a dog which had been poisoned by 57 mgrms. of acid, and buried sixty days.†

From another canine corpse, three days laid in an oven, and left for twenty-seven days at the ordinary temperature, 5·1 mgrms. were recovered out of a fatal dose of 38 mgrms.

The estimation was in each case performed by titrating the distillate with argentic nitrate, the sulphur compounds having been previously got rid of by saturating the distillate with KHO, and precipitating by lead acetate.

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* *Ber. d. deutsch. Chem. Gesellsch.* Berlin, ix. 1023.

† Without wishing to discredit the statements of M. Sokoloff, we may point out that a loss of half a dozen milligrammes only appears rather extraordinary.

§ 12. *How long after Death can Prussic Acid and Cyanide of Potash be Detected?*[*]—Sokoloff[†] appears to have separated prussic acid from the body of hounds at very long periods after death, in one case sixty days; Dragendorff recognised cyanide of potash in the stomach of a hound after it had been four weeks in his laboratory,[‡] and in man eight days after burial. Caspar also, in his 211th case, states that more than 18 mgrms. of anhydrous prussic acid were obtained from a corpse eight days after death,[§] so that even in very advanced stages of putrefaction, and at periods after death extending beyond two months, the detection of prussic acid cannot be pronounced impossible.

§ 13. *Estimation of Hydrocyanic Acid or Potassic Cyanide.*—In all cases the readiest method of estimating prussic acid (whether it be in the distillate from organic substances, or in aqueous solution), is to saturate the liquid with soda or potash, and titrate the alkaline cyanide thus formed with nitrate of silver. The process is based on the fact that there is first formed a soluble compound (KCy, AgCy), which the slightest excess of silver breaks up, and the insoluble cyanide is at once precipitated. If grains are used, 17 grains of nitrate of silver are dissolved in water, the solution made up to exactly 1000 grain measures, each grain measure equalling ·0054 grain of anhydrous hydrocyanic acid. If grammes are employed, the strength of the nitrate of silver solution should be 1·7 grm. to the litre, each cc. then = ·0054 hydrocyanic acid, or ·01302 grm. of potassic cyanide.

Essential oil of bitter almonds may also be titrated in this way, provided it is diluted with sufficient spirit to prevent turbidity from separation of the essential oil. If hydrocyanic acid is determined gravimetrically (which is sometimes convenient, when only a single estimation is to be made), it is precipitated as cyanide of silver, the characters of which have been already described.

Hydric sulphocyanide, HSCN, in very large doses is poisonous. *Sulphocyanide of potash* (according to Dubreuil and Legros),[‖] if

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[*] In opening a body where prussic acid is suspected as the cause of death, it may be well to follow the advice of Caspar, and deviate from the regular course, by opening the head first. The odour of prussic acid will probably be purer and more perceptible in the brain than in the stomach and intestines, in which a very foul smell is nearly always present ("Handbuch der Gerichtlichen Medicin," p. 495). The odour of prussic acid is generally perceptible in poisoning by potassic cyanide, for the latter is so easily decomposed, the former being one of the products.

[†] See *ante*, p. 252.

[‡] Dragendorff, G., *Beitr. zur Gericht. Chem.*, p. 59.

[§] Caspar's "Pract. Handbuch der Gerichtlichen Medicin," p. 561.

[‖] *Compt. Rend.*, t. 64, p. 1256, 1867.

subcutaneously injected, causes first local paralysis of the muscles, and later convulsions.

II.—CHLOROFORM AND CHLORAL.

§ 14. *Chloroform*—$CHCl_3$, specific gravity 1·497, boiling point 61°C. (142°F.)—is a colourless, volatile liquid, of high refracting power, soluble in alcohol and ether, but dissolving very sparingly in water. Accidents from time to time occur from the use of chloroform, and it may come under the notice of the chemist as a poison. Occasionally, but very rarely, it is found adulterated, the common sophistications or impurities being alcohol, wood-spirit, methylated chloroform, aldehyde, free hydrochloric and hydrochlorous acids.

Alcohol.—The chloroform of commerce usually contains a small amount of alcohol, and if this does not exceed 6 per cent. it would be unwise to consider it an adulteration. The detection of alcohol may be effected by Davy's test (see p. 127), or by ferrous dinitro sulphide. The latter may be made by the action of ferric chloride on a mixture of potassic nitrate and ammonic sulphide, and on shaking it up with the chloroform a green colour will be produced, if alcohol is present. Other tests are—(1.) The specific gravity : if there is any considerable adulteration with alcohol, this will, of course, be much under 1·49 ; and (2.) the behaviour in water: if the chloroform be dropped into water, the drops (instead of sinking as pure pellucid beads) will become quite opaque should alcohol be present, and on shaking the mixture up it will become milky.

Methylated Chloroform, owing to the presence of about 6 per cent. of an empyreumatic oil, leaves an unpleasant odour behind it, if permitted to evaporate spontaneously on a cloth.

Aldehyde reduces nitrate of silver, and *hydrochloric acid* can be detected by the reaction of the liquid, and also by the ordinary nitrate of silver test.

§ 15. *The Detection and Separation of Chloroform* from organic substances is not difficult, its low boiling point causing it to distil readily. Accordingly (whatever may be the ultimate modifications, as suggested by different experimenters), the first step is to bring the substances, unless fluid, into a pulp with water, and submit this pulp to distillation by the heat of a water-bath. If the liquid operated upon possesses no particular odour, the chloroform may in this way be recognised in the distillate, which, if necessary, may be redistilled in the same manner, so as to concentrate the volatile matters in a small compass. Generally, however, offensive animal matters present will complicate the analysis, and it will then be necessary to determine chloroform by the fact that its vapour may be decomposed at a red heat into chlorine and hydrochloric acid. The various methods of obtaining this reaction are—

(*a.*) The flask containing the pulp may have a glass tube in connection, dipping into nitrate of silver, and carrying one or two pieces of litmus paper, the tube to be heated in one spot with the flame of a Bunsen burner or spirit lamp.

(*b.*) The tube from the flask may pass through a combustion furnace, and the decomposed vapour be finally drawn (by means of an aspirator) through Liebig's bulbs, containing an acid solution of silver nitrate; or air may be propelled through the whole apparatus by a system of bellows.

(*c.*) The same arrangement as in (*b.*) may be adopted, using pieces of caustic lime in the combustion tube. The chlorine combines with the lime to form chloride of lime, which may be dissolved in dilute nitric acid, and precipitated by nitrate of silver.

In any or all of the above cases, if the weight of the chloride of silver is known, the amount of chloroform may be calculated, $143{\cdot}5$ Ag, $NO_3 = 39{\cdot}83\ CHCl_3$. Should the circumstances of the case permit of a few drops of chloroform itself being obtained pure, it may be identified by what is usually termed Hoffmann's test—viz., warming the chloroform with aniline and alcoholic soda-lye, which produces *isonitril*, easily detected by its odour.*

§ 16. *Chloral.*—This being easily decomposed into chloroform, tests for the latter partly apply to it also. It may, however, be readily separated from its watery solution by petroleum ether, or by ether; the latter is preferable. Chloral, through normal soda solution, is immediately decomposed into formiate of soda and chloroform, a reaction which forms a ready means of quantitative estimation. Excess of soda-lye being added, the liquid is titrated back, 1 cc. of normal soda-lye corresponding to 0·1655 grm. of chloral hydrate. Should an acid already be present, it may be neutralised by carbonate of lime, without injury to the result.

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* Iodoform, bromoform, and chloral also respond to this test.

III.—PHOSPHORUS.

§ 17. *Phosphorus.*—Atomic weight 31, specific gravity 1·77 to 1·840, melting point 44°C., boiling point about 290°C. The phosphorus of commerce is usually in the form of waxy semi-transparent sticks, preserved under water; if exposed to the air, white fumes are given off, with a peculiar onion-like odour; and if observed in the dark, there is emission of a spontaneous light. Phosphorus is easily inflammable, insoluble in water, slightly soluble in alcohol and ether, somewhat more so in fatty and ethereal oils, and to a still greater extent in bisulphide of carbon. Phosphorus exists in, or can be converted into, another allotropic modification,—viz., the red or amorphous phosphorus; this variety is, however, not poisonous,* and therefore need not be described here.†

§ 18. *Phosphuretted Hydrogen.—Phosphine*, PH_3, mol. weight 34, specific gravity 1·178, percentage composition 91·43 phosphorus; 8·57 hydrogen by weight. The absolutely pure gas is not spontaneously inflammable, but that made by the ordinary process is so. It is a colourless, highly poisonous gas, which does not support combustion, but is itself combustible, burning to phosphoric acid ($PH_3 + 2O_2 = PO_4H_3$). Extremely dangerous explosive mixtures may be made by combining phosphine and air or oxygen. Phosphine, when quite dry, burns with a white flame, but if mixed with aqueous vapour it is green; hence a hydrogen flame containing a mixture of PH_3 possesses a green colour.

If sulphur is heated in a stream of phosphine, hydric sulphide and sulphur phosphide are the products. Oxides of the metals, heated with phosphine, yield phosphides with formation of water. Iodine, warmed in phosphine, gives white crystals of iodine phosphonium, and biniodide of phosphorus, $5I + 4PH_3 = 3PIH_4 + PI_2$. Chlorine inflames the gas, the final result being hydric chloride and chloride of phosphorus, $PH_3 + 8Cl = 3ClH + PCl_5$. One of the most important decompositions for our purpose is the action of phosphine on a solution of nitrate of silver; there is a separation of metallic silver, and nitric and phosphoric acids are found in solution, thus, $8AgNO_3 + PH_3 + 4OH_2 = 8Ag + 8HNO_3 + PO_4H_3$.

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* A hound took 200 grms. of red phosphorus in twelve days, and remained healthy.—(*Sonnenschein.*)

† The commercial red phosphorus does, however, contain small quantities of ordinary phosphorus—according to Fresenius, from 0·6 per cent. downwards. It also contains phosphorous acid, and about 4·6 per cent. of other impurities, among which is graphite.—Schrötter, *Chem. News*, Vol. xxxvi., p. 198.

The excess of silver can be separated by hydric chloride, and the phosphoric acid made evident by the addition of molybdic acid in excess—a test which is one of the best we have for phosphine, and hence for phosphorus.

§ 19. *The Medicinal Preparations of Phosphorus* are not numerous; it is usually prescribed in the form of pills, often made by manufacturers of coated pills on a large scale. Besides pills, there is a *phosphorated oil;* that of the French pharmacopeia is made with 1 part of dried phosphorus dissolved in 50 parts of warm almond oil; that of the German has 1 part in 80; the strength of the former is therefore 2 per cent., of the latter 1·25 per cent.

§ 20. *Matches and Vermin Pastes.*— An acquaintance with the percentage of phosphorus in the different pastes and matches of commerce will be found useful. Most of the vermin-destroying pastes contain about 2 per cent. of phosphorus, but matches differ much in composition. Six match-heads, which had been placed in an apple for criminal purposes, and were submitted to Tardieu, were found to contain 20 mgrms. of phosphorus, *i.e.*, 33 grms. in 100. Mayet found in 100 matches 55 mgrms. of phosphorus. Some of the published formularies are as follows :—

(1.)	Glue,	6 parts.	
	Phosphorus,	4 ,,	or 14·8 per cent.
	Nitre,	10 ,,	
	Red Ochre,	5 ,,	
	Blue Smalts,	2 ,,	
(2.)	Phosphorus,	9 parts,	or 16·3 per cent.
	Gum,	16 ,,	
	Nitre,	14 ,,	
	Smalts,	16 ,,	
(3.)	Phosphorus,	4 parts,	or 14·8 per cent.
	Glue,	6 ,,	
	Nitre,	10 ,,	
	Red Lead,	5 ,,	
	Smalts,	2 ,,	
(4.)	Phosphorus,	17 parts,	or 17 per cent.
	Glue,	21 ,,	
	Nitre,	38 ,,	
	Red Lead,	24 ,,	

Phosphorus-poisoning by matches will, however, shortly become very rare, for those containing the ordinary variety of phosphorus are gradually being superseded by matches of excellent quality, which contain no phosphorus whatever.

§ 21. *Phosphorus as a Poison.* — Phosphorus of late years has come into very extensive use in medicine; but in England comparatively few cases of poisoning by its means are on record. In the writer's experience, however, it is very commonly used for the destruction of animals by country people, when prompted by revenge or other underhand motives, the choice of the drug being doubtless owing to the facility with which, under the form of "rat poison," it can be obtained.

§ 22. *Fatal Dose.*—The smallest fatal dose on record is that mentioned by Lobenstein Löbel, of Jena, where, it would appear, a lunatic died from taking one-eighth of a grain. Other cases are also to be found in works of jurisprudence, which prove that less than one grain, taken in a single dose, may destroy life.

§ 23. *The Detection of Phosphorus.*—The following are, in brief, the chief tests for the detection of phosphorus:—*

1. *Mitscherlich's Process.*—The essential feature of this process is simply distillation of free phosphorus, and observation of its luminous properties as the vapour condenses in the condensing tube. The conditions necessary for success are—(1.) that the apparatus should be in total darkness;† and (2.) that there should be no substance present, such as alcohol or ammonia, which, distilling over with the phosphorus-vapour, could destroy its luminosity. A convenient apparatus, and one certain to be in all laboratories, is an ordinary Florence flask, containing the liquid to be tested, fitted to a glass Liebig's condenser, supported on an iron sand-bath (which may, or may not, have a thin layer of sand), and heated by a Fletcher's low temperature burner — the distillate is received into a flask. This apparatus, if in darkness, works well; but should the observer wish to work in daylight, the condenser must be enclosed in a box perfectly impervious to light, and having a hole through which the luminosity of the tube may be seen, the head of the operator and the box being covered with a cloth. If there be a stream of water passing continuously through the condenser, a beautiful luminous ring of light appears in the upper part of the tube, where it remains fixed for some time. Should, however, the refrigeration be imperfect, the luminosity travels slowly down the tube into the receiver. In any case, the delicacy of the test is

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* It has been recommended to dissolve the phosphorus out from organic matters by carbonic disulphide. On evaporation of the latter, the phosphorus is recognised by its physical properties. Such a method is of but limited application, although it may sometimes be found useful. The writer has successfully employed it in the extraction of phosphorus from the crop of a fowl; but on this occasion it happened to be present in large quantity.

† Any considerable amount of phosphorescence can, however, be observed in twilight.

extraordinary.* If the organic liquid is alkaline, or even neutral, there will certainly be some evolution of ammonia, which will distil over before the phosphorus, and retard (or, if in sufficient quantity, destroy) the luminosity. In such a case it is well, as a precaution, to add enough sulphuric acid to fix the ammonia, omitting such addition if the liquid to be operated upon is acid.

2. *The Production of Phosphine*, PH_3.—Any method which produces phosphuretted hydrogen, enabling that gas to be passed through nitrate of silver solution, may be used for the detection of phosphorus. Thus, Sonnenschein states that he has found phosphorus in extraordinarily small amount, mixed with various substances, by heating with potash in a flask, and passing the phosphine into silver nitrate, separating the excess of silver, and recognising the phosphoric acid by the addition of molybdate of ammonia.†

3. *Tests Dependent on the Combustion of Phosphine*, PH_3.—A hydrogen flame, containing only a minute trace of phosphorus, or of the lower products of its oxidation, acquires a beautiful green tint, and possesses a characteristic *spectrum*. In order to obtain the latter in its best form, the amount of phosphine must not be too large, or the flame will become whitish and livid, and the bands lose their defined character, rendering the spectrum continuous. Again, the orifice of the tube whence the gas escapes must not be too small; and the best result is obtained when the flame is cooled.

M. Salet has proposed two excellent methods for the observation of phosphine by the spectroscope:—

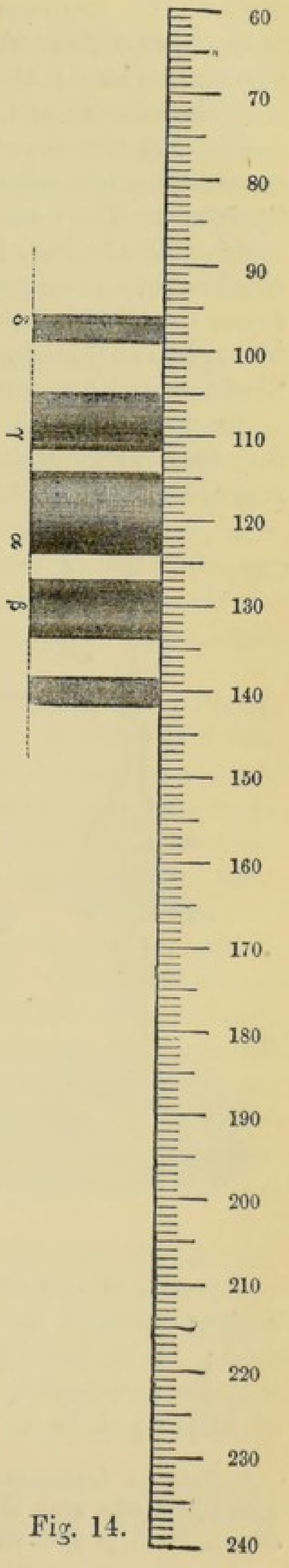

Fig. 14.

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* Fresenius states that he and Neubauer, with 1 mgrm. of phosphorus in 200,000, recognised the light, which lasted for half an hour.—*Zeitschr. f. Anal. Chem.*, i., p. 336.

† Sonnenschein, "Handbuch der Gerichtlichen Chemie." Berlin, 1869.

(1.) He projects the phosphorus-flame on a plane vertical surface, maintained constantly cold by means of a thin layer of running water; the green colour is especially produced in the neighbourhood of the cool surface.

(2.) At the level of the base of the flame, there is an annular space, through which a stream of cold air is continually blown upwards. Thus cooled, the light is very pronounced, and the red band, 597·03 (Fig. 14), which is almost invisible in the ordinary method of examination, is plainly seen. The accompanying diagram (p. 259) is taken from Boisbaudran,* and figures accurately the relative position of the lines of a slightly cooled phosphine flame.

An apparatus (devised by Blondlot, and improved by Fresenius) for the production of the phosphine flame in medico-legal research, is represented in the following diagram:—

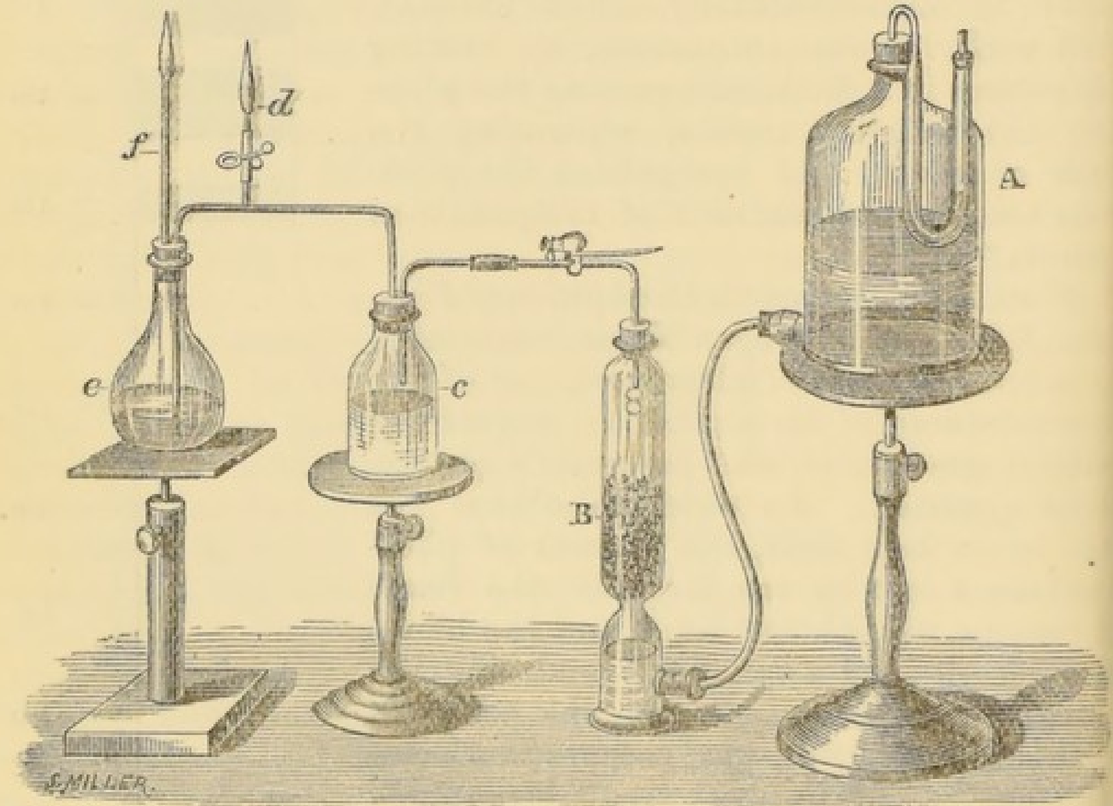

Fig. 15.

Several of the details of this apparatus may be modified at the convenience of the operator. A is a vessel containing sulphuri acid; B is partly filled with granulated zinc, and hydroge may be developed at pleasure; *c* contains a solution of nitrat of silver; *d* is a tube at which the gas can be lit; *e*, a flask

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* *Spectres Lumineux*, par M. Lecoq de Boisbaudran. Paris, 1874. Se also Christofle and Beilstrom's *Abhandlung* in *Fresenius, Zeitchr. f. Anal Chem.*, B. 2, p. 465, and B. 3, p. 147.

containing the fluid to be tested, and provided with a tube, *f*, at which also the gas issuing can be ignited—the orifice should be provided with a platinum nozzle. When the hydrogen has displaced the air, both tubes are lit, and the two flames, being side by side, can be compared. Should any phosphorus come over from the zinc (a possibility which the interposed silver nitrate ought to guard against) it is detected; the last flask is now gently warmed, and if the flame is green, or, indeed, in any case, it should be examined by the spectroscope.*

4. *Lipowitz's Sulphur Test.*—Sulphur has the peculiar property of condensing phosphorus on its surface, and of this Lipowitz proposed to take advantage. Pieces of sulphur are digested some time with the liquid under research, subsequently removed, and slightly dried. When examined in the dark, should phosphorus be present, they gleam strongly if rubbed with the finger, and develop a phosphorous odour. The test is wanting in delicacy, nor can it well be made quantitative; it has, however, an advantage in certain cases, *e.g.*, the detection of phosphorus in an alcoholic liquid.

5. *Scheerer's Test.*—The reducing action of phosphorous acid on silver nitrate furnishes a very delicate test. A piece of filter paper, soaked in solution of nitrate of silver, and suspended in a lask containing phosphorus (or a liquid in which phosphorus is n suspense), soon turns black. SH_2 must of course be excluded, o that its presence should be tested for by a similar paper previously dipped in a solution of lead acetate.†

A combination of these various methods is useful, if phosphorus should be present in very small quantity. The substances re distilled in an atmosphere of CO_2—the distillate (which may leam when shaken up with air, and would thus give evidence of hosphorus) is decomposed by neutral nitrate of silver; the preipitate is collected, washed, and then put in the apparatus for eveloping hydrogen, already figured and described. As an dditional precaution, the gas may be made to pass over pumice-tone moistened with caustic potash.

§ 24. *How long can Phosphorus be recognised after Death?*—ne of the most important matters for consideration, is the time ter death in which free phosphorus, or free phosphoric acids, n be detected. Any phosphorus changed into ammon. mag. hosphate, or into any other salt, is for medico-legal purposes tirely lost, since the expert can only take cognisance of the

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* F. Selmi has proposed the simple dipping of a platinum loop into a uid containing phosphoric acid, and then inserting it into the tip of a drogen flame.

† Arsine also blackens nitrate of silver. (See the article on *Arsenic.*)

substance either in a free state, as phosphine,* or as a free acid.

The question, again, may be asked in court—Does the decomposition of animal substances rich in phosphorus develop phosphine? The answer to this is, that no such reaction has been observed.

A case is related (in *Pharm. Zeitsch. f. Russl.; Jahrg.* 2, p. 87) in which phosphorus was recognised, although the body had been buried for several weeks, and then exhumed.

The expert of pharmacy of the Provincial Government Board of Breslau has also made some experiments in this direction, which are worthy of note:—Four guinea-pigs were poisoned, each by 0·023 grm. of phosphorus; they died in a few hours, and were buried in sandy loam soil 0·5 metre deep. Exhumation of the first took place four weeks after. The putrefying organs—heart, liver, spleen, stomach, and all the intestines, tested by Mitscherlich's distilling method—showed characteristic phosphorescence for nearly one hour.

The second animal was exhumed after eight weeks in a highly putrescent state. Its entrails, on distillation, showed the phosphorescent appearance for thirty-five minutes.

The third animal was taken from the earth after twelve weeks, but no free phosphorus could be detected, although there was evidence of the lower form of oxidation (PO_3) by Blondlot's method.

The fourth animal was exhumed after fifteen weeks, but neither free phosphorus nor PO_3 could be detected.†

A man, as well as a cat, was poisoned by phosphorus. On analysis, twenty-nine days after death, negative results were alone obtained. (*Sonnenschein.*)

It will thus be evident that there is no constant rule, and that, even when decomposition is much advanced, an examination *may* be successful.

The organs to be examined for phosphorus are, principally, the stomach, with its contents, and the liver. If not found in either, it may yet be detected in the intestines, for in one case it would appear that Dragendorff found phosphorus in the cœcum, and nowhere else. The urine should also be tested; in several cases a strong alliaceous odour has been observed, leading to the detection of small quantities of phosphorus.‡

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* A partial change of phosphorus into phosphine in the system is declared to occur by Schnehardt and Dybkowsky; but this again is denied by Bucheim.

† *Vierteljahrsschrift für Gerichtliche Medicin.* Jan. 7, 1876. See also *Zeitschr. f. Anal. Chemie.* 1872.

‡ See Selmi, *Gazz. Chim. Ital.*, iv. 478.

§ 25. *The Quantitative Estimation of Phosphorus* is best carried out by oxidising it into phosphoric acid, and estimating as amm. magnesian phosphate. To effect this, the substances are distilled in an atmosphere of CO_2 into a flask with water, to which a tube containing silver nitrate is attached; the latter retains all phosphine, the former solid phosphorus. If necessary, the distillate may be again distilled into $AgNO_3$; and in any case the contents of the U tube and flask are mixed, oxidised with nitromuriatic acid, filtered from silver chloride, and the phosphoric acid determined in the usual way.

In the case of a child poisoned by lucifer matches, Sonnenschein estimated the free phosphorus in the following way:—The contents of the stomach were diluted with water, a measured part filtered, and the phosphoric acid estimated. The other portion was then oxidised by HCl and potassic chlorate, and the phosphoric acid estimated—the difference being calculated as free phosphorus.

PART III.

ALKALOIDS AND POISONOUS VEGETABLE PRINCIPLES SEPARATED FOR THE MOST PART BY ALCOHOLIC SOLVENTS.

I.—ALKALOIDS.

§ 26. *General Tests for Alkaloids.*—In order to ascertain whether an alkaloid is present or not, a method of extraction must be pursued which, while disposing of fatty matters, salts, &c., shall dissolve as little as possible of foreign substances; such a method, *e.g.*, as the original process of Stas, or one of its modern modifications.

If to the acid aqueous solution finally obtained by this method a dilute solution of soda be added, drop by drop, until it is rendered feebly alkaline, *and no precipitate appear*, whatever other poisonous plant-constituents may be present, alkaloids are absent.

In addition to this negative test, there are also a number of substances which give well-marked crystalline or amorphous precipitates with alkaloids. Such are—tannic, picric, silico-tungstic, phospho-tungstic, and phosphomolybdic acids, a few of which will be described in detail.

(1.) *Phosphomolybdic Acid as a Reagent for Alkaloids.—Preparation:* Molybdate of ammonia is precipitated by phosphate of soda; and the well-washed yellow precipitate is suspended in water and warmed with carbonate of soda, until it is entirely dissolved. This solution is evaporated to dryness, and the ammonia fully expelled by heating. If the molybdic acid is fairly reduced by this means, it is to be moistened by nitric acid, and the heating repeated. The now dry residue is warmed with water, nitric acid added to strong acid reaction, and the mixture diluted with water, so that 10 parts of the solution contain 1 of the dry salt. The precipitates of the alkaloids are as follows:—

Aniline,	Bright-yellow, flocculent.
Morphine,	,, ,,
Narcotine,	Brownish-yellow, ,,
Quinine,	Whitish-yellow, ,,
Cinchonine,	,, ,,
Codeine,	Brownish-yellow, voluminous.
Strychnine,	White-yellow, ,,
Brucine,	Yolk-yellow, flocculent.
Veratrine,	Bright-yellow, ,,
Jervin,	,, ,,
Aconitine,	,, ,,
Emetin,	,, ,,
Theine,	Bright-yellow, voluminous.
Theobromine,	,, ,,
Solanine,	Citron-yellow, pulverulent.
Atropine,	Bright-yellow, flocculent.
Hyoscyamine,	,, ,,
Colchicine,	Orange-yellow, ,,
Delphinine,	Gray-yellow, voluminous.
Berberin,	Dirty-yellow, flocculent.
Conine,	Bright-yellow, voluminous.
Nicotin,	,, ,,
Piperin,	Brownish-yellow, flocculent.

(2.) *Silico-Tungstic Acid as a Reagent for Alkaloids.*—Sodium tungstate is boiled with freshly-precipitated gelatinous silica. To the solution is added mercurous nitrate, which precipitates the yellow mercurous silico tungstate. This is filtered, well washed, and decomposed by an equivalent quantity of hydrochloric acid ; silico-tungstic acid then goes into solution, and mercurous chloride (calomel) remains behind. The clear filtrate is evaporated to lrive off the excess of hydrochloric acid, and furnishes, on sponaneous evaporation, large, shining, colourless octahedra of silicoungstic acid, which effloresce in the air, melt at 36°C., and are asily soluble in water or alcohol.

This agent produces no insoluble precipitate with any metallic alt. Cœsium and rubidium salts, even in dilute solutions, are recipitated by it ; neutral solutions of ammonium chloride give vith it a white precipitate, soluble with difficulty in large quanities of water. It precipitates solutions of the salts of quinine, inchonine, morphine, atropine, &c. ; if in extremely dilute soluion, an opalescence only is produced: for instance it has been bserved that cinchonia hydrochlorate in $\frac{1}{200000}$, quinia hydrohlorate in $\frac{1}{20000}$, morphia hydrochlorate in $\frac{1}{15285}$ dilution, all ave a distinct opalescence. (*Archiv der Pharm.*, Nov., Dr. ichard Godeffroy.)

(3.) *Scheibler's Method for Alkaloids : Phospho-Tungstic Acid.*—rdinary commercial sodium tungstate is digested with half its eight of phosphoric acid, specific gravity 1·13, and the whole allowed to stand for some days, when the acid separates in crystals. A solution of these crystals will give a distinct precipitate with the most minute quantities of alkaloids, $\frac{1}{200000}$ of strychnine, and $\frac{1}{100000}$ of quinine. The alkaloid is liberated by digestion with barium hydrate (or calcium hydrate); and if volatile, may be distilled off; if fixed, dissolved out by chloroform. In complex mixtures colouring matter may be removed by plumbic acetate, the lead thrown out by SH_2, and concentrated, so as to remove the excess of SH_2.

(4.) *Selmi's Process for separating Alkaloids.*—A method of separating alkaloids from an ethereal solution has been recently proposed by Selmi.* The alcoholic extract of the viscera, acidified and filtered, is evaporated at 65°C.; the residue taken up with water, filtered, and decolorised by basic acetate of lead. The lead is thrown out by sulphuretted hydrogen; the solution after concentration repeatedly extracted with ether; and the ethereal solution saturated with dry CO_2, which generally precipitates some of the alkaloids. The ethereal solution is then poured into a clean vessel, and mixed with about half its volume of water, through which a current of CO_2 is passed for 20 minutes; this may cause the precipitation of other alkaloids not thrown down by dry CO_2. If the whole of the alkaloids are not obtained by these means, the solution is dehydrated by agitation with barium oxide, and a solution of tartaric acid in ether is added (care being taken to avoid excess); this throws down any alkaloid still present. The detection of any yet remaining in the viscera is effected by mixing with barium hydrate and a little water, and agitating with *purified* amylic alcohol; from the alcohol the alkaloids may be subsequently extracted by agitation with very dilute sulphuric acid.

§ 27. *Methods of Separation.*

(1.) *Stas's Process.* — The original method of Stas† (afterwards modified by Otto‡), consisted in extraction of the organic matters by strong alcohol, with the addition of tartaric acid; the filtered solution was then carefully neutralised with soda, and shaken up with ether, the ethereal solution being separated by a pipette. Subsequent chemists proposed chloroform instead of ether, § the additional use of amyl-alcohol, || and the

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* F. Selmi, *Gazett. Chim. Ital.*, vj. 153-156, and *Journ. Chem. Soc.*, i., 1877, 93.

† *Annal. d. Chem. u. Pharm.*, 84. 379.

‡ *Ib.* 100. 44. "Anleitung zur Ausmittel d. Gifte."

§ Rodgers and Girwood, *Pharm. Journ. and Trans.*, 16. 497; Prollin's *Chem. Centralb.*, 1857, 231; Thomas, *Zeitschr. fur Analyt. Chem.* i., 517, &c.

|| Erdmann and v. Uslar, *Ann. Chem. Pharm.*, cxx., 121-360.

substitution of acetic, hydrochloric, or sulphuric for tartaric acid.

But to Dragendorff we owe decidedly the best general method of separation, since it is applicable not only to alkaloids, but to glucosides, and other active principles derived from plants. His process is essentially a combination of those already known, and its distinctive features are the shaking up—(1.) of the acid fluid with the solvent, thus removing colouring matters and certain non-alkaloidal principles; and, (2.) of the same fluid made alkaline. The following is his method in full. It may be advantageously used when the analyst has to search generally for vegetable poison, although it is, of course, far too elaborate for every case; and where from any circumstance there is good ground for suspecting the presence of one or two particular alkaloids or poisons, the process may be much shortened and modified. *

(2.) *Dragendorff's Process.*

I. The substance, in as finely-divided form as possible, is digested for a few hours in water acidified with sulphuric acid, at a temperature of 40° to 50°C., and this operation is repeated two or three times, with filtering and pressing of the substances; later, the extracts are united. This treatment (if the temperature mentioned is not exceeded) does not decompose the majority of alkaloids or other active substances; but there are a few (*e.g.*, solanine and colchicine) which would be altered by it; and if such are suspected, maceration at the common temperature is necessary, with substitution of acetic for sulphuric acid.†

II. The extract is next evaporated until it begins to be of a syrupy consistence; the residue mixed with three to four times its volume of alcohol, macerated for twenty-four hours at about 34°C., allowed to become quite cool, and filtered from the foreign matters which have separated. The residue is washed with alcohol of 70 per cent.

III. The filtrate is freed from alcohol by distillation, the watery residue poured into a capacious flask, diluted (if necessary) with water, and filtered. Acid as it is, it is extracted at the common temperature, with frequent shaking, by freshly-rectified petroleum ether; and after the fluids have again separated, the petroleum ether is removed, carrying with it certain impurities

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* Dragendorff's "Gerichtlich chemische Ermittelung von Giften." St. Petersburg, 1876, p. 141.

† When blood is to be examined it is better to dry it, and then powder and extract with water acidified with dilute sulphuric acid. However, if the so-called volatile alkaloids are suspected, this modification is to be omitted.

(colouring matter, &c.), which are in this way advantageously displaced. By this operation ethereal oils, carbolic acid, picric acid, &c., which have not been distilled, besides piperin, may also be separated. The shaking up with petroleum ether is repeated several times (as long as anything remains to be dissolved), and the products are evaporated on several watch-glasses.

RESIDUE OF PETROLEUM ETHER FROM THE ACID SOLUTION.

1. IT IS CRYSTALLINE.

A. *It is yellowish,* and with difficulty volatilised.

α. The crystals are dissolved by concentrated sulphuric acid, with the production of a clear yellow colour, passing into brown and greenish-brown. *Piperin.*

β. The solution in sulphuric acid remains yellow; cyanide of potash and caustic potash colour it, on warming, blood-red. *Picric acid.*

B. IT IS COLOURLESS, LIQUIDISES EASILY, AND SMELLS STRONGLY. *Camphor and similar matters.*

2. IT IS AMORPHOUS.

A. It is fixed.

α. Concentrated sulphuric acid dissolves it immediately—violet, and later greenish-blue: *Constituents of the black hellebore.*

β. It dissolves with a yellow colour, changing into fallow-brown. *Constituents of aconite plant, and products of the decomposition of aconitine.*

B. IT IS WHITE, SHARP-TASTING, AND REDDENS THE SKIN. *Capsicin.*

3. IT IS VOLATILE, with a powerful odour: *ethereal oil, carbolic acid, &c.*

It may be expected that the substances mentioned under the heads 1, 2, and 3, will be, in general, fully obtained by degrees. This is not the case, however, as regards piperin and picric acid.

IV. The watery fluid is now similarly shaken up with benzine, and the benzine removed and evaporated. Should the evaporated residue show signs of an alkaloid (and especially of theine), the watery fluid is treated several times with a fresh mixture of benzine, till a little of the last-obtained benzine extraction leaves on evaporation no residue. The benzine extracts are now united, and washed by shaking with distilled water; again separated and filtered, the greater part of the benzine distilled from the filtrate, and the remainder of the fluid divided and evaporated on several watch-glasses.

The evaporated residue may contain theine, colchicine, cubebin, digitaline, cantharidin, colocynthin, elaterin, caryophylline, absynthin, cascarillin, populin, santonin, &c., and traces of veratrine, delphinine, physostigmine, and berberin.

A remnant of piperin and picric acid may remain from the previous treatment with petroleum ether.

THE BENZINE RESIDUE FROM THE ACID SOLUTION.

1. IT IS CRYSTALLINE.

A. WELL-FORMED, COLOURLESS CRYSTALS.

α. Sulphuric acid dissolves the hair-like crystals without change of colour; evaporation with chlorine water, and subsequent treatment with ammonia, gives a murexide reaction. *Theine.*

β. Sulphuric acid leaves the rhombic crystals uncoloured. The substance, taken up by oil, and applied to the breast, produces a blister. *Canthardin.*

γ. Sulphuric acid leaves the scaly crystals at first uncoloured, then slowly develops a reddening. It does not blister; warm alcoholic potash-lye colours it a transitory red. *Santonin.*

δ. Sulphuric acid dissolves the spherical grains orange-yellow, and this solution is coloured by nitric acid a transitory violet.

ε. Sulphuric acid colours the crystals almost black, whilst it takes itself a beautiful red colour. *Cubebin.*

2. IT IS AMORPHOUS.

A. COLOURLESS OR PALE YELLOW RESIDUE.

α. Sulphuric acid dissolves it at first yellow; the solution becoming later red. Fröhde's reagent does not colour it violet. *Elaterin.*

β. Sulphuric acid dissolves red; Fröhde's reagent violet-red; tannic acid does not precipitate. *Populin.*

γ. Sulphuric acid dissolves it extremely red; Fröhde's reagent a beautiful cherry-red; tannic acid precipitates a yellowish-white. *Colocynthinin.*

δ. Sulphuric acid colours it gradually a beautiful red, whilst tannin does not precipitate. *Constituents of the Pimento.*

B. Crystals Pale to Clear Yellow.

α. *Piperin.*

β. *Picric Acid.*

γ. Caustic potash dissolves it purple. *Aloetin.*

C. Mostly undefined Colourless Crystals.

α. Sulphuric acid dissolves it green brown; bromine colours this solution red; dilution with water again green. The substance renders the heart-action of a frog slower. *Digitaline.*

β. Sulphuric acid dissolves it orange, then brown, lastly red-violet. Nitric acid dissolves it yellow, and water separates as a jelly out of the latter solution. Sulphuric acid and bromine do not colour it red. *Gratiolin.*

γ. Sulphuric acid dissolves it red-brown. Bromine produces in this solution red-violet stripes. It does not act on frogs. *Cascarillin.*

B. Pure Yellow Residue.

α. Sulphuric acid dissolves it yellow; on the addition of nitric acid, this solution is green, quickly changing to blue and violet. *Colchicine.*

β. Sulphuric acid dissolves with separation of a violet powder; caustic potash colours it red; sulphide of ammonia violet, and, by heating, indigo-blue. *Chrysammic acid.*

C. A Greenish Bitter Residue, which dissolves brown in concentrated sulphuric acid; in Fröhde's reagent, likewise, at first brown, then at the edge green, changing into blue-violet, and lastly violet.

Constituents of wormwood, with absynthin, besides quassiin, menyanthin, ericolin, daphnin, cnicin, and others.

D. Generally Undefined Yellow Crystallisation.—Sulphuric acid dissolves it olive green. The alcoholic solution gives with iodide of potash a colourless and green crystalline precipitate. *Berberin.*

V. As a complete exhaustion of the watery solution is not yet attained by the benzine agency, another is tried.

THE WATERY SOLUTION IS NOW EXTRACTED IN THE SAME WAY BY CHLOROFORM.

In chloroform the following substances are especially taken up:—Theobromine, narceine, papaverin, cinchonine, jervin, besides picrotoxin, syringin, digitaline, helleborine, convallamarin, saponin, senegin, smilacin. Lastly, portions of the bodies named in Process IV., which benzine failed to extract entirely, enter into solution, as well as traces of brucin, narcotine, physostigmine, veratrine, delphinine. The evaporation of the chloroform is conducted at the ordinary temperature in four or five watch-glasses.

THE CHLOROFORM RESIDUE FROM THE ACID SOLUTION.

1. The Residue is more or less markedly crystalline.

A. *It gives in the sulphuric acid solution evidence of an alkaloid by its action towards iodine and iodide of potash.*

α. Sulphuric acid dissolves it without the production of colour, and chlorine and ammonia give no murexide reaction. *Cinchonine.*

β. Sulphuric acid dissolves it without colour, chlorine and ammonia give as with theine a murexide reaction. *Theobromine.*

1. The Residue is Amorphous.

A. *In acetic acid solution it renders the action of the frog's heart slower, or produces local anæsthesia.*

αα. It does not produce local anæsthesia.

α. Sulphuric acid dissolves it red-brown, bromine produces a beautiful purple colour, water changes it into green, hydrochloric acid dissolves it greenish-brown. *Digitaline.*

β. Sulphuric acid dissolves it yellow, then brown-red; on addition of water this solution becomes violet. Hydrochloric acid, on warming, dissolves it red. *Convallamarin.*

bb. It produces local anæsthesia.

α. Sulphuric acid dissolves it brown. The solution becomes, by extraction with water, violet, γ. Sulphuric acid does not colour in the cold; on warming, the solution becomes a blue violet. *Papaverin.*

δ. Sulphuric acid dissolves it in the cold with the production of a blue colour.

Unknown impurities, many commercial samples of Papaverin.

ε. Sulphuric acid dissolves it at first grey-brown; the solution becomes in about twenty-four hours blood-red. Iodine water colours it blue.

Narceine.

B. IT GIVES NO ALKALOID REACTION.

α. Sulphuric acid dissolves it with a beautiful yellow

and can even be diluted with two volumes of water without losing its colour. *Saponin.*

β. Sulphuric acid dissolves it yellow. On diluting with water the same reaction occurs as in the previous case, but more feebly, and leaves behind, on evaporation, the yellow chloroform solution. *Senegin.*

γ. Sulphuric acid dissolves brown, and the solution becomes red by the addition of a little water. The action is very weak. *Smilacin.*

cc. Sulphuric acid dissolves it with the production of a dirty red, hydrochloric acid, in the cold, with that of a reddish-brown colour, and the last solution becomes brown on boiling.

Constituents of the hellebore, particularly Jervin.

b. Is inactive, and becomes blue by sulphuric acid; by Fröhde's reagent dark cherry red. Hydrochloric acid dissolves it red. The solution becomes by boiling colourless.

Syringin.

colour; mixed with nitre, then moistened with sulphuric acid, and lastly treated with concentrated soda-lye, it is coloured a brick-red. *Picrotoxin.*

β. Sulphuric acid dissolves it with the production of a splendid red colour. The substance renders the heart-action of a frog slower. *Helleborine.*

VI. THE WATERY FLUID IS NOW AGAIN SHAKEN UP WITH PETROLEUM ETHER,

In order to take up the rest of the chloroform, and the watery fluid is saturated with ammonia. The watery solution of *aconite* and *emetin* is liable to undergo, through free ammonia, a partial decomposition; but on the other hand, it is quite possible to obtain, with very small mixtures of these substances, satisfactory reactions, even out of ammoniacal solutions.

VII. THE AMMONIACAL WATERY FLUID WITH PETROLEUM ETHER.

In the earlier stages Dragendorff advises the shaking up with petroleum ether at about 40°, and the removal of the ether as quickly as possible whilst warm. This is with the intention of separating by this fluid strychnine, brucin, emetin, quinine, veratrine, &c. Finding, however, that a full extraction by petroleum ether is either difficult or not practicable, he prefers, as we have seen, to conclude the operation by other agents, coming back again upon the ether for certain special cases. Such are the volatile alkaloids; and here he recommends treatment of the fluid by *cold* petroleum ether, taking care *not* to hasten the removal of the latter. Strychnine and other fixed alkaloids are then only taken up in small quantities, and the greater portion remains for the later treatment of the watery fluid by benzine.

A portion of the petroleum ether, supposed to contain in solution volatile alkaloids, is evaporated in two watch-glasses; to the one strong hydrochloric acid is added, the other being evaporated without this agent. On the evaporation of the petroleum ether, it is seen whether the first portion is crystalline or amorphous, or whether the second leaves behind a strongly smelling fluid mass, which denotes a volatile alkaloid. If the residue in both glasses is without odour and fixed, the absence of volatile acid and the presence of fixed alkaloids (strychnine, emetin, veratrine, &c.) are indicated.

THE PETROLEUM ETHER RESIDUE FROM AMMONIACAL SOLUTION.

1. IT IS FIXED AND CRYSTALLINE.	2. IT IS FIXED AND AMORPHOUS.	3. IT IS FIXED AND ODOROUS.
A. *The crystals volatilise with difficulty.*		A. *On adding to the watch-glass a littl hydrochloric acid, crystals are left behind.*
aa. Sulphuric acid dissolves it without colour.		*aa.* Its solution is not precipitated by platin chloride.
α. Chromate of potash colours this solution a transitory blue, then red. *Strychnine.*	α. The purest sulphuric acid dissolves it almost without colour; sulphuric, containing nitric acid, red, quickly becoming orange. *Brucine.*	α. The crystals o the hydrochloric compound act on polarised light, and are mostly needle shaped and colum nar. *Conia and Methyl Conia.*
β. Chromate of potash does not colour it blue. With chlorine, water, and ammonia, it gives a green colour. *Quinine.*	β. Sulphuric acid dissolves it yellow, becoming deep red. *Veratrine.*	β. The crystal are cubical or tetra hedral. *Alkaloid from cap sicum.*
	γ. Sulphuric acid dissolves it brown-green; Fröhde's reagent red, changing into green. *Emetin.*	
		bb. The solutio of the hydrochlorat of the alkaloid i precipitated by pla tin chloride. *Sarracinin*
b. Sulphuric acid dissolves it yellow,		*b.* The residue o the hydrochlorate o

and the solution becomes gradually a beautiful deep red.

Sabadilline.

c. The crystals are easily volatilised.

Conia.

the alkaloid is amorphous, or, by further additions of HCl, becomes crystalline.

aa. Its diluted aqueous solution is precipitated by platin chloride.

α. The hydrochlorate salt, being quickly treated with Fröhde's re-agent, gives after about two minutes a deep violet solution, which gradually fades.

Lobeliin.

β. The hydrochlorate smells like nicotin, and becomes by Fröhde's reagent yellow, and after twenty-four hours pale red. *Nicotin.*

The hydrochlorate is without odour, the free base smells faintly like aniline.

Sparteine.

bb. The substance is not precipitated from a diluted solution by platin chloride.

α. Its petroleum ether solution produces no turbidity with a solution of picric acid in petroleum ether; but it leaves behind, when mixed with the above, crystals mostly of three-sided plates.

Trimethylamin.

β. The petroleum ether solution gives, on evaporation, when treated similarly, moss-like crystals. The substance is made blue by chloride of lime, as well as by diluted sulphuric acid and bichromate of potash. *Aniline.*

γ. The alkaloid does not smell like methylamin, and is not coloured by chloride of lime, sulphuric acid, or chromate of potash.

Volatile alkaloid of the Pimento.

VIII. THE AMMONIACAL SOLUTION IS SHAKEN UP WITH BENZINE.

In most cases petroleum ether, benzine, and chloroform, are more easily separated from acid watery fluids than from ammoniacal, benzine and chloroform causing here a difficulty which has perhaps deterred many from using this method. Dragendorff, however, maintains that he has never examined a fluid in which he could not obtain a complete separation of the benzine and water. If the upper benzine layer is fully gelatinous and emulsive, the under layer of water is to be removed with a pipette as far as possible, and the benzine with a few drops of absolute alcohol and filtration. As a rule, the water goes through first alone, and by the time the greater part has run through, the jelly in the filter, by dint of stirring, has become separated from the benzine; finally, the jelly shrinks up to a minimum, and the clear benzine filters off. Dragendorff filters mostly into a burette, from which ultimately the benzine and the water are separated.

The principal alkaloids which are dissolved in benzine are—strychnine, methyl and ethyl strychnine, brucine, emetin, quinine, cinchonine, atropine, hyoscyamine, physostogmin, aconitine, nepalin, the alkaloid of the Aconitum lycoctonum, aconellin, napellin, delphinine, veratrine, sabatrin, sabadilline, codeine, thebaine, and narcotine.

THE BENZINE RESIDUE DERIVED FROM THE AMMONIACAL SOLUTION.

1. IT IS FOR THE MOST PART CRYSTALLINE.

a. Sulphuric acid dissolves it without colour, the solution being coloured neither on standing nor on the addition of nitric acid.

aa. It dilates the pupil of a cat.

α. Platin chloride does not precipitate the aqueous solution. The sulphuric acid solution gives on warming a peculiar smell. *Atropine.*

β. Platin chloride applied to the solution precipitates. *Hyoscyamine.*

bb. It does not dilate the pupil.

α. The sulphuric acid solution becomes blue by chromate of potash.

αα. The substance applied to a frog produces tetanus. *Strychnine.*

ββ. It lowers the number of respirations in a frog. *Ethyl and Methyl Strychnine.*

β. Sulphuric acid and bichromate of potash do not colour it blue.

2. IT IS FOR THE MOST PART AMORPHOUS.

a. Pure sulphuric acid dissolves it either whitish-red or yellowish.

α. The solution becomes by nitric acid immediately red, then quickly orange. *Brucine.*

β. The solution becomes by little and little brownish-red. The substance is coloured red by chloride of lime solution, and it contracts the pupil. *Physostogmin.*

αα The sulphuric acid watery solution is fluorescent, and becomes green on the addition of chlorine water and ammonia. *Quinine and Cinchonine.* (The last is more difficult to dissolve in petroleum ether than quinine).	
ββ. The solution is not fluorescent. *Cinchonine.*	
b. Sulphuric acid dissolves it at first colourless; the solution takes on standing a rose or violet-blue; on addition of nitric acid, a blood-red or brown coloration.	*b.* Pure sulphuric acid dissolves it yellow, and the solution becomes later beautiful red (with delphinine, more quickly a darker cherry-red).
α. A solution in diluted sulphuric acid becomes, on heating, gradually deep blood-red, and, when cooled, violet, with nitric acid. The aqueous solution is precipitated by ammonia. *Narcotine.*	*α.* The hydrochloric acid solution becomes red on heating.
	αα. The substance acts on a frog, causing, in large doses, tetanus. *Veratrine.* It is almost without action on frogs. *Sabatrin.*
β. The solution in diluted sulphuric acid becomes, on heating, a beautiful blue. Excess of ammonia does not precipitate in a diluted watery solution. *Codeine.*	*β.* The hydrochloric acid solution does not, on heating, become red. *Delphinine.*
c. Sulphuric acid dissolves it with the production of a yellow colour.	*c.* Pure sulphuric acid dissolves it yellow, and the solution becomes later red-brown, and gradually violet-red.
α. The solution remains yellow on standing. *Acolyctin.*	*α.* The substance even in small doses paralyses frogs, and dilates the pupil of a cat's eye. Ether dissolves it with difficulty. *Nepalin.*

β. It becomes beautifully red. *Sabadilline.*	*β*. It is easily soluble in ether, its effects are not so marked, and it does not dilate the pupil. *Aconitine.* Its effects are still feeble; it does not dilate the pupil, and is with difficulty dissolved by ether. *Napellin.*
d. Sulphuric acid dissolves it with an immediate deep red-brown colour. *Thebaine.*	*d*. Sulphuric acid dissolves it with a dark green colour, and the solution becomes, even after a few seconds, a beautiful blood-red. *Alkaloidal substances out of the Aconitum lycoctonum.*
e. Sulphuric acid dissolves it immediately blue. *Substances accompanying the papaverins.*	*e*. Sulphuric acid dissolves it brown-green, and Fröhde's reagent red, becoming beautifully green. *Emetin.*

IX. SHAKING OF THE AMMONIACAL WATERY SOLUTION WITH CHLOROFORM.

This extracts the remainder of the cinchonine and papaverin, narceine, and a small portion of morphia, as well as an alkaloid from the celandine.

The Residue from the Chloroform.

aa. The solution, on warming, is only slightly coloured.

α But after it is again cooled, it strikes with nitric acid a violet-blue; chloride of iron mixed with the substance gives a blue colour; Fröhde's reagent also dissolves it violet.
Morphia.

β. It is not coloured by nitric acid; it is also indifferent to chloride of iron. *Cinchonine.*

bb. The solution becomes by warming violet-blue.
Papaverin.

b. Sulphuric acid dissolves it greenish-brown, and the solution becomes, on standing, blood-red. *Narceine.*

c. Sulphuric acid dissolves it a violet-blue.
Alkaloidal constituent of the Celandine.

X. SHAKING UP OF THE WATERY FLUID WITH AMYL ALCOHOL.

From this process, besides morphia and solanine, as well as salicin, the remnants of the convallamarin, saponin, senegin, and narceine, are also to be expected.

The Amyl Alcohol Residue.

a. Sulphuric acid dissolves it without colour in the cold.
Morphia (see above).

b. Sulphuric acid dissolves it with the production of a clea yellow-red, and the solution becomes brownish. Iodine wate colours it a deep-brown. The alcoholic solution gelatinises.
Solanine.

c. Sulphuric acid dissolves it green-brown, becoming red.
Narceine (see above).

d. Sulphuric acid dissolves it yellow, then brown-red, becoming violet on dilution with water. Hydrochloric acid dissolves it, and it becomes red on warming. It stops the heart-action in the systole. *Convallamarin.*

β. Hydrochloric acid dissolves it for the most part without colour. *Saponin.*

γ. As the foregoing, but acting more feebly.
Senegin.

e. Sulphuric acid dissolves it immediately a pure red. On warming with sulphuric acid and bichromate of potash, a smell of salicylic acid is developed. *Salicin.*

XI. DRYING THE WATERY FLUID WITH THE ADDITION OF POWDERED GLASS, AND EXTRACTION OF THE FINELY-DIVIDED RESIDUE BY CHLOROFORM.

The residue of the first chloroform extract lessens the number of respirations of a frog; the residue of the second and third chloroform extract becomes, by sulphuric acid and bichromate of potash, blue, passing into a permanent red.

Another portion of this residue becomes red on warming with diluted sulphuric acid. *Curarine.*

(3.) SHORTER PROCESS FOR SEPARATING SOME OF THE ALKALOIDS.

A shorter process, recommended conditionally by Dragendorff, for brucine, strychnine, quinine, cinchonine, and emetin, is as follows:—

The substance, if necessary, is finely divided, and treated with sulphuric acid (dilute) until it has a marked acid reaction. To every 100 cc. of the pulp (which has been diluted with distilled water to admit of its being filtered later), at least 5 to 10 cc. of diluted sulphuric acid (1 : 5) are added. It is digested at 50°C. for a few hours, filtered, and the residue treated again with 100 cc. of water at 50°C. This extract is, after a few hours, again filtered; both the filtrates are mixed and evaporated in the water-bath to almost the consistence of a thin syrup. The fluid, however, must not be concentrated too much, or fully evaporated to dryness. The residue is now placed in a flask, and treated with three to four times its volume of alcohol of 90 to 95 per cent.; the mixture is macerated for twenty-four hours, and then filtered. The filtrate is distilled alcohol-free, or nearly so, but a small amount of alcohol remaining is not objectionable. The watery fluid is diluted to about 50 cc., and treated with pure benzine; the mixture is shaken, and after a little time the benzine removed—an operation which is repeated. After the removal the second time of the benzine, the watery fluid is made alkaline with ammonia, warmed to 40° or 50°C., and the free alkaloid extracted by twice shaking it up with two different applications of benzine. On evaporation of the latter, if the alkaloid is not left pure, it can be dissolved in acid, precipitated by ammonia, and again extracted by benzine.

(4.) *Scheibler's Process.*

A method very different from those just described is one practised by Scheibler. This is to precipitate the phospho-tungstate of the alkaloid, and then to liberate the latter by digesting the precipitate with either hydrate of barium or hydrate of calcium, dissolving it out by chloroform, or, if volatile, by simple distillation. The convenience of Scheibler's process is great, and it admits of very general application. In complex mixtures, it will usually be found best to precede the addition of phospho-tungstic acid[*] by that of acetate of lead, in order to remove colouring

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[*] The method of preparing this reagent is as follows:—Ordinary commercial sodium tungstate is treated with half its weight of phosphoric acid, specific gravity 1·13, and then allowed to stand for some days. Phospho-tungstic acid separates in crystals.

matter, &c.; the excess of lead must in its turn be thrown out by SH_2, and the excess of SH_2 be got rid of by evaporation. Phospho-tungstic acid is a very delicate test for the alkaloids, giving a distinct precipitate with the most minute quantities ($\frac{1}{2000000}$ of strychnine and $\frac{1}{1000000}$ of quinine). A very similar method is practised by Sonnenschein and others with the aid of phosphomolybdic acid. The details of Scheibler's process are as follows:—

The organic mixture is repeatedly extracted by water strongly acidified with sulphuric acid; the extract is evaporated at 30° to the consistence of a thin syrup, then diluted with water, and, after several hours' standing, filtered in a cool place. To the filtered fluid phosphomolybdic acid is added in excess, the precipitate filtered, washed with water to which some phosphomolybdic acid and HNO_3 have been added, and whilst still moist rinsed into a flask. Caustic baryta or carbonate of potash is added to alkaline reaction, and after the flask has been connected with bulbs containing HCl, it is heated at first slowly, then more strongly. Ammonia and any volatile alkaloids are driven over into the acid, and are there fixed, and can be examined later by suitable methods. The residue in the flask is carefully evaporated to dryness (the excess of baryta having been precipitated by CO_2), and then extracted by strong alcohol. On evaporation of the alcohol, the alkaloid is generally sufficiently pure to be examined, or, if not so, it may be obtained pure by re-solution, &c.

§ 28. *Identification of the Alkaloids.*—Having obtained, in one way or other, a crystalline or amorphous substance, supposed to be an alkaloid, or, at all events, an active vegetable principle, the next step is to identify it. If the tests given in Dragendorff's process have been applied, the observer will have already gone a good way towards the identification of the substance; but it is, of course, dangerous to trust to one reaction.

In medico-legal researches there is seldom any considerable quantity of the material to work upon. Hence the greatest care must be taken from the commencement not to waste the substance in useless tests, but to study well at the outset what—by the method of extraction used, the microscopic appearance, the reaction to litmus paper, and the solubility in different menstrua—it is likely to be. However minute the quantity may be, it is essential to divide it into different parts, in order to apply a variety of tests; but as any attempt to do this on the solid substance will probably entail loss, the best way is to dissolve it in a watch-glass in half a cc. of alcohol, ether, or other suitable solvent. Droplets of this solution are then placed on watch glasses or slips of microscopic glass, and to these drops, by the aid of a glass rod, different reagents can be applied, and the changes watched under the microscope as the drops slowly evaporate.*

(1.) *Action of Sulphuric Acid.*—A test very generally applicable to the alkaloids is the colour, or absence of colour, they produce when treated by strong acids, such as sulphuric or nitric. A drop of the solution is allowed to evaporate to dryness on a piece of porcelain, and then a droplet of strong pure acid is mixed with it, the action being first observed in the cold, and the plate afterwards heated. The following useful short table is given by Dr. Guy †:—

	Sulphuric Acid.			Nitric Acid.
	Cold.	Warm.	Hot.	
Cantharidin, .	0	0	0	0
Strychnine, .	0	0	Yellow ^{1} ‡	Pink^2
Brucine, . .	0	0	Yellow^2	Red^3
Morphine, .	0	0	Brown	Orange^3
Atropine, . .	0	0	Brown^3	0
Aconitine, .	0	Brown	Black	0
Picrotoxin, .	0	Yellow	Brown	0
Veratrine, .	Orange^3	Scarlet	Claret	0
Digitaline, .	Red-brown^1	Red-brown^2	Red-brown^3	0
Solanine, . .	Yellow^3	Brown^3	Brown^3	0

(2.) *Sublimation of the Alkaloids.*—A very beautiful and elegant aid to the identification of alkaloids, and vegetable principles generally, is their behaviour towards heat.

Alkaloids, glucosides, the organic acids, &c., when carefully heated, either—(1) sublime wholly without decomposition (like theine, cytisin, and others); or, (2) partially sublime with decom-

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* The modern chemist who aims at being a forensic expert will be of necessity compelled to make himself intimately acquainted with all the chief vegetable alkaloids. Since the discovery by Sertürner of morphia (the first alkaloid ever isolated) in the beginning of this century, alkaloidal criminal poisoning has kept pace, one may almost say, with the discovery of the alkaloids themselves; and the scientific criminals who arise from time to time will certainly choose some poison not met with in ordinary commerce.

† "Forensic Medicine," p. 679.

‡ The small figures denote degrees of intensity.

position; or, (3) are changed into new bodies (as, for example, gallic acid); or, (4) melt and then char; or, (5) simply char and burn away.

Many of these phenomena are striking and characteristic, taking place at definite temperatures, subliming in characteristic forms, or leaving characteristic residues.

One of the first to employ sublimation systematically, as a means of recognition of the alkaloids, &c., was Helwig.* His method was to place a small quantity (from $\frac{1}{2}$ to $\frac{1}{1000}$ of a milligram) in a depression on platinum foil, cover it with a slip of glass, and then carefully heat by a small flame. After Helwig, Dr. Guy† greatly improved the process by using porcelain discs, and more especially by the adoption of a convenient apparatus, which may be termed "the subliming cell." It is essentially composed of a ring of glass from $\frac{1}{8}$ to $\frac{2}{3}$ of an inch in thickness, such as may be obtained by sections of tubing, the cut surfaces being ground perfectly smooth. This circle is converted into a closed cell by resting it on one of the ordinary thin discs of glass used as a covering for microscopic purposes, and supporting a similar disc. The cell was placed on a brass plate, provided with a nipple, which carried a thermometer, and was heated by a small flame applied mid-way between the thermometer and the cell; the heat was raised very gradually, and the temperature at which any change took place was noted. In this way Dr. Guy made determinations of the subliming points of a large number of substances, and the microscopic appearances of the sublimates were described with the greatest fidelity and accuracy. The writer, however, on repeating with care Dr. Guy's determinations, could in no single instance agree with his subliming points, nor with the apparatus he figures and describes could two consecutive observations exactly coincide. Further, on examining the various subliming temperatures of substances, as stated by different authors, the widest discrepancies were found—differences of two or even three degrees might be referred to errors of observation, a want of exact coincidence in the thermometers employed, and the like; but to what, for example, can we ascribe the irreconcilable statements which have been made with regard to theine? According to Strauch, this substance sublimes at 177°C.; according to Mulder, at 184·7°. But that both of these observations deviate more than 70 degrees from the truth may be proved by any one who cares to place a few milli-

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* "Das Mikroscop in der Toxicologie."

† *Pharm. Journ. Trans.* [2], viij. 719; ix. 10, 58. "Forensic Medicine." London, 1875.

grams of theine, enclosed between two watch-glasses, over the water-bath; in a few minutes a distinct sublimate will condense on the upper glass, and, in point of fact, theine will be found to sublime several degrees below 100°.

Since this great divergency of opinion is not found either in the specific gravity, or the boiling points, or any of the like determinations of the physical properties of a substance, it is self-evident that the processes hitherto used for the determination of subliming points are faulty. The sources of error are chiefly—

(1.) Defects in the apparatus employed,—the temperature read being rather that of the metallic surface in the immediate vicinity of the thermometer, than of the substance itself.

(2.) The want of agreement among observers as to what should be called a sublimate; one considering a sublimate only that which is evident to the naked eye, another taking cognisance of the earliest microscopic film.

(3.) No two persons employing the same process.

With regard to the apparatus employed, the present writer adopts Dr. Guy's subliming cell; but the cell, instead of resting on a metallic solid, floats on a metallic fluid; for any temperature a little above 100°C. this fluid is mercury, but for higher temperatures fusible metal is preferable.

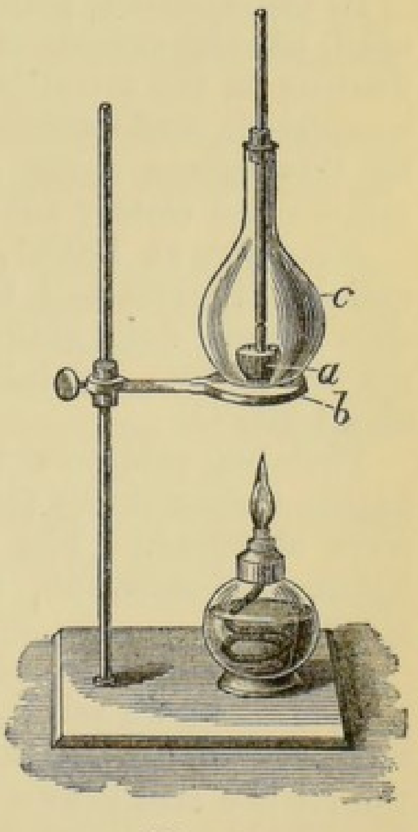

Fig. 16.

The exact procedure is as follows:—A porcelain crucible (see Fig. 16, *a*), about 3 inches in diameter, is nearly filled with mercury or fusible metal, as the case may be; a minute speck (or two or three crystals of the substance to be examined) is placed on a thin disc of microscopic covering glass, floated on the liquid, and the cell is completed by the glass ring and upper disc. The porcelain crucible is supported on a brass plate (*b*), fixed to a retort stand in the usual way, and protected from the unequal cooling effects of currents of air by being covered with a flask (*c*), from which the bottom has been removed. The neck of the flask conveniently supports a thermometer, which passes through a cork, and the bulb of the thermometer is immersed in the bath of liquid metal. In the first examination of a substance the temperature is raised somewhat rapidly, taking off the upper disc with a forceps at every 10 degrees, and exchanging it for a fresh disc, until the substance is destroyed. The second examination is conducted much more slowly, and the discs exchanged at every four or five degrees, whilst the final determination is effected by raising the temperature with great caution, and exchanging the discs at about the points of change (already partially determined) at every half degree. All the discs are examined microscopically. The most convenient definition of a sublimate is this—the most minute films, dots, or crystals, which can be observed by a $\frac{1}{4}$-inch power, and which are obtained by keeping the subliming cell at a definite temperature for sixty seconds. The commencement of many sublimates assumes the shape of dots of extraordinary minuteness, quite invisible to the unaided eye; and, on the other hand, since the practical value of sublimation is mainly as an aid to other methods for the recognition of substances, if we go beyond *short* intervals of time, the operation, otherwise simple and speedy, becomes cumbersome, and loses its general applicability.

There is also considerable discrepancy of statement with regard to the melting point of alkaloidal bodies; in many instances a viscous state intervenes before the final complete resolution into fluid, and one observer will consider the viscous state, the other complete fluidity, as the melting point.

In the melting points given below the same apparatus was used, but the substance was simply placed on a thin disc of glass floating on the metallic bath before described (the cell not being completed), and examined from time to time microscopically, for by this means alone can the first drops formed by the most minute and closely adherent crystals to the glass be discovered.

Morphine, at 150°C., clouds the upper disc with nebulæ; the nebulæ are resolved by high magnifying powers into minute dots; these dots gradually become coarser, and are generally converted into crystals at 188°C.; the alkaloid browns at or about 200°C.

Thebaine sublimes in theine-like crystals at 135°C.; at higher temperatures (160° to 200°C.), needles, cubes, and prisms were observed. The residue on the lower disc, if examined before carbonisation, is fawn-coloured with non-characteristic spots.

Narcotine gives no sublimate; it melts at 155°C. into a yellow liquid, which on raising the temperature ever becomes browner to final blackness. On examining the residue before carbonisation, it is a rich brown amorphous substance; but if narcotine be heated two or three degrees above its melting point, and then cooled slowly, the residue is crystalline; long, fine needles radiating from centres being common.

Narceine gives no sublimate; it melts at 134°C. into a colourless liquid, which undergoes at higher temperatures the usual transition of brown colours; the substance heated a few degrees above its melting point, and then allowed to cool slowly, shows a straw-coloured residue, divided into lobes or drops containing feathery crystals.

Papaverin gives no sublimate, it melts at 130°C. The residue heated a little above its melting point, and then slowly cooled, is amorphous, of a light-brown colour, and in no way characteristic.

Hyoscyamine gives no crystalline sublimate; it melts at 89°C., and appears to volatilise in great part without decomposition. It melts into an almost colourless fluid, which when solid may exhibit a network not unlike vegetable parenchyma; on moistening the network with water, interlacing crystals immediately appear. If, however, hyoscyamine be kept at 94° to 95° for a few minutes, and then slowly cooled, the edges of the spots are arborescent, and the spots themselves crystalline.

Atropine (daturine) melts at 97°C.; at 123°C. a faint mist appears on the upper disc. Crystals cannot be obtained; the residue is not characteristic.

Solanine.—The upper disc is dimmed with nebulæ at 190°C., which are coarser and more distinct at higher temperatures; at 200°C. it begins to brown, and then melts; the residue consists of amber-brown, non-characteristic drops.

Strychnine gives a minute sublimate of fine needles, often disposed in lines at 169°C.; about 221°C. it melts, the residue (at that temperature) is resinous.

Brucine melts at 151°C. into a pale yellow liquid, at higher temperatures becoming deep-brown. If the lower disc after melting be examined, no crystals are observed, the residue being quite transparent, with branching lines like the twigs of a leafless tree; light mists, produced rather by decomposition than by true sublimation, condense on the upper disc at 185°C., and above.

Saponin neither melts nor sublimes; it begins to brown about 145°C., is almost black at 185°C., and quite so at 190°C.

Delphinine begins to brown about 102°C.; it becomes amber at 119°C., and melts, and bubbles appear. There is no crystalline sublimate; residue not characteristic.

Pilocarpine gives a distinct crystalline sublimate at 153°C.; but thin mists, consisting of fine dots, may be observed as low as 140°C. Pilocarpine melts at 159°C.; the sublimates at 160° to 170°C., are in light yellow drops; if these drops are treated with water, and the water evaporated, feathery crystals are obtained; the residue is resinous.

Theine wholly sublimes; the first sublimate is minute dots, at 79°C.; at half a degree above that very small crystals may be obtained; and at such a temperature as 120°C., the crystals are often long and silky.

Theobromine likewise wholly sublimes; nebulæ at 134°C., crystals at 170°C., and above.

Delphinine gives no crystalline sublimate. It begins to brown at 119°C., and melts, the melted mass containing bubbles. The residue is not characteristic.

Salicin melts at 170°C.; it gives no crystalline sublimate. The melted mass remains up to 180°C. almost perfectly colourless; above that temperature browning is evident. The residue is not characteristic.

Picrotoxin gives no crystalline sublimate. The lowest temperature at which it sublimes is 128°C.; the usual nebulæ then make their appearance; between 165° and 170° there is slight browning; at 170° it melts. The residue, slowly cooled, is not characteristic.

Cantharidin sublimes between 82° and 83°C., very scantily at 85°C. The sublimate is copious.

Quinetum begins to sublime in distinct crystals, composed of short prisms, needles, and plates, at 147°C.; at 139°C. the substance is found melted in drop-like forms, not crystalline. The residue, from a sublimate of such temperature as 150° to 160°C., is intermixed with well-formed crystals.

Quinidine begins to brown very slightly about 100°C. If kept above that temperature up to 180°C., a rich brown residue is left on the lower disc, which has a peculiar reticulated appearance.

The active principles of plants may, in regard to their behaviour to heat, be classed for practical purposes into—

1. Those which give a decided crystalline sublimate:
    - (*a.*) Below 100°, *e.g.*, theine, thebaine, cantharidin.
    - (*b.*) Between 100° and 150°, *e.g.*, quinetum.
    - (*c.*) Between 150° and 200°, *e.g.*, strychnine, morphine, pilocarpine.

2. Those which melt, but give no crystalline sublimate:
    - (*a.*) Below 100°, *e.g.*, hyoscyamine, atropine.
    - (*b.*) Between 100° and 150°, *e.g.*, papaverin.
    - (*c.*) Between 150° and 200°, *e.g.*, salicin.
    - (*d.*) Above 200°, *e.g.*, solanine.

3. Those which neither melt nor give a crystalline sublimate, *e.g.*, saponin.

§ 29. *Quantitative Estimation of the Alkaloids.*—For medico-legal purposes the alkaloid obtained is usually weighed directly, but for technical purposes other processes are used. One of the most convenient of these is titration with normal or decinormal sulphuric acid, a method applicable to a few alkaloids of marked basic powers—*e.g.*, quinine is readily and with accuracy estimated in this way, the alkaloid being dissolved in a known volume of the acid, and then titrated back with soda. If a large number of observations are to be made, an acid may be prepared so that each cc. equals 1 mgrm. of quinine. A reagent of general application is found in the so-called *Mayer's reagent*, which consists of 13,546 grms. of mercuric chloride, and 49·8 grms of iodide of potash in the litre of water. Each cc. of such solution precipitates—

Of Strychnine,	·0167	grm.
,, Brucine, .	·0233	,,
,, Quinine, .	·0108	,,
,, Cinchonine,	·0102	,,
,, Quinidine,	·0120	,,
,, Atropine,	·0145	,,
,, Aconitine,	·0268	,,
,, Veratrine,	·0269	,,
,, Morphine,	·0200	,,
,, Narcotine,	·0213	,,
,, Nicotine,	·00405	,,
,, Coneine,	·00416	,,

The final reaction is found by filtering, from time to time, a drop on to a glass plate, resting on a blackened surface, and adding the test until no precipitate appears. The results are only accurate when the strength of the solution of the alkaloid is about 1 : 200; so that it is absolutely necessary first to ascertain approximately the amount present, and then to dilute or concentrate, as the case may be, until the proportion mentioned is obtained

A convenient method of obtaining the sulphate of an alkaloid or quantitative purposes, and especially from organic fluids, is that recommended by Wagner. The fluid is acidulated with sulphuric acid, and the alkaloid precipitated by a solution of odine in iodide of potash. The precipitate is collected and disolved in an aqueous solution of hyposulphite of soda. The ltered solution is again precipitated with the iodine reagent, nd the precipitate dissolved in sulphurous acid, which, on vaporation, leaves behind the pure sulphate of the base.

II.—OPIUM.

§ 30. Opium is a gummy mass, consisting of the juice of the incised unripe fruit of the *Papaver somniferum*, hardened in the air, and containing a large quantity of definite, highly-complex crystalline principles. The following analyses by Schindler, although somewhat imperfect, give an idea as to the relative proportion of the chief constituents :—

	Smyrna.	Constant.	Egyptian.
Morphia,	10·30	4·50	7·00
Codeia,	·25	·52	...
Narcotine,	1·30	3·47	2·68
Narceia,	·71	·42	
Meconin,	·08	·30	
Meconic acid,	4·70	4·38	
Peculiar resin,	10·93	8·10	
Vegetable mucus - caoutchouc, acid, fat, and vegetable fibre,	26·25	17·18	
Brown acid, soluble in water and alcohol,	1·04	·40	
Brown acid, soluble only in water, also gum,	40·13	56·46	
Lime,	0·40	0·02	
Magnesia,	0·07	0·40	
Alumina, ferric oxide, silica, calcic phosphate,	0·24	·22	
Salts and vegetable oil,	0·36	0·36	
About.	96·76	96·73	

Several of the best processes for extracting morphine and th chief crystalline substances, with a view to their valuation, ar as follows :—

(1.) *Schacht's Method.* — Five to ten grms. of dry, finely powdered opium are digested with sufficient distilled water t make a thin pulp. After twenty-four hours the whole is throw on a weighed filter, and washed until the washings are almos colourless and tasteless. The portion insoluble in water is drie at 100°C., and weighed; in good opium this should not excee 40 per cent. The filtrate is evaporated until it is about one-fift of the weight of the opium taken originally; cooled, filtered and treated with pure animal charcoal until the dark-brow colour is changed into a brownish-yellow. The liquid is the re-filtered, precipitated with a slight excess of ammonia, allowe to stand in an open vessel until all odour of ammonia di appears, and at the same time frequently stirred, in order tha the precipitate may not become crystalline — a form which is always more difficult to purify. The precipitate is now collected on a tared filter, washed, dried, and weighed. With an opium containing 10 per cent. of morphine its weight is usually 14 per cent. A portion of the precipitate is then detached from the filter, weighed, and exhausted, first with ether, and afterwards with boiling alcohol (0·81 specific gravity). Being thus purified from narcotine, and containing a little colouring matter only, it may now be dried and weighed, and the amount of morphine calculated on the whole from the data obtained.

(2.) *Kiefer's* ingenious method,* which is based on the fact that morphine changes ferridcyanide of potash into ferrocyanide of potash, gives, according to C. Schacht, no satisfactory result.

(3.) *Fleury* has proposed a titration by oxalic acid as follows:—2 grms. of the powdered opium are macerated a few hours with 8 cc. of aqueous oxalate of ammonia, brought on a filter, and washed with 5 cc. of water. To the filtrate an equal volume of 80 per cent. alcohol and ammonia to alkaline reaction is added; and after standing twenty-four hours in a closed flask, it is filtered, and the flask rinsed out with some cc. of 40 per cent. alcohol. The filter, with its contents after drying, is placed in the same flask (which should not be cleansed), a few drops of alcoholic logwood solution are added, with an excess of oxalic acid solution of known strength, the whole being made up to 100 cc. This is divided into two parts, and the excess of acid titrated back with diluted soda-lye. If the oxalic acid solution is of the strength of 4·42 grms. to the litre, every cc. of the oxalic acid solution which has become bound up with morphine, corresponds to 0·02 grm. of morphine.

(4.) *Hager's Method* has the merit of being speedy, although the results are not perfectly accurate:—5 grms. of the powdered opium are thoroughly mixed in a mortar with previously slaked lime, and then heated in a flask for an hour with 50 grms. of distilled water at a boiling temperature. The whole is thrown on a small filter, and washed with hot water until the filtrate weighs 80 grms. This filtrate is concentrated in the water-bath to 50 grms., and placed in a conical glass; 1·5 grm. of ether and six drops of good benzine are then added, which hasten the separation of morphine, and hinder the adhesion of crystals to the sides of the glass. The liquid is well stirred, and 3·5 grms. of chloride of ammonium are added. After three hours the morphia is thus precipitated, separated by filtration, and weighed. The precipitate may be purified by washing with ether; some morphine

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* *Ann. Chem. Pharm.*, ciii. 271.

always remains in solution; but it may, as Dragendorff suggests, be recovered by shaking the alkaline solution with amyl alcohol.

§ 31. *Medicinal and other Preparations of Opium.*—The chief mixtures, pills, and other forms, officinal and non-officinal, in which opium may be met with, are as follows:—

(1.) *Officinal.*

Compound Tincture of Camphor, P. B.*—Opium, camphor, benzoic acid, oil of anise, and proof spirit.

Opium, . .	41	by weight in 100 by measure.
Benzoic Acid, .	41	,, ,, ,,
Camphor, .	31	,, ,,

One grain of opium is contained in half an ounce of the tincture.

Ammoniated Tincture of Opium.—Strong solution of ammonia, rectified spirit, opium, oil of anise, saffron, and benzoic acid.

Opium,	1·04	parts by weight in 100 by measure.
Benzoic acid,	1·87	,, ,, ,,

One grain of opium in every 96 minims.

The Compound Powder of Kino, P. B.

Opium, ...	5 per cent.
Cinnamon, ...	20 ,,
Kino, ...	75 ,,

The Compound Powder of Opium, P. B.

Opium, ...	10·00 per cent.
Black Pepper, ...	13·33 ,,
Ginger, ...	33·33 ,,
Caraway fruit, ...	40·00 ,,
Tragacanth, ...	3·33 ,,

Tincture of Opium (*Laudanum*).—Opium and proof spirit. One grain of opium in 14·8 min.; that is, about 6·7 parts by weight in 100 by measure.

Pill of Lead and Opium, P. B.

Acetate of Lead, ...	75·0 per cent.
Opium, ...	12·5 ,,
Confection of Roses, ...	12·5 ,,

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* The common appellation of this tincture is *Paregoric*, or Paregoric Elixir.

Aromatic Powder of Chalk and Opium.—Opium 2·5 per cent., the rest of the constituents being cinnamon, nutmeg, saffron, cloves, cardamoms, and sugar.

Compound Powder of Ipecacuanha (Dover's Powder).

Opium,	10 per cent.
Ipecacuanha,	10 ,,
Sulphate of Potash,	80 ,,

Confection of Opium (*Confectio opii*) is composed of syrup and compound powder of opium; according to its formula, it contains 2·4 per cent. of opium by weight.

Extract of Opium contains the solid constituents capable of extraction by water; its strength is about the same as opium itself.

Liquid Extract of Opium contains 5 per cent. of extract of opium.

Liniment of Opium is composed of equal parts of laudanum and soap liniment; it contains about 3·7 per cent. dry opium.

The Compound Soap-pill is made of soap and opium, one part of opium in every five of the mass—*i.e.*, 20 per cent.

Ipecacuanha and Morphine Lozenges, as the last, with the addition of ipecacuanha; each lozenge contains $\frac{1}{36}$ grain (1·8 mgrm.) morphine hydrochlorate, $\frac{1}{12}$ grain (5·4 mgm.) ipecacuanha.

Morphia Suppositories are made with hydrochlorate of morphia, benzoated lard, white wax, and oil of theobroma; each suppository contains $\frac{1}{2}$ grain (32·4 mgrm.) of morphine salt.

Opium Lozenges are composed of opium extract, tincture of tolu, sugar, gum, extract of liquorice, and water. Each lozenge contains one-tenth of a grain (6·4 mgrms.) of extract of opium.

The Ointment of Galls and Opium contains one part of opium in 14·5 parts of the ointment—*i.e.*, opium 6·9 per cent.

Opium Wine, P.B.—Sherry, opium extract, cinnamon, and cloves. About 4·5 of opium extract by weight in 100 parts by measure (22 grains to the ounce).

Solutions of Morphia, both of the acetate and hydrochlorate, P.B., are made with a little free acid, and with rectified spirit. The strength of each is half a grain in each fluid drachm (·0324 grm. in 3·549), or ·91 part by weight in 100 by measure.

Morphia Lozenges are made with the same accessories as opium lozenges, substituting morphia for opium; each lozenge contains $\frac{1}{36}$ grain of hydrochlorate of morphia (1·8 mgrm.).

Syrup of Poppies.—The ordinary syrup of poppies is sweetened laudanum. It should, however, be what it is described—viz., a syrup of poppy-heads. As such, it is said to contain one grain of extract of opium to the ounce.

(2.) *Patent and other Non-Officinal Preparations of Opium.*

Godfrey's Cordial is made on rather a large scale, and is variable in strength and composition. It usually contains about 1½ grain of opium in each fluid ounce,* and, as other constituents, sassafras, molasses or treacle, rectified spirit, and various flavouring ingredients, especially ginger, cloves, and coriander; aniseed and caraways may also be detected.

Grinrod's Remedy for Spasms consists of hydrochlorate of morphia, spirit of sal-volatile, ether, and camphor julap; strength, 1 grain of the hydrochlorate in every 6 ounces.

Lemaurier's Odontalgic Essence is acetate of morphia dissolved in cherry-laurel water; strength, 1 grain to the ounce.

Nepenthe is a preparation very similar to *Liq. Opii sedativ.*, and is of about the same strength as laudanum.†

Black Drop (known also by various names, such as Armstrong's Black Drop) is essentially an acetic acid solution of the constituents of opium. It is usually considered to be of four times the strength of laudanum. The wholesale receipt for it is: Laudanum, 1 ounce, and distilled vinegar 1 quart, digested for a fortnight. The original formula proposed by the Quaker doctor of Durham, Edward Tunstall, is—Opium, sliced, ½ lb.; good verjuice,‡ 3 pints; and nutmeg, 1½ ounce; boiled down to a syrupy thickness; ¼ lb. of sugar and 2 teaspoonfuls of yeast are then added. The whole is set in a warm place for six or eight weeks, after which it is evaporated in the open air until it becomes of the consistence of a syrup. It is lastly decanted and filtered, a little sugar is added, and the liquid made up to 2 pints.

Dalby's Carminative—

Carbonate of magnesia, . . .	40 grains.
Tincture of castor, and compound tincture of cardamoms, of each .	15 drops.
Laudanum, ...	5 ,,
Oil of aniseed, ...	3 ,,
Oil of nutmeg, ...	2 ,,
Oil of peppermint, ...	1 ,,
Peppermint water, ...	2 fl. ounces.

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* If made according to Dr. Paris' formula, 1⅙ grain in an ounce.

† It may be regarded as a purified alcoholic solution of meconate of morphia, with a little excess of acid, and of about the same strength as laudanum. (*Taylor.*)

‡ Verjuice is the juice of the wild crab.

Dose, from a half to one teaspoonful. Another receipt has no laudanum, but instead syrup of poppies.

Chlorodyne.—Brown's chlorodyne is composed of—

Chloroform,	6 drachms.
Chloric ether,	1 „
Tincture of capsicum,	½ „
Hydrochlorate of morphine,	8 grains.
Scheele's prussic acid,	12 drops.
Tincture of Indian hemp,	1 drachm.
Treacle,	1 „

Atkinson's Infant Preserver—

Carbonate of magnesia,	6 drachms.
White sugar,	2 ounces.
Oil of aniseed,	20 drops.
Spirit of sal-volatile,	2½ drachms.
Laudanum,	1 „
Syrup of saffron,	1 ounce.
Caraway water, to make up,	1 pint.

Boerhave's Odontalgic Essence—

Opium,	0½ drachm.
Oil of cloves,	2 „
Powdered camphor,	5 „
Rectified spirit,	1½ fl. ounce.

§ 32. *Doses of Opium and Morphia.*—Opium in the solid state is prescribed for adults in quantities not exceeding 3 grains, the usual dose being from ¼ to 1 grain (16·2 mgrms. to 64·8 mgrms.). The extract of opium is given in exactly the same proportions (special circumstances, such as the habitual use of opium, excepted); the dose of all the compounds of opium is mainly regulated by the proportion of opium contained in them.

The dose for children (who bear opium ill) is usually very small; single drops of laudanum are given to infants at the breast, and the dose cautiously increased up to ten years old. Most practitioners would consider half a grain a very full dose; and in cases requiring it, would seldom prescribe at first more than $\frac{1}{16}$ to ¼ grain.

The dose of solid opium for a horse is from ½ drachm to 2 drachms (1·77 grm. to 7·08 grms.); in extreme cases, however, 4 drachms (14·16 grms.) have been given.

The dose for large cattle is from 10 to 60 grains (·648 to 3·88 grms.); for calves, 10 grains (·648 grms.); for dogs it is greatly regulated by the size of the animal, ¼ grain to 2 grains (16·2 to 129·6 mgrms.).

Fatal Dose.—Cases are recorded of infants dying from extremely small doses of opium—*e.g.*, $\frac{1}{90}$, $\frac{1}{15}$, and $\frac{1}{8}$ of a grain ;* but in such instances one cannot help suspecting some mistake. It may, however, be freely conceded that a very small quantity might be fatal to infants, and that half a grain given to a child under one year would probably develop serious symptoms.

The smallest dose of solid opium known to have proved fatal to adults was equal to 4 grains (·256 grms.) of crude opium (*Taylor*) ; and the smallest dose of the tincture (laudanum), 2 drachms (7·0 cc.) (*Taylor*) ; the latter is, however, rather uncertain in its composition.

A dangerous dose (save under special circumstances) is :—For a horse, 4 drachms (14·17 grms.) ; for cattle, 2 drachms (7·04 grms.) ; for a dog of the size and strength of a foxhound, 3 grains (·182 grm.).

§ 33. *General Method for the Detection of Opium.*—It is usually laid down in forensic works that where poisoning by opium is suspected, it is sufficient to detect the presence of meconic acid in order to establish that of opium. In a case of adult poisoning there is generally substance enough available to obtain one or more alkaloids, and the presence of opium may, without a reasonable doubt, be proved, if meconic acid (as well as either morphia, narcotine, thebaia, or other opium alkaloid) has been detected. Pills containing either solid opium or the tincture, usually betray the presence of the drug by the odour, and in such a case there can be no possible difficulty in isolating morphine and meconic acid, with probably one or two other alkaloids. The method of extraction from organic fluids is the same as before described, but it may, of course, be modified for any special purpose. If opium, or a preparation of opium, be submitted to Dragendorff's process (see p. 267), the following is a sketch of the chief points to be noticed.

If the solution is *acid*—

(1.) *Benzine* mainly extracts *meconin*, which dissolves in sulphuric acid very gradually (in twenty-four to forty-eight hours), with a green colour passing into red. Meconin has no alkaloidal reaction.

(2.) *Amyl alcohol* dissolves small quantities of *meconic acid*, identified by striking a blood-red colour with ferric chloride.

If now the amyl alcohol is removed with the aid of petroleum ether, and the fluid made alkaline by ammonia—

(1.) *Benzine* extracts *narcotine, codeine*, and *thebaine*. On evaporation of the benzine the alkaloidal residue may be dissolved

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* ·7, 4·3, and 8·1 mgrms.

in water, acidified with sulphuric acid, and after filtration, on adding ammonia *in excess, thebaine and narcotine* are precipitated, *codeine* remaining in solution. The dried precipitate, if it contain thebaine, becomes blood-red when treated with cold concentrated sulphuric acid, while narcotine is shown by a violet colour developing gradually when the substance is dissolved in dilute sulphuric acid 1 : 5, and gently warmed. The codeine in the ammoniacal solution can be recovered by shaking up with benzine, and recognised by the red colour which the solid substance gives when treated with a little sugar and sulphuric acid.

(2.) *Chloroform* especially dissolves the *narceine*, which on evaporation of the chloroform may be identified by its general characters, and by its solution in Fröhde's reagent* becoming a beautiful blue colour. Small quantities of morphine may be extracted with codeine.

(3.) *Amyl alcohol* extracts from the alkaline solution morphine, identified by its physical characters, turning violet with Fröhde's reagent, blue by chloride of iron, and reducing iodine out of iodic acid; further, by its solution in concentrated sulphuric acid becoming, after a few hours, a red violet on the addition of a little nitric acid.

§ 34. The principal alkaloids in opium are—*Morphia, narcotine, codeine, narceine, papaverin, thebaine, meconin, opianyl, and meconic acid.*

Morphia (morphine) ($C_{17}H_{19}NO_3 + H_2O$), the most important alkaloid in opium, is contained in quantities which are somewhat variable. According to Guibourt, Smyrna opium yields 11·7 to 21·46 per cent., the mean being 12 to 14 per cent.; Egyptian, from 5·8 to 12 per cent.; Persian, 11·37 per cent. In East Indian Patna opium, for medical use, he found 7·72; in a sample used for smoking, 5·27 per cent.; in Algerian opium, 12·1 per cent.; in French opium, 14·8 to 22·9 per cent. All the above determinations are calculated on the drug dried at 100°C.

Morphine occurs in commerce as a white powder, usually in the form of more or less perfect six-sided prisms, but sometimes in that of white silky needles. When heated in the subliming cell (described at p. 284), faint nebulæ, resolved by high microscopic powers into minute dots, appear on the upper disc at 150°C. As the temperature is raised the spots become coarser, and at 188°C. distinct crystals may be obtained, the best being formed at nearly 200°C., at which temperature morphia begins distinctly to brown, melt, and carbonise. At temperatures below 188°C., instead of minute dots, the sublimate may consist

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* 1 ctgrm. of molybdate of soda in 1 cc. of concentrated sulphuric acid.

of white circular spots or foliated patterns. It dissolves in 960 to 1000 parts of cold water, in 400 to 500 parts of boiling water, and is scarcely soluble in ether and benzine. Absolute alcohol, according to Pettenkofer, dissolves in the cold one-fortieth of its weight, boiling, one-thirtieth. Amyl alcohol, in the cold, dissolves one-fourth per cent., and still more if the alkaloid be thrown out of an aqueous acid solution by ammonia in the presence of amyl alcohol; for under such circumstances the morphine has no time to become crystalline. According to Schlimpert, one part of morphine requires 60 of chloroform for solution; according to Pettenkofer, 175.

Morphine is easily soluble in dilute acids, as well as in solutions of the caustic alkalies and alkaline earths; carbonated alkalies and chloride of ammonium also dissolve small quantities. The acid watery, and the alcoholic solutions, turn the plane of polarisation to the left; for sulphuric, nitric, and hydrochloric acids $[\alpha]r = 89{\cdot}8^\circ$; in alkaline solution the polarisation is less, $[\alpha]r = 45{\cdot}22^\circ$. It is alkaline in reaction, neutralising acids fully; and, in fact, a convenient method of titrating morphine is by the use of a centinormal sulphuric acid—each cc. equals 2·85 mgrm. of anhydrous morphine.

Products of Decomposition Tests.—If morphine is separated, its behaviour to heat (already described) is very characteristic, and assists greatly in its identification. One of the best confirmatory tests is the action of iodic acid:—If a little of the latter be mixed with a drop of freshly-made thin starch paste,* on a white plate, and morphine or one of its salts be added, iodine is set free, and colours the starch blue.

Another test is its reducing action on bichromate of potash:—If the latter salt, with a little strong sulphuric acid, be added to morphine, and heated, the oxide of chromium (giving first a brown and then a green tint) is produced.

Concentrated nitric acid dissolves morphine, first reddening it, and the resulting resinous product, heated with potash, develops methylamin.

Concentrated sulphuric acid dissolves morphine in the cold

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* Instead of starch paste bisulphide of carbon may be used. A little iodic acid is put in a test-tube with a few drops of bisulphide of carbon. The suspected substance is then added, and, on shaking, if morphine be present, the bisulphide of carbon is coloured from a rose to a dark red. Again, instead of iodic acid, iodate of potash may be employed. It is unnecessary to say that, for this purpose, it must contain no trace of iodide. The latter may be detected by putting the iodate in a test-tube with a little water, sulphuric acid, and carbon bisulphide; the latter fluid must then show no red colour.—*Mohr.*

vithout the production of colour; but on heating, the solution ecomes first red-violet, then dirty green.*

If morphine is heated for from two to three hours in a closed ube with dilute hydrochloric acid, water is eliminated—

$$(C_{17}H_{19}NO_3 = C_{17}H_{17}NO_2 + H_2O),$$

nd the hydrochlorate of apo-morphine is produced. If morphine s heated with iodide of methyl and absolute alcohol in a closed ube for half an hour at 100°C., methyl iodide of morphine is btained in colourless, glittering, quadratic crystals, easily oluble in water, $C_{17}H_{19}(CH_3)NO_3I + H_2O$; similarly the ethyl odide compound can be produced.

If concentrated sulphuric acid be digested on morphine for welve to fifteen hours (or heated for half an hour at 100°C.), on dding to the cooled violet-coloured solution either a crystal of itrate of potash, or of chlorate of potash, or a drop of dilute itric acid, a beautiful violet-blue colour is produced, which asses gradually into a dark blood-red. $\frac{1}{100}$ of a mgrm. will espond distinctly to this test. Fröhde's reagent strikes with orphine a beautiful violet colour, passing from blue into dirty reen, and finally almost vanishing. $\frac{1}{200}$ of a mgrm. will respond o the test, but it is not in itself conclusive, since papaverin and ertain glucosides give an identical reaction.

One of the most conclusive tests for morphine is the blue colour vhich it strikes with neutral chloride of iron. The best way to repare the solution of iron is to sublime some ferric chloride, nd dissolve the product, or (as suggested by Mohr) to use the erro-ammonium alum.

If morphine is not detected in the contents of the stomach, it ay yet be found in the intestines.† Dragendorff and Kaufann, in their experiments on animals, recognised morphine in he bowels several days after the ingestion of the poison. If earch be made for the absorbed alkaloid, the liver is the organ which it has been most frequently detected; it has also been ound in the blood.

§ 35. *Narcotine* ($C_{22}H_{23}NO_7$) crystallises out of alcohol or ther in colourless, transparent, glittering needles, or groups of eedles, belonging to the orthorhombic system.

It is only slightly soluble in boiling, and almost insoluble in old water. One part requires 100 parts of cold, and 20 of boil-

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* The sulphuric acid solution, whether heated or not, usually contains ome unchanged morphine.

† Voit examined the urine and fæces of a man who had taken morphine r years; none was detected in the urine, but it was separated readily from he fæces. *Arch. Pharm.* [3], vii. 23-26.

ing 85 per cent. alcohol; 126 parts of cold, 48 of boiling ether (specific gravity 0·735); 2·69 parts of chloroform; 400 of olive oil; 60 of acetic ether; 300 of amyl alcohol; and 22 parts of benzine, for solution. The neutral solution of narcotine turns the plane of polarisation to the left, $[a]r = 130{\cdot}6$; the acid solution to the right.

Narcotine gives no crystalline sublimate; its behaviour in the subliming cell is described at p. 286.

Behaviour of Narcotine with Reagents.—Narcotine, dissolved in dilute hydrochloric acid, and then treated with a little bromine gives a yellow precipitate, which on boiling is dissolved; by gradually adding solution of bromine and boiling, a fine rose colour is produced, but readily destroyed by excess of bromine This is perhaps the best test for the presence of narcotine. Concentrated sulphuric acid dissolves narcotine; the solution in the cold is at first colourless, after a few minutes yellow, and in the course of a day or longer the tints gradually deepen. If the solution is warmed, it first becomes orange-red, then at the margin violet-blue; and if heated until hydric sulphate begins to volatilise, the colour is an intense red-violet. If the heating is not carried so far, but the solution allowed to cool, a delicate cherry red hue slowly develops. If the sulphuric acid solution contains 1 : 2000 of the alkaloid, this test is very evident; with 1 : 40,000 the colour is only a faint carmine (*A. Husemann*).

A solution of narcotine in pure sulphuric acid, to which a drop of nitric acid has been added, becomes of a red colour; if the solution is warmed to 150°C., hypochlorite of soda develops a carmine-red; and chloride of iron first a violet, then a cherry-red The precipitants of narcotine are: phosphomolybdic acid, picric acid, sulphocyanide of potash, potassio cadmic iodide, mercuric chloride, platinic chloride, auric chloride, and several other reagents

Narcotine is poisonous, and from 2 to 3 grms. have proved fatal to small dogs and cats. It has been given medicinally—as much as 1·5 grm. in divided doses during the twenty-four hours.

From the brown mass left after heating narcotine above 200°C., hydrochloric acid extracts a small portion of a base but little studied. The residue consists of humopic acid ($C_{40}H_{19}O_{14}$) which can be obtained by dissolving in caustic potash, precipitating with HCl, dissolving the precipitate in boiling alcohol and finally throwing it down by water.

§ 36. *Codeine* ($C_{18}H_{21}NO_3$) is an alkaloid contained in opium in small quantity only. Mulder, indeed, quotes ·66 to ·75 per cent as present in Smyrna opium, but Merck and Schindler give ·2 per cent. Schindler found, in Constantinople, ·5 per cent.; and Merck, in Bengal, ·5 per cent. also.

Codeine crystallises out of dry ether in small, colourless, anhydrous crystals; but crystallised slowly from an aqueous solution, the crystals are either in well-defined octahedra, or in prisms, containing one atom of water, and melting in boiling water to an oily fluid.

It requires 80 parts of cold, 17 of boiling water, 10 parts of benzole, and 7 parts of amyl alcohol respectively, for solution. Alcohol, ether, and chloroform freely dissolve it, but in petroleum ether it is almost insoluble. Further, it is also soluble in aqueous ammonia, and in dilute acids, but insoluble in excess of caustic potash or soda, and may thus be thrown out of an aqueous solution. A solution of codeine turns the plane of polarisation to the left, $[a]r = 118{\cdot}2°$.

Concentrated sulphuric acid dissolves codeine without colour, but after eight days the solution becomes blue; this reaction is quicker if the acid contains a trace of nitric acid. If the sulphuric acid solution be warmed to 150°C., and a drop of nitric acid be added after cooling, a blood-red colour is produced. Fröhde's reagent (see p. 297, *footnote*) produces a dirty green colour, soon becoming Prussian blue, and terminating after twenty-four hours in a pale yellow.

§ 37. *Narceine* ($C_{23}H_{29}NO_9$) crystallises out of water, alcohol, or diluted acetic acid, in long, white, four-sided, rhombic prisms, or fine bushy united needles. It has a somewhat bitter taste, and is without odour.

The crystals generally contain water of crystallisation. One part of narceine dissolves in 375 parts of cold, 230 of boiling, water. Very concentrated potash-lye precipitates narceine from its watery solution as an oil, weaker alkaline liquids dissolve it. One part of narceine is dissolved in 945 parts of 80 per cent. alcohol. It is easily soluble in boiling alcohol and in hot acetic acid, but is insoluble in ether. Benzole and petroleum ether extract narceine neither from acid nor alkaline solutions; amyl alcohol and chloroform only from alkaline aqueous solutions in small quantities. Narceine turns the plane of polarisation to the left, $a[r] = 66°7$.

It melts at 134°C., but gives no crystalline sublimate. The melted substance is at first colourless; but on raising the temperature, the usual transitions of colour through different shades of brown to black are observed. If melted, and kept a few degrees above its melting point, and then cooled slowly, the residue is straw-coloured, divided into lobes, most of which contain feathery crystals.

At high temperatures narceine develops a herring-like odour; the residue becomes darkish blue with iron chloride. Concentrated nitric acid dissolves it with a yellow colour ; on heatin red vapours are produced ; the fluid contains crystals of oxal acid, and develops with potash a volatile base. Concentrat sulphuric acid colours pure narceine brown ; but if impure, blood-red or blue colour may be produced.

Fröhde's reagent colours it first yellow-brown, then yello and lastly the solution becomes colourless. Narceine form precipitates with bichromate of potash, chloride of gold, chloride of platinum, and several other reagents. The o formed by the addition of potassio zinc iodide is in hair-li crystals, which after twenty-four hours become blue.

Narceine has been experimented upon by a large number observers ; it is undoubtedly a narcotic, and in large doses poison. It has been given subcutaneously in doses of ·02 a ·06 grm. of the hydrochlorate.

§ 38. *Papaverin* ($C_{21}H_{21}NO_4$)* crystallises from alcohol white needles or scales. It possesses scarcely any alkali reaction, and has but little effect on a plane of polarised ligh It is almost insoluble in water ; alcohol and ether dissolve it the cold with difficulty; boiling, copiously, but the alkaloid part separates on cooling. One part of the alkaloid is dissolved 36·6 of benzine, and in 76 parts of amyl alcohol. Petroleu ether dissolves it by the aid of heat, but the alkaloid separates crystals on cooling. Chloroform extracts it from either acid alkaline solutions. Papaverin gives no crystalline sublimate. melts at 130°C. ; the residue is amorphous, light brown, and is n characteristic. Concentrated sulphuric acid colours it a de violet-blue, and dissolves it to a violet, slowly fading. Th solution, by permanganate of potash, is first green and then gre Fröhde's reagent gives a beautiful violet colour, which becom blue, and vanishes after twenty-four hours. Diluted solutio of salts of papaverin are not precipitated by phosphomolybd acid. This is unusual with alkaloids, and may assist in i identification.

§ 39. *Thebaine* ($C_{10}H_{21}NO_3$). — Opium seldom contains mu more than 1 per cent. of this alkaloid. It usually forms needl or short crystals. It is strongly alkaline, and by rubbi becomes negatively electric. It is almost insoluble in wat aqueous ammonia, and solutions of the alkalies. It requires t parts of cold alcohol for solution, and dissolves readily in h Ether, hot or cold, is also a good solvent. 100 parts of benzi are required for 5·27 parts of thebaine, and 100 of amyl alco for 1·67 parts. Chloroform dissolves thebaine with difficulty o

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* Merck gave the formula $C_{20}H_{21}NO_4$, Hesse $C_{21}H_{21}NO_4$; the latt has been recently confirmed by Beckett and Wright.

of both acid and alkaline solutions; petroleum ether extracts it from neither. Thebaine sublimes at 135°C. The sublimate is in minute crystals, similar to theine; at higher temperatures (160° to 200°C.) needles, cubes, and prisms are obtained. The residue is fawn-coloured. Fröhde's reagent (as well as concentrated sulphuric acid) dissolves it, with the production of a blood-red colour, passing gradually into yellow. The precipitate with picric acid is yellow and amorphous; with tannic acid, yellow; with gold chloride, red-yellow; and with platinic chloride, citron-yellow, gradually becoming crystalline.

Thebaine is a powerful poison. Drs. Crum Brown and Fraser found ·012 grm. fatal to kittens; and Bernard 1 grm. fatal to dogs of from 7 to 8 kilogrms. weight, if injected into the veins. Müller, however, using the same quantity subcutaneously, did not obtain a fatal result. The symptoms noticed hitherto are very similar to those produced by strychnine—viz., tetanic convulsions.

§ 40. *Meconin* (*Opianyl*) ($C_{10}H_{10}O_4$) is in the form of white glittering needles, which melt under water at 77°C., and in air at 90°C., again coagulating at 75°C. It may be sublimed in beautiful crystals. It is soluble in 22 parts of boiling, and 700 of cold, water; dissolves easily in alcohol, ether, acetic acid, and ethereal oil, and is not precipitated by acetate of lead. Its solution in concentrated sulphuric acid becomes, on warming, purple, and gives, on the addition of water, a brown precipitate. It appears to be without toxic action on human beings and animals.

§ 41. *Meconic Acid* ($C_7H_4O_7$) crystallises in white shining scales, or small rhombic prisms, with three atoms of water ($C_7H_4O_7 + 3\,H_2O$); but at 100°C. this is lost, and it becomes an opaque white mass. It reddens litmus, and has a sourish taste. It is but little soluble in cold, but dissolves in four parts of boiling, water; it dissolves easily in alcohol, less so in ether. It forms well-marked salts; the barium and calcium salt crystallise with one atom of water, the former having the composition $C_7H_2Ba_2O_7 + H_2O$; the latter, if ammonium meconate is precipitated by calcium chloride, $C_7H_2Ca_2O_7 + H_2O$; but if calcium chloride is added to the acid itself, the salt has the composition $C_7H_3CaO_7 + H_2O$. If meconic acid is gently heated, it decomposes into carbon dioxide and comenic acid, $C_6H_4O_5$. If the heat is stronger, pyromeconic acid, $C_5H_4O_3$—carbon dioxide, water, acetic acid, and benzole are formed. Pyromeconic acid is readily sublimed in large transparent tables. Chloride of iron, and soluble iron salts generally, give with meconic acid (even in great dilution) a lively red colour, which is not altered by heat, nor by the addition of HCl, nor by that of gold chloride. Sugar of lead and nitrate of silver each give a white precipitate; and mercurous and mercuric nitrates white and yellow precipitates.

In a special research amongst organic fluids for meconic acid, the substances are extracted by alcohol *feebly* acidulated with nitric acid; on filtration the alcohol, after the addition of a little water, is distilled off, and to the remaining fluid a solution of acetate of lead is added, and the whole filtered. The filtrate will contain any alkaloids, whilst meconic acid, if present, is bound up with the lead on the filter. The meconate of lead may be either washed or digested in strong acetic acid, to purify it, suspended in water, and freed from lead by SH_2; the filtrate from the lead sulphide may be tested by ferric chloride, or preferably, at once evaporated to dryness, and weighed. After this operation it is identified. If the quantity is so small that it cannot be conveniently weighed, it may be estimated colorimetrically, by having a standard solution of meconic acid, containing 1 mgrm. in every cc. A few drops of neutral ferric chloride are added in a Nessler cylinder to the liquid under examination; and the tint thus obtained is imitated in the usual way, in another cylinder, by means of ferric chloride, the standard solution and water. It is also obvious that the weight of the meconic acid may be increased by converting it into the barium salt—100 parts of anhydrous baric meconate, $C_7H_2Ba_2O$, being equivalent to 42·3 of meconic acid, $C_7H_4O_7$.

In any case where the analyst has found only meconic acid, the question may be raised in court as to whether it is a poison or not. The early experiments of Sertürner,[*] Langer, Vogel, Sömmering, and Grape,[†] showed that in comparatively speaking large doses it had but little, if any, action on dogs or men. Albers [‡] has, however, experimented on frogs, and found that in doses of ·1 to ·2 grm. there is, first, a narcotic action, and later convulsions and death. According to Schroff[§] there is a slight narcotic action on man. Hence it follows that the question of its poisonous action is still undecided.

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[*] *Ann. Phys.*, xxv. 56; xxvij. 183.

[†] *De opio et de illis quibus constat partibus.* Berol., 1822.

[‡] *Arch. Path. Anat.*, xxvj. 248.

[§] *Med. Jahresb.* 1869.

III.—NUX VOMICA.

§ 42. Nux vomica is found in commerce both in the entire state and as a powder. It is the seed of the *Strychnos nux vomica,* or Koochla tree. The seed is about the size of a shilling, round, flattened, concavo-convex, of a yellowish-grey or light-brown colour, covered with a velvety down of fine radiating, silky hairs; the texture is tough, leathery, and not easily pulverised; the taste is intensely bitter. The powder is not unlike that of liquorice, and if met with in the pure state gives a dark orange-red colour with nitric acid, which is destroyed by chloride of tin; the aqueous infusion gives a precipitate with tincture of galls, is reddened by nitric acid, and gives an olive-green tint with persulphate of iron. The best method, however, of recognising quickly and with certainty that the substance under examination is nux vomica powder, is to extract strychnine from it by the following simple process:—The powder is completely exhausted by boiling alcohol (90 per cent.),* the alcoholic extract evaporated to dryness, and then treated with water; the aqueous solution is passed through a wet filter, and concentrated by evaporation to a small bulk. To this liquid a drop or so of a concentrated solution of chromate of potash is added, and the yellow precipitate of chromate of strychnine thus obtained is separated, and identified both by its form and by the colour reactions to be described (p. 311).

§ 43. *Chemical Composition.*—Nux vomica contains at least four distinct principles—

(1.) Strychnine.
(2.) Brucia.
(3.) Igasuria.
(4.) Strychnic or igasuric acid.

§ 44. *Strychnine* ($C_{21}H_{22}N_2O_2$) is contained in the bean of *S. Ignatius,* in the bark (*false angustura bark*) and seeds of the *Strychnos nux vomica,* in the *Strychnos colubrina,* L., in the *Strychnos Tiente,* Lesch, and probably in various other plants of the same genus.

Commercial strychnine is met with either in colourless crystals or as a white powder, the most usual form being that of the alkaloid itself; but the nitrate, sulphate, and acetate are also old to a small extent.

The *microscopical appearance* of strychnine, as thrown down

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* Instead of this process, the more exhaustive one described at page 310, an of course be used.

by the solution or vapour of ammonia, may be referred to three leading forms :—the long rectangular prism, the short hexagonal prism, or the regular octahedron (*Guy*). If obtained from the slow evaporation of an alcoholic solution, it is usually in the form of four-sided pyramids or long prisms ; but if obtained by speedy evaporation or rapid cooling, it appears as a white granular powder. If obtained from a benzole solution, the deposit is usually crystalline, but without a constant form, though at times the crystals are extremely distinct, the short six-sided prism prevailing; but triangular plates, dodecahedral, rhomboidal, and pentagonal, may also be met with (*Guy*). An ethereal solution on evaporation assumes dendritic forms, but may contain octahedra and four-sided prisms. A chloroform solution deposits rosettes, veined leaves, stellate dotted needles, circles with broken radii, and branched and reticulated forms of great delicacy and beauty (*Guy*).

Strychnine is very insoluble in water, although readily dissolved by acidulated water. According to Wormley's repeated experiments, one part of strychnine dissolves in 8333 parts of cold water; and, according to Pelletier and Cahor, it dissolves in 6667 parts of cold, and 2500 parts of boiling, water. It may be convenient, then, to remember that a gallon of cold water would hardly dissolve more than 10 grains (·142 grm. per litre); the same amount, if boiling, about 30 grains of strychnine (·426 grm. per litre). The solubility of one part of strychnine in other menstrua is as follows :—Cold alcohol, 0·833 specific gravity, 120, boiling, 10 parts (*Wittstein*); cold alcohol, 0·936 specific gravity, 240 parts (*Merck*); cold alcohol, 0·815 specific gravity, 107 parts (*Dragendorff*). Amyl alcohol, 181 parts; benzine, 164; chloroform, 6·9 (*Schlimpert*), 5 (*Pettenkofer*); creosote and essential and fixed oils also dissolve strychnine.

Of all the above solvents, it is evident that chloroform is the best for purposes of separation, and next to chloroform, benzine

If a speck of strychnine be placed in the subliming cell, it wil be found to sublime usually in a crystalline form at 169°C. A common form at this temperature, according to the writer's own observations, is minute needles, disposed in lines; but, as Dr Guy has remarked, the sublimate may consist of drops, of waving patterns, and various other forms; and, further, while the sublimates of morphia are made up of curved lines, those of strychnine consist of lines either straight or slightly curved, with parallel feathery lines at right angles. On continuing the heat strychnine melts at about 221°C., and the lower disc, if removed and examined, is found to have a resinous residue, but it stil continues to yield sublimates until reduced to a spot of carbon.

Strychnine is so powerfully bitter, that one part dissolved in 70,000 of water is distinctly perceptible; it is a strong base, with a marked alkaline reaction, neutralising the strongest acids fully, and precipitating many metallic oxides from their combinations, often with the formation of double salts. Most of the salts of strychnine are crystalline, and all extremely bitter.

An alcoholic solution of strychnine turns the plane of polarisation to the left, $[a]\ r = -132{\cdot}08°$ to $136{\cdot}78°$ (*Bouchardat*); but acid solutions show a much smaller rotatory power.

The salts used in medicine are—the *sulphate*, officinal only in the French pharmacopeia; the *nitrate*, officinal in the German, Austrian, Swiss, Norse, and Dutch pharmacopeias; and the *acetate*, well known in commerce, but not officinal.

The *Sulphate* ($2C_{21}H_{22}N_2O_2H_2SO_4 + 7H_2O$) is a neutral salt, crystallising in four-sided, orthorhombic prisms, and soluble in about 50 parts of cold water.

The *Nitrate* ($C_{21}H_{22}N_2O_2HNO_3$) crystallises on evaporation from a warm solution of the alkaloid in dilute nitric acid, in silky needles, mostly collected in groups. The solubility of this salt is considerable, one part dissolving in 50 of cold, in 2 of boiling, water; its solubility in boiling and cold alcohol (80 per cent.) is almost the same, taking 60 of the former and 2 of the latter.

The *Acetate* crystallises in tufts of needles; as stated, it is not officinal in any of the European pharmacopeias.

The chief precipitates or sparingly soluble crystalline compounds of strychnine are—

(1.) The *Chromate of Strychnine* ($C_{21}H_{22}N_2O_2CrHO_2$), formed by adding a neutral solution of chromate of potash to a solution of a strychnine salt, crystallises out of hot water in beautiful, very insoluble, orange-yellow needles, mixed with plates of various size and thickness. This salt is of great practical use to the analyst; for by its aid strychnine may be separated from a variety of substances, including brucine, the colour tests being either applied direct to the strychnine chromate, or the chromate decomposed by ammonia, and the strychnine recovered from the alkaline liquid by chloroform.

(2.) *Sulphocyanide of Strychnine* ($C_{21}H_{22}N_2O_2CNHS$) is a thick, white precipitate, produced by the addition of a solution of potassic sulphocyanide to that of a strychnine salt; on warming it dissolves, but on cooling reappears in the form of long silky needles.

(3.) *Double Salts.*—The platinum compound obtained by dding a solution of platinic chloride to one of strychnine hloride has the composition $C_{21}H_{22}N_2O_2HClPtCl_2$, and crystal-ses out of weak boiling alcohol (in which it is somewhat soluble) in gold-like scales. The similar palladium compound, $C_{21}H_{22}N_2O_2HCl, PdCl$, is in dark-brown needles; and the gold compound, $C_{21}H_{22}N_2O_2HClAuCl_3$, in orange-coloured needles.

(4.) *Strychnine Trichloride.*—The action of chlorine on strychnine, by which chlorine is substituted for a portion of the hydrogen, has been proposed as a test. The alkaloid is dissolved in very dilute HCl, so as to be only just acid; on now passing through chlorine gas, a white insoluble precipitate is formed, which may be recrystallised from ether; it has probably the composition $C_{21}H_{19}Cl_3N_2O_2$, and is extremely insoluble in water.

(5.) *The Iodide of Strychnine* ($C_{21}H_{22}N_2O_2HI_3$) is obtained by the action of iodine solution on strychnine sulphate; on solution of the precipitate in alcohol, and evaporation, it forms violet-coloured crystals, very similar to those of potassic permanganate. Brucine forms a corresponding salt in bronze-coloured needles.

§ 45. *Fatal Dose of Strychnine.*—The fatal dose varies according to age, constitution, and other circumstances. There are instances on record in which 5 mgrms. ($\frac{1}{14}$ grain), when given in solution by the stomach, has caused poisonous symptoms; such cases are, however, exceptional. Eulenberg has observed poisonous symptoms produced in adults by the subcutaneous injection of 6 mgrms. ($\frac{1}{11}$ grain), and of 10 mgrms. ($\frac{1}{6}$ grain). Bois observed marked poisonous symptoms from the similar subcutaneous administration of 8 mgrms. to a child six years old, and of 4 mgrms. to a child four years old. According to Christison, a child of from two to three years of age was killed by $\frac{1}{16}$ of a grain (·0162 grm.). The smallest fatal dose on record, as regards adults, is related by Wurner, in which ·015 to ·03 grm. of sulphate of strychnine (about $\frac{1}{5}$ to $\frac{2}{5}$ grain) caused a fatal result. Taylor estimates the fatal dose for adults as from $\frac{1}{2}$ to 2 grains (·0324 to ·1296 grm.); Guy puts the minimum at $\frac{1}{4}$ of a grain (·0162 grm.).

On the other hand, recovery has taken place from larger doses. Darwin describes recovery from $1\frac{1}{2}$ grain (·0972 grm.); Taylor from 3 grains (·1944 grm.); and Husemann from 3 to 7 grains (·1944 to ·4536 grm.).

With regard to the poisonous doses for animals, it may be stated generally, that if the smallest dose producing tetanic spasms be increased by one-third, it becomes lethal. According to Christison's researches, ·02 grm. (about $\frac{1}{3}$ grain) is fatal t swine; ·03 grm. ($\frac{1}{2}$ grain) to bears, if injected into the pleura 1 to 3 grains (·0648 to ·1944 grm.) is given to horses in cases o paralysis, although 3 grains cannot but be considered a dangerou dose, unless smaller doses have been previously administere without effect; 10 grains would probably kill a horse, and 1 grains (·972 grm.) have certainly done so.

The dose for dogs is $\frac{1}{16}$ of a grain, cautiously increased; the fatal dose depends upon the size and weight of the dog. A sheep dog would be killed by about the same dose as an adult man; hence half a grain to such a dog would be a dangerous dose, if it were administered without beginning with smaller quantities. According to Rosenthal and Leube the fatal dose for kittens is 1·2 mgrm. (·018 grain) for every pound weight of the body. Guinea-pigs require 6 mgrms. (·09 grain); doves, 2·4 mgrms. (·036 grain). Frogs are very susceptible; sometimes so small a dose as ·01 mgrm. ($\frac{1}{1000}$ grain) is sufficient to excite tetanus. Fowls, on the other hand, are very unsusceptible, requiring, if of moderate size, 24 mgrms. (·36 grain) to induce a fatal result. Certain birds also, such as the *Buceros rhinoceros*, enjoy a special immunity, and are said to feed on the fruit of the strychnos tree.

§ 46. *Separation of Strychnine from Organic Matters.*—The separation of strychnine from organic matters, &c., is undertaken strictly on the general principles already detailed (p. 266). It may happen, however, that in cases of poisoning there is the strongest evidence from symptoms in the person or animal that strychnine alone is to be sought for. In an instance of the kind, if a complex organic liquid (such as the contents of the stomach) is under examination, it is best to remove the solid substances by filtration through glass-wool or linen, and evaporate nearly to dryness over the water-bath, acidifying with acetic acid, and then exhausting the residue repeatedly with boiling alcohol of 80 per cent. The alcoholic extract is in its turn evaporated to dryness, and taken up with water; the aqueous solution is passed through a wet filter, and then shaken up with the usual succession of fluids, viz., petroleum ether, benzole, chloroform, and amyl alcohol, which will remove a great number of impurities, but will not dissolve the strychnine from the acid solution. The amyl alcohol may lastly be removed by petroleum ether; and on removal of the final extractive (which should be done as thoroughly as possible) chloroform is added, and the fluid is alkalised by ammonia, which precipitates the alkaloid in the presence of the solvent. Should the reverse process be employed—that is, ammonia added first, and then chloroform—the strychnine is not so perfectly dissolved, since it has time to assume a crystalline condition; on separation and evaporation of the chloroform, the residue (if much discoloured, or evidently impure) may be dissolved in alcohol or benzole, and recrystallised several times; this by practice can be done without any loss of substance.

Should search be made for minute portions of strychnine in the tissues, considering the small amount of the poison which may produce death, it is absolutely necessary to operate on a very large quantity of material. It would be advisable to take the whole of the liver, the brain, spinal cord, spleen, stomach, duodenum, kidneys, all the blood that can be obtained, and a considerable quantity of muscular tissue, so as to make in all about one-eighth to one-tenth of the whole body; this may be cut up into small pieces, and boiled in capacious flasks with alcohol, acidified with acetic acid. Evaporation must be controlled by adapting to the cork an upright condenser.

Should the analyst not have apparatus of a size to undertake this at one operation, it may be done in separate portions; the filtrate from any single operation being collected in a flask, and the spirit distilled off in order to be used for the next. In this way, a large quantity of the organs and tissues can be exhausted by half a gallon of alcohol. Finally, most of the alcohol is distilled off, and the remainder evaporated at a gentle heat in a capacious dish, the extract being treated by water, &c., as described. It is only by working on this large scale that there is any probability of detecting absorbed strychnine in those cases where only one or two grains have destroyed life, and even then it is possible to miss the poison.

Strychnine has been detected in the blood of dogs and cats in researches specially undertaken for that purpose, but sometimes a negative result has been obtained, without apparent cause (*Dragendorff.*)* Dragendorff gave dogs the largest possible dose of strychnine daily. On the first few days no strychnine was found in the urine, but later it was detected, especially if food was withheld. M'Adam was the first who detected the absorbed poison, recognising it in the muscles and urine of a poisoned horse, and also in the urine of a hound. Dragendorff has found it in traces in the kidneys, spleen, and pancreas; Guy, in different parts of the central nervous system and in the saliva. So far as the evidence goes, the liver is the best organ to examine for strychnine; but all parts supplied with blood, and most secretions may contain small quantities of the alkaloid. At one time it was believed that strychnine might be destroyed by putrefaction; but the question of the decomposition of the poison in putrid bodies may be said to be settled. So far as all evidence goes, strychnine is an extremely stable substance, and no amount of putrescence will destroy it. M'Adam found it in a horse a month after death, and in a duck eight weeks after; Nuneley in fifteen animals forty-three days after death, when the bodies were much decomposed; Roger in a body after five weeks interment; and

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* In an animal rapidly killed by a subcutaneous injection of acetate of strychnine, no strychnine was detected either in the blood or liver.—*Dragendorff.*

lastly, Richter in putrid tissues exposed for eleven years to decomposition in open vessels.

§ 47. *Identification of the Alkaloid.*—A residue containing strychnine, or strychnine mixed with brucine, is identified—

(1.) By its alkaline reaction and its bitter taste. No substance can possibly be strychnine unless it taste markedly bitter.

(2.) By its behaviour in the subliming cell already described; tests may be applied to any of the sublimates, or to the substance itself. Dr. Guy has proposed to treat a sublimate with a drop of a solution of dilute picric acid, $\frac{1}{250}$; in a few seconds or minutes small, round, greenish-brown spots show themselves, which spread, often coalesce, and become the centres of delicate arborescent crystalline groups, the elementary form in all of which is a large section of a small circle, a rare form, and one eminently characteristic.

(3.) By the extremely insoluble chromate of strychnine, already described.* A fluid containing 1 : 1000 of strychnine gives with chromate of potash (if allowed to stand over night) a marked precipitate, dissimilar to all others, except those of lead and baryta chromates, neither of which can possibly occur if any of the processes described are followed.

(4.) If the chromate just described is treated on a porcelain plate with a drop of pure strong sulphuric acid, a deep rich blue colour, passing through purple into red, rapidly makes its appearance. Dr. Guy, neglecting intermediate colours, aptly compares the succession—(1.) to the rich blue of the Orleans plum; (2.) to the darker purple of the mulberry; and, (3.) to the bright clear red of the sweet orange.

(5.) These colours may be also obtained by mixing a drop of sulphuric acid with strychnine and a crystal, or speck, of any one of the following substances—ferridcyanide of potash, permanganate of potash, peroxide of lead, or peroxide of manganese.

(6.) Letheby's galvanic colour test:—If a minute strychnine residue, obtained by the evaporation of a drop of dilute solution of strychnine, in a cup-shaped depression in a piece of platinum foil, be treated with a drop of concentrated sulphuric acid, and the foil connected with the positive pole of a Grove or Smee's battery, on touching the acid with the negative pole a violet colour flashes out, and on removing the pole the tint remains.

(7.) Sonnenschein has proposed the sesquioxide of cerium and

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* 1 grm. of strychnine gave 1·280 grms. of the chromate, = 78·1 per cent. of strychnine; 3 gave 3·811 of the chromate, = 78·77 per cent. of strychnine. —*Mohr.*

sulphuric acid as a test for strychnine: the colours produced are a beautiful blue, passing slowly into violet, and terminating in a long enduring cherry-red.

These colour tests are supposed to be employed upon the more or less pure substance. If, however, strychnine be mixed with no great quantity of starch or dextrine, tartar emetic, tartaric acid, or argol, it will still respond.

Brucine, if in large quantity, renders the tests for strychnine uncertain; but, as already pointed out, the strychnine may be converted into chromate, and thus separated from brucine. The pharmaceutical preparations, moreover, do not contain sufficient brucine to interfere seriously with the colour tests. In mixture with santonin it is easily detected. Dragendorff obtained evidence of its presence when only so small a quantity as ·32 mgrm. was present. In mixture with quinine and cinchonine, it can also be detected. Dragendorff was able to render evident ·025 mgrm. mixed with twenty times its weight of quin. sulphate; the same observer likewise recognised ·04 mgrm. of strychnine in thirty-three times its weight of caffeine. Veratrine is likewise not injurious. Since morphine is used as an antidote, it might be separated with strychnine; Reese* recognised in a mixture of equal parts of strychnine and morphine, $\frac{1}{50000}$ grm. when the proportion was 1 : 2; $\frac{1}{30000}$ grm. when 1 : 3; $\frac{1}{15000}$ grm. when 1 : 4; $\frac{1}{10000}$ grm. when 1 : 5; $\frac{1}{8000}$ grm. when 1 : 10; $\frac{1}{1000}$ grm. when 1 : 20; but these alkaloids are easily separated, absolute alcohol dissolving out the morphine, and leaving the strychnine.

(8.) *The Physiological Test* consists in administering the substance to some small animal (preferably to a frog), and inducing the ordinary tetanic symptoms. It may be at once observed that if definite chemical evidence of strychnine has been obtained, the physiological test is quite unnecessary; and, on the other hand, should the application of a liquid or substance to a frog induce tetanus, while chemical evidence of the presence of strychnine was wanting, it would be hazardous to assert that strychnine was present, seeing that caffeine, carbolic acid, picrotoxin, and many other substances induce similar symptoms. The test has, however, this value for an analyst, that it would indicate immediately the presence of some poison. The best method (if the test is used at all) is to take two frogs,† and insert under the skin of the one the needle of a subcutaneous syringe, previously charged with a solution of the

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* *Pharm. Zeitschr. f. Russl. Jahrg.*, i., p. 277.

† A very practical disadvantage of the physiological test is the great difficulty of obtaining frogs exactly when wanted.

substance, injecting a moderate quantity. The other frog is treated similarly with a very dilute solution of strychnine, and the two are then placed under small glass shades, and the symptoms observed and compared. It is not absolutely necessary to inject the solution under the skin, for if applied to the surface the same effects are produced; but if accustomed to manipulation, the operator will find the subcutaneous application more certain, especially in dealing with minute quantities of the alkaloid.*

§ 48. *Brucine*, $C_{23}H_{26}N_2O_4$,† occurs associated with strychnine in the plants already mentioned; its best source is the so-called *false angustura* bark, which contains but little strychnine. Its action is similar to that of strychnine. If crystallised out of dilute alcohol it contains 4 atoms of water, easily expelled either in a vacuum over sulphuric acid or by heat. Crystallised thus, it forms transparent four-sided prisms, or arborescent forms, like boric acid. If thrown down by ammonia from a solution of the acetate, it presents itself in needles or in tufts.

The recently crystallised alkaloid has a solubility different from that which has effloresced, the former dissolving in 320 parts of cold, and 150 parts of boiling, water; whilst the latter (according to Pelletier and Caventou), requires 500 of boiling, and 850 parts of cold, water for solution. Brucine is easily soluble in absolute, as well as in ordinary, alcohol; 1 part dissolves in 1·7 of chloroform, in 60·2 of benzine. Petroleum ether, the volatile and fatty oils and glycerine, dissolve the alkaloid slightly, amyl alcohol freely; it is insoluble in *anhydrous* ether. The behaviour of brucine in the subliming cell is described at p. 287. The alcoholic solution of brucine turns the plane of polarisation to the left, $[\alpha]r = -11·27°$. The taste is bitter and acrid. Soubeiran maintains that it can be recognised if one part is dissolved in 500,000 parts of water. Brucine fully neutralises acids, and forms salts which are for the most part crystalline. The neutral sulphate ($C_{23}H_{25}N_2O_4SH_2O_4 + 3\frac{1}{2}H_2O$) is in long needles, easily soluble in water. The acetate is not crystalline, that of strychnine is so (p. 307).

The precipitants of solutions of the salts of brucine are—ammonia, the caustic and carbonated alkalies, sulphocyanide of

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* Methyl strychnine, as well as methyl brucine, has been shown by Brown and Fraser to have an effect exactly the opposite to that of strychnine, paralysing the muscles like curari. In the case, therefore, of the methyl compounds, a physiological test would be very valuable, since these compounds do not respond to the ordinary tests.

† Sonnenschein has asserted that brucine may be changed into strychnine by the action of NO_3; this statement has been investigated by A. J. Cownley, but not confirmed.—*Pharm. Journ.* [3], vi. 841.

potash, chloride of platinum, phosphomolybdic acid, and a large number of general alkaloidal reagents.

The only really trustworthy test for the presence of brucine is its behaviour with nitric acid: with that reagent it produces a scarlet colour, passing into blood-red, into yellow-red, and finally ending in yellow. This can be made something more than a mere colour-test, for it is possible to obtain a crystalline body from the action of nitric acid on brucine. If a little of the latter be put in a test-tube, and treated with nitric acid of 1·4 specific gravity (immersing the test-tube in cold water to moderate the action), the scarlet colour is produced, and there is a development of nitric oxide and carbon dioxide, and the formation of methyl nitrite, oxalic acid, and kakotelin, $C_{23}H_{20}N_2O_4 + 5NHO_3 = C_{20}H_{22}N_4O_9 + N(CH_3)O_2 + C_2H_2O_4 + 2NO + 2H_2O$. On diluting abundantly with water, the kakotelin separates in yellow flocks, and may be crystallised out of dilute hydrochloric or dilute nitric acid in the form of yellow or orange-red crystals, very insoluble in water, but dissolving readily in dilute acid. On removal by dilution of the product just named, neutralisation with ammonia and addition of a solution of chloride of calcium, the oxalate of lime is thrown down. This combined test—viz., the production by the action of nitric acid, (1.) of a red colour; (2.) of yellow scales or crystals insoluble in water; (3.) of oxalic acid—can belong to no alkaloid except brucine.

There are other methods of producing the colour test. If a few drops of nitric acid are mixed with the substance in a test-tube, and then sulphuric acid cautiously added, so as to form a layer at the bottom, at the junction of the liquids a red zone passing into yellow, is seen.

A solution of brucine is also coloured red by chlorine gas, ammonia changing the colour into yellow.

§ 49. *Fatal Dose of Brucine.*—There has been some confusion relative to the quantity of brucine required to produce fatal results, owing, probably, to the alkaloid having been contaminated with strychnine, or otherwise rendered impure. Pelletier considered it, in comparison with strychnine, 10 times, Majendie, 12 times, and Andral 24 times weaker; it is, however, now held to be, when perfectly pure, about from 6 to 7 times weaker than strychnine. The experiments of Abée and Falcke have also shown that much depends not only on attendant circumstances but also on the form in which it is administered—whether as an alkaloid, or combined with citric or acetic acid, &c.*

In regard to the separation of brucine from organic fluids o

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* Abée: Experimentale Untersuchungen über den Einfluss des Brucin auf die Thierische Organisation. Marburg, 1861.

tissues, the process already detailed for strychnine suffices. It is of very great importance to ascertain whether both strychnine and brucine are present or not—the presence of both pointing to nux vomica or one of its preparations. The presence of brucine may, of course, be owing to impure strychnine; but if found in the tissues, that solution of the question is improbable, the commercial strychnine of the present day being usually pure, or at the most containing so small a quantity of brucine as would hardly be separated from the tissues.

§ 50. *Igasurin* is an alkaloid as yet but little studied; it appears that it can be obtained from the boiling-hot watery extract of nux vomica seeds, through precipitating the strychnine and brucine by lime, and evaporation of the filtrate. According to Desnoix* it forms white crystals containing 10 per cent. of water of crystallisation.

It is said to be poisonous, its action being similar to that of strychnine and brucine, and in activity standing midway between the two.

§ 51. *Strychnic Acid.*—Pelletier and Caventou obtained by boiling with spirit small, hard, warty crystals of an organic acid, from *S. Ignatius*, as well as from nux vomica seeds. The seeds were first exhausted by ether, the alcohol solution was filtered and evaporated, and the extract treated with water and magnesia, filtered, and the residue first washed with cold water, then with hot spirit, and boiled lastly with a considerable quantity of water. The solution thus obtained was precipitated with acetate of lead, the lead thrown out by SH_2, and the solution evaporated, the acid crystallising out. It is a substance as yet imperfectly studied, and probably identical with malic acid.

§ 52. *Pharmaceutical and other Preparations of Nux Vomica and Strychnine, with Suggestions for their Valuation.*

An aqueous extract of nux vomica, officinal in the German pharmacopeia, appears to contain principally brucine, with a small percentage of strychnine; the proportion of brucine to strychnine being about four-fifths to one-fifth. Blossfield found in a sample 4·3 per cent. of total alkaloid, and two samples examined by Grundmann consisted of (No. 1) strychnine, 0·6 per cent., brucine 2·58 per cent., total, 3·18 per cent.; (No. 2), strychnine, 0·68 per cent., brucine, 2·62 per cent., total, 3·3 per cent. A sample examined by Dragendorff yielded, strychnine 0·8 per cent., brucine 3·2 per cent., total ·4 per cent.

The spirituous extract of nux vomica, officinal in the British and all the Continental pharmacopeias, differs from the aqueous

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* Desnoix, *Journ. Pharm.* (3), xxv. 202.

in containing a much larger proportion of alkaloids, the total percentage varying from 7 to 8·6 per cent., and about half the total quantity being strychnine.

There is also an *extract of St. Ignatius bean* which is used in the States, and is more active than the extract of nux vomica, since nearly the whole of its alkaloid may be referred to strychnine.

The tincture of nux vomica varies somewhat in strength. Lieth found in one sample 0·122 per cent. of strychnine, and 0·09 per cent. brucine; and two samples examined by Wissel consisted respectively of 0·353 per cent. and 0·346 per cent. of total alkaloids. Dragendorff found in two samples ·2624 per cent. and ·244 per cent. of total alkaloids, about half of which was strychnine.

Analysis.—Either of the extracts may be treated for a few hours on the water-bath, with water acidulated by sulphuric acid, filtered, the residue well washed, the acid liquid shaken up with benzine to separate impurities, and, on removal of the benzine, alkalised with ammonia, and shaken up two or three times with chloroform; the chloroform is then evaporated in a tared vessel, and the total alkaloids weighed. Strychnine, as before stated, may be separated from brucine by dissolving the latter out with absolute alcohol. The tincture is analysed on precisely similar principles, the spirit being got rid of by distillation, and the residue treated by acidified water, &c.

The nux vomica powder itself may be valued as follows:—15 to 20 grms., pulverised as finely as possible, are treated three times with 150 to 300 cc. of water, acidified with sulphuric acid, well boiled, and after each boiling filtered and thoroughly pressed. The last exhaustion must be destitute of all bitter taste. The united filtrates are then evaporated to the consistence of a thick syrup, which is treated with sufficient burnt magnesia to neutralise the acid. The extract is now thoroughly exhausted with boiling alcohol of 90 per cent.; the alcoholic extract, in its turn, is evaporated nearly to dryness, and treated with acidulated water; this acid solution is freed from impurities by shaking up with benzine, and lastly alkalised with ammonia, and the alkaloids extracted by shaking up with successive portions of chloroform. The chloroformic extract equals the total alkaloids, which may be separated in the usual way.

In four samples of nux vomica examined by Dragendorff, the total alkaloids ranged from 2·33 to 2·42 per cent. Grate found in two samples 2·88 per cent. and 2·86 per cent. respectively; while Karing from one sample separated only 1·65 per cent. The strychnine and brucine are in about equal proportions, Dragendorff* finding 1·187 per cent. strychnine, and 1·145 per cent. brucine.†

The *vermin-killers* in use in this country are: Miller's rat-powder, Battle's vermin-killer, and Butler's vermin-killer.

Miller's rat-powder consists of 1 oz. of nux vomica, and 1 lb. of oatmeal, *i.e.*, about 5·8 per cent. of nux vomica. Since the average amount of strychnine in nux vomica is ·4 per cent., and brucine three times that quantity, viz., 1·2 per cent., the probability is that this powder contains about ·023 per cent. strychnine and ·067 per cent. brucine.

Battle's vermin-killer (according to an analysis by Tardieu) contains the following in each packet.

Strychnine, ...	0·10
Potato Starch, ...	1·00
Prussian Blue, ...	0·20
	1·30 grms.

In other words, each packet weighs 19 grains (or nearly a scruple), and contains about 1½ grain of strychnine, or about 7·7 per cent.

Butler's vermin-killer is a mixture of flour, soot, and strychnine, but sometimes Prussian blue is substituted for soot. It is sold in threepenny and sixpenny packets. The latter Taylor found to weigh a drachm (3·8 grms.), and to contain from 2 to 3 grains (·13 to ·19 grm.) of strychnine; the threepenny packet about half this quantity.

The amount of strychnine and brucine in Miller's rat-powder is valued exactly as in the case of nux vomica powder.

Battle's or Butler's vermin-powder merely requires exhaustion by benzole or chloroform; if not pure, purification is easy on well known principles.

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* Dragendorff, "Die Chemische Werthbestimmung einiger Starkwirkenden Droguen." St. Petersburg, 1874.

† These details are very necessary, as bearing on the question of the fatal dose of nux vomica, which Taylor tells us (*Med. Jurisprud.*, I. 409) was of some importance in *Reg.* v. *Wren*, in which 47 grains were attempted to be given in milk. The fatal dose of nux vomica must be ruled by its alkaloidal content, which may be so low as 1 per cent., and as high as nearly 3 per cent. 30 grains have proved fatal (*Taylor*); if the powder in this instance was of he ordinary strength, the person died from less than a grain (·0648 grm.) f the united alkaloids.

IV.—BELLADONNA.

§ 53. The *Atropa belladonna,* or deadly nightshade, is indigenous, and may be found in some parts of England, although it cannot be said to be very common. It belongs to the *Solanaceæ,* and is a herbaceous plant, with broadly ovate entire leaves, and lurid-purple axillary flowers on short stalks; the berries are violet-black, and the whole of the plant is highly poisonous. The juice of the leaves stain paper a purple colour. The seeds are very small, kidney-shaped, weighing about 90 to the grain; they are covered closely with small, round projections, and are easily identified by an expert, who may be supposed to have at hand (as is most essential) samples of different poisonous seeds for comparison. The nightshade owes its poisonous properties to *atropine.*

§ 54. *Atropine* (*Daturine*), $C_{17}H_{23}NO_3$.—This important alkaloid has been found in all parts of the *Atropa belladonna,* or deadly nightshade, in the *Datura stramonium,* and in the seeds of the *Datura arborea.* It probably exists in all the species of *Datura.* The yield of the different parts of belladonna, according to Gunther,* is as follows:—

	Quantity of Alkaloids in the Fresh Substance, per cent.		Quantity of Alkaloids in the Dry Substance, per cent.	
	(*a*.) By Weighing.	(*b*) By Titration.	(*a*) By Weighing.	(*b*) By Titration.
Leaves, . .	0·2022	0·20072	0·838	0·828
Stalk, . .	0·0422	—	0·146	—
Ripe fruit, .	0·2128	0·20258	0·821	0·805
Seed, . .	0·26676	—	0·407	—
Unripe fruit, .	0·1870	0·1930	0·955	0·955
Root, . .	0·0792	—	0·210	—

Atropine appears to exist in the plant in combination with mali acid. Another alkaloid has been described, *Belladonin;* but thi is probably only a product of the decomposition of atropine, an has not yet been sufficiently studied.

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* *Pharm. Zeitschr. f. Russl.*, Feb., 1869. Dragendorff, "Die Chemisch Werthbestimmung einiger Starkwirkenden Droguen." St. Petersburg, 187

Atropine forms colourless crystals (mostly in groups or tufts of needles and prisms), which are heavier than water, and possess no smell, but an unpleasant, long-enduring, bitter taste. According to actual experiments, it melts about 97°C. (other chemists give 90°); it is also said to sublime scantily in a crystalline form, but the writer has been unable to obtain any crystals by sublimation; about 123°C. faint mists collect on the upper disc, but they are perfectly amorphous.*

Its reaction is alkaline; one part requires, of cold water, 300; of boiling, 58; of ether, 30; of benzole, 40; and of chloroform, 3 parts for solution. In alcohol and amyl alcohol it dissolves in almost every proportion. It turns the plane of polarisation weakly to the left.

Atropine mixed with nitric acid exhibits no change of colour. The same is the case with concentrated sulphuric acid in the cold; but on heating, there ensues the common browning, with development of a peculiar odour, likened by Gulielmo to orange flowers, by Dragendorff to the flowers of the *Prunus padus*, and by Otto to the *Spiræa ulmaria*—a sufficient evidence of the untrustworthiness of this as a distinctive test. The odour, indeed, with small quantities, is certainly not powerful, nor is it strongly suggestive of any of the plants mentioned. A far more decided odour is given off if a speck of atropine is evaporated to dryness with a few drops of strong solution of baryta, and heated strongly; the scent is decidedly analogous to that of hawthorn-blossom, and unmistakably agreeable.

By the action of fuming hydrochloric acid, or that of caustic alkalies, atropine is decomposed into tropine ($C_8H_{15}NO$) and tropic acid ($C_9H_{10}O_3$).† Tropine is a white, crystalline, strongly alkaline mass, melting at 60°C., and volatilising at 230°C. undecomposed. It is soluble in water, alcohol, and ether, and gives precipitates with tannic acid, iodised hydriodic acid, Mayer's reagent, gold chloride, and mercuric chloride.‡ Atropic acid $C_9H_3O_2$) and isatropic acid ($C_9H_8O_2$) may also be obtained by he action of hydrochloric acid; the first, in radiating crystals, melting at 106·5°, and capable of distillation; the second, in thin hombic plates, melting about 200°C., and not volatile.

The precipitate which atropine gives with chloride of gold in ydrochloric acid solution assumes the form of foliated groups; its omposition is $C_{17}H_{23}NO_3HClAuCl_3$. Carbazotic acid also gives precipitate of beautiful plates, but neither of these can be said

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* Doubtless crystals could be obtained by sublimation *in vacuo*.

† The reaction may be represented thus, $C_{17}H_{23}NO_3 + H_2O = C_8H_{15}NO + C_9H_{10}O_3$.

‡ Selmi, *Journ. Chem. Soc.*, I., 1877, 94.

to be characteristic or decisive of atropine. The most reliabl test is the peculiar odour with baryta before-mentioned, and the physiological action on the pupil of the eye, a solution o atropine, even when so weak as 1 : 130000, dilating the iris This action on the iris has been studied by Ruyter,* Donders and Von Graefe.† It is entirely a local action, taking effect when in dilute solution only on the eye to which it has been applied ; and it has been produced on the eyes of frogs, not only in the living subject, but after the head has been severed from the body and deprived of brain. The thinner the cornea, th quicker the dilatation ; therefore, the younger the person o animal, the more suitable for experiment. In frogs, with solution of 1 : 250, dilatation commences in about five minutes in pigeons, seven minutes ; and in kittens, ten minutes. I man, a solution of 1 : 120 commences to act in about six to seve minutes, reaches its highest point in from ten to fifteen minutes and persists more or less for six to eight days. A solution 1 : 480 acts first in fifteen to twenty minutes, and reaches it greatest point in twenty minutes ; a solution of 1 : 48000 require from three-quarters of an hour to an hour to show its effect Dogs and cats are far more sensible to its influence than man and therefore more suitable for experiment. If the exper chooses, he may essay the proof upon himself, controlling th dilatation by Calabar bean ; but it is seldom necessary or advis able to make personal trials of this nature.

§ 55. *Pharmaceutical Preparations.*—It would appear that mos of the pharmaceutical preparations can be titrated by addin Mayer's reagent (diluted one-half) to an acid aqueous solution the active principle, each cc. being equal to 6·25 mgrms. atropine, when a solution of the approximate strength of 1 : 50 is operated upon. Or the alkaloid may be precipitated by th undiluted Mayer's reagent, the precipitate collected on a filte washed with water, and dissolved in alcohol of 90 to 95 per cen The alcoholic solution is then evaporated and weighed ; it co tains 44·9 per cent. of atropine.‡ The various pharmaceutic preparations are—The leaves, root, extract of the leaves, an oin ment and a plaster made with the extract, a tincture of th leaves, a liniment (which is practically a tincture of the roo flavoured with camphor), atropine itself, a weak alcoholic solutio of atropine (·83 per cent.), an ointment of atropine (1·66 per cent the sulphate of atropine, and, lastly, a solution of sulphate atropine (·83 per cent.)

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* Dr. Ruyter—"De actione atropæ Belladonnæ in iridem." Traj. Rhen, 1852.

† Von Graefe, *Arch. Opthal.*, ix. 262, 1864.

‡ Dragendorff, *op cit.*

§ 56. *Fatal Dose.*—The exact quantity which may cause death, it is impossible to state with precision, atropine being one of those substances whose effect, varying in different cases, seems to depend on special constitutional tendencies, or idiosyncracies, of the individual. Some persons take a comparatively large amount with impunity, while others scarcely bear a very moderate dose without exhibiting unpleasant symptoms. Eight mgrms. ($\frac{1}{8}$ grain) have been known to produce poisonous symptoms; and ·129 grm. (2 grains), death; we may therefore infer that about ·0648 grm. (1 grain) would, unchecked by remedies, probably act fatally. Different animals show various degrees of susceptibility to the drug. Cats suffer, but generally recover, from subcutaneous administration in quantities of 6 grms. (9·0 grains) of the sulphate; and rats, guinea-pigs, and hedgehogs, bear equally large doses.

Atropine is used in veterinary practice, from 32·4 to 64·8 mgrms. [$\frac{1}{2}$ to 1 grain] and more being injected subcutaneously, but the extent to which this may be done with safety is not yet established.

§ 57. *Separation of Atropine from Organic Tissues, &c.*

From the contents of the stomach atropine may be separated by acidulating strongly with sulphuric acid (15 to 20 cc. of dilute H_2SO_4 to 100 cc.), digesting for some time at a temperature not exceeding 70°C., and then reducing any solid matter to a pulp by friction, and filtering, which can generally be effected by the aid of a filter-pump. The liver, muscles,* and coagulated blood, &c., may also be treated in a precisely similar way. The acid liquid thus obtained is first, to remove impurities, shaken up with amyl alcohol, and after the separation of the latter in the usual manner, it is agitated with chloroform, which will take up any of the remaining amyl alcohol,† and also serve to purify further. The chloroform is then removed by a pipette (or the separating flask before described), and the fluid made alkaline, and shaken up with ether, which on removal is allowed to evaporate spontaneously. The residue will be found to contain atropine, if present, and, possibly, sulphate of ammonia. If the latter is suspected, the residue should be treated with absolute alcohol, in which ammonia sulphate is insoluble.

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* Neither amyl alcohol nor chloroform removes atropine from an *acid* olution.

† Atropine goes into the blood, and appears to be present in the different organs in direct proportion to the quantity of blood they contain. Dragen-orff has found in the muscles of rabbits fed upon belladonna sufficient atropine for quantitative estimation.

From the urine* atropine may be extracted by acidifying with sulphuric acid, and agitation with the same series of solvents.

V.—HENBANE.

§ 58. The seeds, the leaves, and the root of the *Hyoscyamus niger*, as well as those of the *Hyoscyamus alba*, all contain a very powerful alkaloid, *hyoscyamine.*

Hyoscyamine, as separated in the course of analysis, is a resinoid, sticky, amorphous mass, difficult to dry, and possessing a tobacco-like odour. It can, however, be obtained in well-marked odourless crystals, which melt at 90°C., a portion subliming unchanged. According to Thovroy,† hyoscyamine crystallises out of chloroform in rhombic tables, and out of benzole in fine needles; but out of ether or amyl alcohol it remains amorphous. When perfectly pure, it dissolves with difficulty in cold, but more readily in hot, water; if impure, it is hygroscopic, and its solubility is much increased. In any case, it dissolves easily in alcohol, ether, chloroform, amyl alcohol, benzole, and dilute acids. Hyoscyamine neutralises acids fully, and forms crystallisable salts, which assume for the most part the form of fine needles.

§ 59. *Pharmaceutical and other Preparations of Henbane.*—The leaves are alone officinal in the European pharmacopeias; but the seeds and the root, or the flowers, may be met with occasionally, especially among herbalists. The table ‡ on next page will give an idea of the alkaloidal content of the different parts of the plant.

In order to ascertain the percentage of the alkaloid in any part of the plant, the process followed by Thorey has the meri of simplicity. The substance is first exhausted by petroleum ether, which frees it from fat; after drying, it is extracted wit 85 per cent. alcohol at a temperature not exceeding 40°C. Th alcoholic extracts are then united, the alcohol distilled off, an the residue filtered. The filtrate is now first purified by agitation with petroleum ether, then saturated by ammonia, an shaken up with chloroform. The latter, on evaporation, leave

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* Dragendorff has found atropine in the urine of rabbits fed with bell donna; the separation by the poison is so rapid that it often can only b recognised in the urine during the first hour after the poison has bee taken.

† *Pharm. Zeitschr. f. Russl.*, 1869.

‡ This table, taken from Dragendorff's "Chemische Werthbestimmun einiger Starkwirkenden Droguen," embodies the researches of Thorey.

	Plant Destitute of Flowers.				Plant in Flower.				Plant in Fruit.			
	Hyosc.-Albus.		Hyosc.-Niger.		Hyosc.-Albus.		Hyosc.-Niger.		Hyosc.-Albus.		Hyosc.-Niger.	
	1868.	1869.	1868.	1869.	1868.	1869.	1868.	1869.	1868.	1869.	1868.	1869.
Seeds, ...	...	...	...	...	...	...	...	...	0·162	0·172	0·075	0·118
Leaves,. . . .	0·588	0·469	0·154	0·192	0·359	0·329	0·147	0·206	0·211	0·153	0·065	0·110
Stalk, ...	0·012	...	0·070	0·017	0·036	0·048	0·032	0·030	0·027	0·029	0·009	0·010
Root, ...	0·128	0·176	0·027	0·080	0·146	0·262	0·127	0·138	0·106	0·086	0·028	0·056

the alkaloid only slightly impure, and after washing with distilled water, if dissolved in dilute sulphuric acid, a crystallin sulphate may be readily obtained.

A tincture and an extract of henbane leaves are officinal i most pharmacopeias; an extract of the seeds in that of France

An oil of hyoscyamus is officinal in all the Continental pharmacopeias, but not in the British.

An ointment, made of one part of the extract to nine of simpl ointment, is officinal in the German.

The tincture (after distilling off the spirit) and the extract (on proper solution) may be conveniently titrated by Mayer' reagent (p. 288), which, for this purpose, should be diluted one half; each cc. then, according to Dragendorff, equalling 6·9 mgrms. of hyoscyamine. Kruse found 0·042 per cent. of hyoscyamine in a Russian tincture, and ·28 per cent. in a Russia extract. Any preparation made with extract of henbane will b found to contain nitrate of potash, for Attfield has shown th extract to be rich in this substance. The ointment will requir extraction of the fat by petroleum ether; this accomplished, th determination of its strength is easy.

The oil of hyoscyamus is poisonous, and contains the alkaloi An exact quantitative research is difficult; but if 20 grms. the oil are shaken up for some time with water acidified by su phuric acid, the fluid separated from the oil, made alkalin shaken up with chloroform, and the latter removed and ev porated, sufficient will be obtained to test successfully for t presence of the alkaloid, by its action on the pupil of the eye.

§ 60. *Dose.*—·006 grm. ($\frac{1}{10}$ grain) is the utmost dose of hyo cyamine which can be given with safety to an adult; and eve this quantity, according to Schroff, in the case of a young ma suffering from chronic bronchitis, threw the patient into a dee sleep, with hallucinations on awakening, dryness of the throa dilated pupils, frequency of the pulse, &c. A poisonous do would probably be half a grain; a fatal dose a grain.

§ 61. *Separation of Hyoscyamine from Organic Matters.*—T isolation of the alkaloid from organic tissues or fluids, in cas where a medical preparation of henbane, or of the leaves, ro &c., has been taken, is possible, and should be carried out on t principles already detailed (pp. 265-280). Hyoscyamine is main identified by its power of dilating the pupil of the eye. It is sa that so small a quantity as ·0083 mgrm. ($\frac{1}{4000}$ grain) will in fifte minutes dilate the eye of a kitten. It is true that atropi also dilates the pupil; but if sufficient of the substance shou have been isolated to apply other tests, it can be distinguish from atropine by the fact that the latter gives no precipitate wi platinic chloride, whilst hyoscyamine is precipitated by a small quantity of platinic chloride, and dissolved by a larger amount.

Hyoscyamine gives precipitates with tincture of iodine, chloride of gold, and most of the common alkaloidal reagents, but exhibits no peculiar reaction. The observation of Kletzinsky,* that the action of soda-lye changes hyoscyamine into ammonia and santonin might, if correct, probably be utilised in identifying the alkaloid.

VI.—CONIUM (HEMLOCK).

§ 62. The *Conium maculatum*, or spotted hemlock, is a rather common umbelliferous plant, growing in waste places, and flowering from about the beginning of June to August. The stem is from three to five feet high, smooth, branched, and spotted with purple; the leaflets of the partial involucres are unilateral, ovate, lanceolate, with an attenuate point shorter than the umbels; the seeds are destitute of vittæ, and have five prominent crenate wavy ridges. The whole plant is fœtid and poisonous. Conium owes its active properties to a volatile liquid alkaloid, *Coniine*, united with a crystalline alkaloid, *Conhydrine*.

§ 63. *Coniine*, conia, conicine ($C_8H_{15}N$)—specific gravity 0·878 to 0·89, boiling point 163·5°C.—is a clear oily fluid, possessing a peculiarly unpleasant, mousey odour. One part is soluble in 100 parts of water, in six parts of ether, and in almost all proportions of amyl alcohol, chloroform, and benzine. It readily volatilises, and, provided air is excluded, may be distilled unchanged. It ignites readily, and burns with a smoky flame. It acts as a strong base, precipitating the oxides of metals and alkaline earths from their solutions, and it coagulates albumen. Coniine forms salts with hydrochloric acid ($C_8H_{15}N.HCl.$), phosphoric acid, iodic acid, and oxalic acid, which are in well-marked crystals. The sulphate, nitrate, acetate, and tartrate are, on the other hand, non-crystalline.

If coniine is oxidised with nitric acid, or bichromate of potash, and diluted sulphuric acid, butyric acid is formed; and since the latter has an unmistakable odour, and other characteristic properties, it has been proposed as a test for coniine. This may be conveniently performed thus,—A crystal of potassic bichromate is put at the bottom of a test-tube, and some diluted sulphuric acid

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* *Schweiz. Wochenschr. Pharm.*, 1866, 85.

with a drop of the supposed coniine added; on heating, t
butyric acid reveals itself by its odour, and can be distilled in
baryta water, the butyrate of baryta being subsequently sep
rated in the usual way, and decomposed by sulphuric acid, &c.

Another test for coniine is the following:—If dropped into
solution of alloxan, the latter is coloured after a few minut
an intense purple-red, and white needle-shaped crystals a
separated, which dissolve in cold potash-lye into a beautif
purple-blue, and emit an odour of the base.* Dry hydrochlor
acid gives a purple-red, then an indigo-blue colour with coniin
but if the acid is not dry, there is formed a bluish-green cryst
line mass. This test, however, is of little value to the to
cologist, the pure substance alone responding with any defini
result.

The ordinary precipitating agents, according to Dragendor
act as follows:—

Potass. bismuth iodide.
  1 : 2000, a strong orange precipitate.
  1 : 3000. The drop of the reagent is surrounded with muddy border.
  1 : 4000. The drop of the reagent is surrounded with muddy border.
  1 : 5000, still perceptible.
  1 : 6000. The last limit of the reaction.

Phosphomolybdic acid gives a strong yellow precipitat
limit, 1 : 6000.

Potass. mercuric iodide gives a cheesy precipitate; limit, 1 : 10
in neutral, 1 : 800 in acid, solutions.

Potass. cadmic iodide gives an amorphous precipitate, 1 : 30

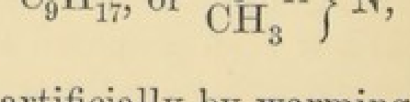
Of all these tests the most satisfactory are—

(1.) The formation of microscopic needles of hydrochlorate
coniine, doubly refracting light, and evolving a mousey odo
when breathed upon.

(2.) The formation of butyric acid in oxidation.

(3.) The reaction with alloxan.

Most of the coniine of commerce contains—

Methyl coniine, . . 

C_9H_{17}, or $\left.\begin{matrix} C_8H_{14} \\ CH_3 \end{matrix}\right\} N$,

a substance which can be formed artificially by warming conii

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* Schwarzenbach, *Vierteljahrsschr. f. Pract. Pharm.* viij., 170.

with methyl iodide, treating the mixture with soda-lye, and distilling. It is very similar to coniine in appearance; and Drs. Crum Brown and Fraser have established the fact that its toxic action is both qualitatively and quantitatively equal to that of coniine. Ethyl coniine and methyl coniine are also similar in action to coniine.

§ 64. *Conhydrine* ($C_8H_{17}NO$) is frequently present in coniine, from which it may be separated by cooling down to 5°C., filtering through glass wool, and purifying the crystals on the filter by petroleum ether, in which fluid conhydrine does not readily dissolve. Conhydrine forms colourless glittering crystals, which melt about 120·6°C., the resulting fluid boiling at 226·3°C.; at higher temperatures it volatilises without residue. It dissolves somewhat in water, and easily in alcohol and ether; the solution is strongly alkaline.

Conhydrine is a poison similar to, but not quite so powerful as, coniine. It has little medico-legal interest. Wertheim's experiments appear to show that for every 100 of coniine, hemlock only contains 5·7 of conhydrine.

§ 65. *Pharmaceutical Preparations.*—The percentage of coniine in the plant itself, and in pharmaceutical preparations, can be approximately determined by distilling the coniine over, in a partial vacuum,* and titrating the distillate with Mayer's reagent, each cc. = about ·0125 grm. of coniine. It appears to be necessary to add powdered chloride of potash and a small quantity of diluted sulphuric acid before titrating, or the precipitate does not separate. In any case the end of the reaction is difficult to observe.†

The fresh plant is said to contain from about ·04 to ·09 per cent., and the fruit about 7 per cent. of coniine.

The officinal preparations are—the leaves, the fruit, a tincture of the fruit, an extract of the leaves, the juice of the leaves (*Succus conii*), a compound hemlock pill (composed of extract of hemlock, ipecacuanha, and treacle), an inhalation of coniine (*Vapor conii*), and a poultice (*Cataplasma conii*) made with the leaves.

§ 66. *Separation of Coniine from Organic Matters or Tissues.*—The substances are digested with water, acidulated with H_2SO_4, at a temperature not exceeding 40°C., and then filtered. If the

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* This is easily effected by uniting a flask containing the alkaloid fluid, air-tight, with a Liebig's condenser and a receiver, the latter being connected with Bunsen's water-pump, or one of the numerous exhausting apparatuses now in use in every laboratory.

† Dragendorff, "Die Chemische Werthbestimmung einiger Starkwirkenden Droguen." St Petersb., 1874.

filtrate should be excessive, it must be concentrated ; alcohol then added, the liquid refiltered, and from the filtrate th alcohol separated by distillation.

On cooling, the acid fluid is agitated with benzine, and th latter separated in the usual way. The fluid is now alkalise with ammonia, and shaken up once or twice with its own volum of petroleum ether; the latter is separated and washed wi distilled water, and the alkaloid is obtained almost pure. the petroleum ether leaves no residue, it is certain that th alkaloid was not present in the contents of the stomach intestine.

The affinity of coniine with ether or chloroform is such, th its solution in either of these fluids, passed through a *dry* filte scarcely retains a drop of water. In this way it may be co veniently purified, the impurities dissolved by water remaini behind.

In searching for coniine, the stomach, intestines, blood, urin liver, and lungs, are the parts which should be examine According to Dragendorff, it has been discovered in the body a cat six weeks after death.

Fatal Dose.—The fatal dose of coniine is not known ; in th case of Louise Berger, 10 to 15 drops appear to have cause death in a few minutes. The auto-experiments of Dworza Heinrich, and Dillaberger, would indicate that one drop ma cause unpleasant symptoms. Albers, in the treatment of woman suffering from cancer of the breast, witnessed convulsio and loss of consciousness from a third dose of 4 mgrms. (·0 grain); and Eulenberg, its full narcotic effects on a child aft subcutaneous injection of 1 mgrm. (·015 grain).

VII. TOBACCO.*

§ 67. The various species of tobacco found in commerce a contain a liquid, volatile, poisonous alkaloid, *Nicotine,* probabl united in the plant with citric and malic acids. There is als present in tobacco an unimportant camphor, *nicotianin.* Th general composition of the plant may be gathered from th following table:—

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* The adulterations of tobacco, and processes for their detection, do n enter into the plan of this work.

FRESH LEAVES OF TOBACCO (POSSELT and REINMANN).

Nicotina,	0·060
Concrete volatile oil,	0·010
Bitter extractive,	2·870
Gum with malate of lime,	1·740
Chlorophyl,	0·267
Albumen and gluten,	1·308
Malic acid,	0·510
Lignine and a trace of starch,	4·969
Salts (sulphate, nitrate, and malate of potash, chloride of potassium, phosphate and malate of lime, and malate of ammonia,	0·734
Silica,	0·088
Water,	88·280
	100·836

§ 68. *Quantitative Estimation of Nicotine in Tobacco.*—The best process (although not a perfectly accurate one) is the following:—25 grms. of the tobacco are mixed with milk of lime, and allowed to stand until there is no odour of ammonia; the mixture is then exhausted by petroleum ether, the ether shaken up with a slight excess of normal sulphuric acid, and titrated back by baryta water; the sulphate of baryta may be collected and weighed, so as to control the results with regard to the percentage of nicotine in commercial tobacco. Kosutany found from 1·686 to 3·738 per cent. in dry tobacco; Letheby, in six samples, from 1·5 to 3·2 per cent.; whilst Schlössing gives for Havanna 2 per cent., Maryland 2·29 per cent., Kentucky 6·09 per cent., Virginian 6·87 per cent., and for French tobacco, quantities varying from 3·21 to 7·96 per cent. Again, Lenoble found in Paraguay tobacco from 1·8 to 6 per cent.; and Wittstein, in six sorts of tobacco in Germany, 1·54 to 2·62 per cent. We are thus driven to the conclusion that the alkaloid varies within very wide limits, although it is quite possible that the processes of extraction and estimation by these various observers are of unequal value.

§ 69. *Nicotine* ($C_{10}H_{14}N_2$), when pure, is an oily, colourless fluid, of 1·027 specific gravity at 15°C. It evaporates under 100°C. in white clouds, and boils about 240°C., at which temperature it partly distils over unchanged, and is partly decomposed, a brown resinous product remaining. It volatilises with aqueous and amyl alcohol vapour notably, and is not even fixed at $-10°$. It has a strong alkaline reaction, and rotates a ray of polarised light to the left. Its odour, especially on warming, is strong and unpleasantly like tobacco, and it has a sharp caustic taste. It absorbs water exposed to the air, and dissolves in water in all proportions, partly separating from such solution by caustic alkalies. The aqueous solution acts in many respect like ammonia, saturating acids fully, and may therefore be i certain cases estimated with accuracy by titration, 49 parts c H_2SO_4 corresponding to 126 of nicotine.

Alcohol and ether dissolve nicotine in every proportion; such solutions are distilled, nicotine goes over first. The salt which it forms with hydrochloric, nitric, and phosphoric acid crystallise with difficulty; tartaric and oxalic acid form whit crystalline salts, and the latter, oxalate of nicotine, is soluble i alcohol, a property which distinguishes it from the oxalate c ammonia. The oxalate of nicotine is the best salt from which t regenerate nicotine in a pure state.

Hydrochlorate of nicotine is more easily volatilised than th pure base. Nicotine is precipitated by alkalies, &c., also b many oxyhydrates, lead, copper, &c. By the action of light i is soon coloured yellow and brown, and becomes thick, in whic state it leaves, on evaporation, a brown resinous substance, onl partly soluble in petroleum ether.

Chlorine gas colours nicotine blood-red or brown; the produc is soluble in alcohol, and separates on evaporation in crystals.

Cyanogen also colours nicotine brown; the product out c alcohol is not crystalline. Platin chloride throws down a reddis crystalline precipitate, soluble on warming; and gallic acid give a flocculent precipitate. A drop of nicotine, poured on dr chromic acid, blazes up, and gives out an odour of tobacco-camphor; if the ignition does not occur in the cold, it is produced b a gentle heat. It is scarcely possible to confound nicotine wit ammonia, by reason of its odour; and, moreover, ammonia ma always be excluded by converting the base into the oxalate, an dissolving in absolute alcohol.

On the other hand, a confusion between coniine and nicotin is apt to occur when small quantities only are dealt with. I may, however, be guarded against by the following tests:—

(1.) If coniine be converted into oxalate, the oxalate dissolve in alcohol, and coniine regenerated by distillation (best *in vacu* with caustic lye, and then hydrochloric acid added, a crystallin hydrochlorate of coniine is formed, which doubly refracts light, an is in needle-shaped or columnar crystals, or dendritic moss-lik forms. The columns afterwards become torn, and little rows o cubical, octahedral, and tetrahedral crystals (often cross o dagger-shaped) grow out of yellow amorphous masses. Crysta line forms of this kind are rare, save in the case of dilute solution of chloride of ammonium (the presence of the latter is, of course rendered by the treatment impossible); and nicotine does no give anything similar to this reaction.

(2.) Coniine coagulates albumen; nicotine does not.

(3.) Nicotine yields a characteristic crystalline precipitate with an aqueous solution of mercuric chloride; the similar precipitate of coniine is amorphous.

§ 70. *Fatal Dose.*—Extremely unpleasant symptoms have arisen from the absorption of 2 to 4 mgrms. of nicotine; but the data are not sufficient to form an opinion as to the smallest quantity required to produce fatal results.

§ 71. *Separation of Nicotine from Organic Matters*, &c.—The process for the isolation of nicotine is precisely that used for coniine (see p. 326). It appears that it is unaltered by putrefaction, and may be separated and recognised by appropriate means a long time after death. Orfila detected it in an animal two or three months after death; Melsens discovered the alkaloid unmistakably in the tongues of two dogs, which had been buried in a vessel filled with earth for seven years! and it has been found in animals buried for shorter periods by several experimenters. Nicotine should always be looked for in the tongue and mucous membrane of the mouth, as well as in the usual viscera. The case may be much complicated if the person supposed to be poisoned should have been a smoker; for the defence would naturally be that there had been either excessive smoking or chewing, or even swallowing accidentally a quid of tobacco.*

VIII.—CALABAR BEAN.

§ 72. The ordeal bean of Calabar (*Physostigma faba*) is a large, all but tasteless, kidney-shaped bean, about an inch in length and half an inch thick; its convex edge has a furrow with elevated ridges, and is pierced by a small hole at one extremity. The integuments are coffee-brown in colour, thin, hard, and brittle; they enclose two white cotyledons, easily pulverisable, and weighing on an average 3·98 grms. (46 grains.) The seed contains at least one alkaloid, termed *Physostogmine* (first separated in 1864 by Jobst and Hesse), and possibly a second, according to Harnach and Witkowsky, who have discovered in association with physostogmine a new alkaloid, which they call *Calaburine*, and which differs from physostogmine in being insoluble in ether, and soluble in water. It is also soluble in alcohol, and further,

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* In an experiment of Dragendorff's, nicotine is said to have been detected in 35 grms. of the saliva of a person who had half an hour previously smoked a cigar.

the precipitate produced by potassium iodohydrargyrate in calabarine solutions is insoluble in alcohol.

§ 73. *Physostogmine*, or Eserin, is not easily obtained in a crystalline state, being most frequently extracted as a colourless varnish, drying into brittle masses. It is, however, quite possible to obtain it in the form of partially crystalline crusts, or even rhombic plates, by care being taken to perform the evaporation, and all the operations, at as low a temperature as possible, and preferably in a dimly-lit room; for if the temperature rises to 40°C. much of the alkaloid will be decomposed. Hesse recommends that the beans be extracted by alcohol, the alcoholic solution alkalised by sodic carbonate, and the liquid shaken up with ether, which will retain the alkaloid. The ether solution is now separated, and acidified slightly with very dilute sulphuric acid; the fluid, of course, separates into two layers, the lower of which contains the alkaloid as a sulphate, the upper is the ether, which is withdrawn, and the acid fluid passed through a moist filter. The whole process is then repeated as a purification.

Again, Vée, who has repeatedly obtained the alkaloid in a crystalline condition, directs the extraction of the beans by alcohol, the alcoholic solution to be treated as before with soda and then with ether; the ethereal solution to be evaporated to dryness, dissolved in dilute acid, precipitated by sugar of lead, and the filtrate from this precipitate alkalised by potassic bicarbonate, and then shaken up with ether. The ethereal solution is permitted to evaporate spontaneously, and the crystalline crusts dissolved in a little dilute acid; and the solution is lastly alkalised by bicarbonate of potash, when, after a few minutes, crystalline plates are formed.

For the extraction of physostogmine from the fluids of the body, Dragendorff recommends benzole: the alcoholic filtered extract (first acidified) may be agitated with such solvents as petroleum and benzine, in order to remove colouring matter; then alkalised and shaken up with benzine, and the latter allowed to evaporate spontaneously,—all the operations being, as before stated, carried on under 40°C. If much coloured, it may be purified according to the principles before mentioned. In cases where enough of the extract (or other medicinal preparation) has been taken to destroy life, the analyst, with proper care, would probably not have much difficulty in separating a small quantity of the active principle. It is rapidly eliminated by the saliva and other secretions under putrefaction. The formula ascribed to physostogmine is $C_{15}H_{21}N_3O_2$. It is strongly alkaline, fully neutralising acids, and forming tasteless salts. It is easily melted (and perhaps partly decomposed) at a temperature of 45°C.; at

100°C. it is certainly changed, becoming of a red colour, and forming with acids a red solution. It dissolves easily in alcohol, ether, chloroform, and bisulphide of carbon; but is not easily soluble in water.

The salts formed by the alkaloid with the acids are generally hygroscopic and uncrystallisable, but an exception is met with in the hydrobromide, which crystallises in stellate groups.[*] If CH_2 is passed into water containing the alkaloid in suspension, a clear solution is obtained; but the slightest warmth decomposes the soluble salt, and reprecipitates the alkaloid. The hydrargyc hydroiodide, $C_{15}H_{21}N_3O_2HI2HgI$, is a white precipitate, insoluble in water, becoming yellow on drying, soluble in ether and alcohol, and from such solutions obtained in crystalline prismatic groups. A heat of 70°C. melts the crystals, and they solidify again in the amorphous condition.

The most delicate chemical test is probably that of Dragendorff, viz., the production of a marked red colour in a solution of the sulphate by means of bromine water; it succeeds with less than ·06 of a mgrm.[†]

Concentrated sulphuric acid dissolves physostogmine with the production of a yellow colour, changing into olive-green; nitric acid (conc.) also gives a yellow colour. Ammonia and the carbonated alkalies precipitate the alkaloid from an acetic acid solution in the form of oily drops. Other precipitants are tannic acid, which throws down from a solution of the hydrochloride, a reddish-white flocculent precipitate, not easily soluble in hydrochloric acid; chloride of gold, a blue, with quick reduction of gold; mercuric chloride, a reddish-white precipitate, easily soluble in hydrochloric acid. It gives no precipitate with platinic chloride.

In most cases it will be necessary to identify physostogmine by its physiological activity, as well as by its chemical characters. For this purpose a small quantity of the substance should be inserted in the eye of a kitten; if it contains the alkaloid in question, in twenty minutes, at the very latest, there will be a strong contraction of the pupil, and a congested state of the conjunctival vessels. Further researches may be made with a small quantity on a bird or frog.[‡]

The chief symptoms observed will be those of paralysis of the respiratory and voluntary muscles, followed by death. If a solu-

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[*] M. Duquesnel, *Pharm. J. Trans.* [3], v. 847.

[†] Husemann's "Jahresbericht." 1872.

[‡] It may be noted in passing that it is seldom advisable to inject poison *subcutaneously* into birds of so small a size as sparrows, since the wound and the fright obscure the symptoms. Nothing is easier than to administer it by the beak.

tion is applied to the web of a frog's foot, the blood-vessels become dilated; if applied to voluntary or involuntary muscular fibre the contractility is, according to the dose, either destroyed or much weakened. It may thus be shown to retard and weaken the heart's action. Physostogmine also appears, according to Dragendorff and Pander, to act as an irritant, for they always observed gastro-enteritis as a result of the poison, even when injected subcutaneously. The enhanced secretion from all mucous surfaces, and the enlargement of the blood-vessels, are also very constant symptoms. Death appears to occur principally from paralysis of the respiratory muscles.

Of all these characteristics, the contraction of the pupil is, for legal purposes, the principal. A substance extracted from the tissues or other organic matters, in the manner mentioned, strongly contracting the pupil and giving the bromine reaction, would, in the present state of our knowledge, be indicative of physostogmine, and of that alone.

§ 74. *Pharmaceutical Preparations.*—The only preparation officinal in this country and abroad, is a spirituous extract (*Extractum physostigmatis*), used principally for external application, the dose of which is not more than a quarter of a grain.

§ 75. *Fatal Dose of Physostogmine.*—1 mgrm. (·015 grain) as sulphate, given by Vèe to a woman subcutaneously, caused vomiting, &c., after half an hour. A pupil of Gubler's took 2 mgrms. without apparent effect; but another mgrm., a little time after, caused great contraction of the pupil and very serious symptoms, which entirely passed off in four hours. It would thus be just to call 1 mgrm. a poisonous, but not necessarily, fatal dose.

IX.—COCCULUS INDICUS.

§ 76. The berries of the *Menispermum cocculus* comprise at least three definite crystalline principles: *menispermine*, *paramenispermine* (nitrogen-containing bases), and *picrotoxin*, which possesses some of the characters of an acid.

§ 77. *Menispermine* ($C_{18}H_{24}N_2O_2$?), discovered in 1834 by Pelletier and Courbe, is associated with a second named *paramenispermine.* The powdered berries are extracted by alcohol of 36°; the picrotoxin removed by hot water from the alcoholic extract; the menispermine and paramenispermine dissolved out together by acidulated water, and from this solution precipitated by ammonia. The brown precipitate is dissolved in acetic acid, filtered, and again precipitated by ammonia. This precipitate is dried, treated with cold alcohol, to separate a yellow resinous substance, and lastly with ether, which dissolves out the menispermine, but leaves the paramenispermine.

Menispermine forms white semi-transparent four-sided, truncated prisms, melting at 120°C., decomposed at a higher temperature, insoluble in water, but dissolving in warm alcohol and ether. Combined with eight atoms of water it crystallises in needles and prisms. The crystals are without any taste; in combination with acids, salts may be formed.

§ 78. *Paramenispermine* forms four-sided prisms, or radiating crystalline masses, melting at 250°C., and subliming undecomposed. The crystals are soluble in absolute ether, insoluble in water, and scarcely soluble in ether.

Menispermine dissolves in acids, but apparently without forming definite salts.

§ 79. *Picrotoxin* ($C_{12}H_{14}O_5$) was discovered in 1820 by Boullay. It is usually prepared by extracting the berries with boiling alcohol, distilling the alcohol off, boiling the alcoholic residue with a large quantity of water, purifying the watery extract with sugar of lead, concentrating the colourless filtrate by evaporation, and crystallising the picrotoxin out of water.

Picrotoxin crystallises out of water, and also out of alcohol, in colourless, flexible, four-sided prisms, often arborescent, and possessing a silky lustre. They are unalterable in the air, soluble in 150 parts of cold, and 25 parts of boiling water, dissolving easily in acidified water, in spirit, in ether, in amyl alcohol, and chloroform. They are without smell, but have an extremely bitter taste. Caustic ammonia is also a solvent.

The crystals are neutral and bitter. They melt at a gentle heat to a yellow mass; at higher temperatures giving off an acid vapour, with a caramel-like odour, and lastly carbonising. Picrotoxin in cold concentrated sulphuric acid dissolves with the production of a beautiful gold-yellow to saffron yellow colour, which becomes on the addition of a trace of potassic-bichromate violet, passing into brown. An alcoholic solution turns a ray of polarised light to the left $[a]j = -28{\cdot}1°$.

Picrotoxin behaves towards strong bases like a weak acid. Its compounds with the alkalies and alkaline earths are gummy and not easily obtained pure. Compounds with quinine, cinchonine, morphia, strychnine, and brucine can be obtained in the crystalline condition. Dilute sulphuric acid transforms it, with assimilation of water, into a weak gummy-like acid, which corresponds to the formula $C_{12}H_{16}O_6$. Nitric acid oxidises it to oxalic acid. Nitropicrotoxin and bromopicrotoxin

($C_{12}H_{13}(NO_2)O_5$, and $C_{12}H_{12}Br_2O_5$), can by appropriate treatme be obtained.

Concentrated aqueous solutions of alkalies and ammonia compose picrotoxin fully on warming. It reduces alkaline copp solution, and colours bichromate of potash a beautiful gree The best test for its presence is, however, as follows:—T supposed picrotoxin is mixed with thrice its bulk of saltpetre, t mixture moistened with sulphuric acid, and then decompos with soda-lye in excess, when there is produced a transito brick-red colour. For the reaction to succeed, the picrotox should be tolerably pure.

Solutions of picrotoxin are not precipitated by the chlorides platinum, mercury, and gold, iodides of potash, ferro and ferri cyanides of potash, nor by picric nor tannic acids.

Picrotoxin is a poison. Vossler killed a cat in two hou with a dose of ·12 grm. (1·8 grain); and another cat, with t same dose, died in 45 minutes. Falcke destroyed a young houn with ·06 grm. (·92 grain) in 24 to 26 minutes. Given by subc taneous or intravenous injection, it is, as might be expected, sti more lethal and rapid in its effects. In an experiment of Falcke' ·03 grm. (·46 grain), injected into a vein, destroyed a stron hound within 20 minutes; ·016 grm. (·022 grain), injected unde the skin, killed a guinea pig in 22 minutes; and ·012 grm (1·8 grain) a hare in 40 minutes. Hence it may be inferre that from 2 to 3 grains (12·9 to 19·4 centigrms.) would, in a probability, be a dangerous dose for an adult person.

The toxic action of picrotoxin on fish and frogs has been pro posed as a test. The symptoms observed in fish are mainly a follows:—The fish, according to the dose, show uncertain motion of the body, lose their balance, and finally float to the surface lying on one side, with frequent opening of the mouth and gill covers. These symptoms are, however, in no way distinguish able from those induced by any poisonous substance in th water, or by many diseases to which fish are liable. Neverthe less, it may be conceded that in certain cases the test may b valuable—if, *e.g.*, beer be the matter of research, none of th methods used for the extraction of picrotoxin will be likely to extract any other substance having the poisonous actio described on fish, so that, as a confirmatory test, this may b of use.

Frogs, under the influence of picrotoxin, become first uneasy and restless, and then somewhat somnolent; but after a short time tetanic convulsions set in, which might lead the inexperienced to imagine that the animal was poisoned by strychnine. There is, however, one marked distinction between the two—viz., that in picrotoxin poisoning an extraordinary swelling of the abdomen has been observed, a symptom which, so far as known, is due to picrotoxin alone. The frog is, therefore, in this instance, the most suitable subject for physiological tests.

Beer extract containing picrotoxin is fatal to flies; but no conclusion can be drawn from this, since many bitter principles (notably quassia) are in a similar manner fatal to insect life The separation of picrotoxin from beer is described at p. 165.

X.—ACONITE.

§ 80. The officinal *aconite* is the *Aconitum napellus*—monkshood or wolfsbane—a very common garden plant in this country, and one cultivated for medicinal purposes. Many varieties of aconite exist in other regions, which either are, or could be, imported; of these the most important is the *Aconitum ferox*, a native of he Himalayan mountains, imported from India.

All the aconites, so far as known, are extremely poisonous, nd it appears probable that different species contain different lkaloids. The root of *A. napellus* is from two to four inches long, onical in shape, brown externally and white internally. The eaves are completely divided at the base into five wedge-shaped obes, each of the five lobes being again divided into three near segments. The numerous seeds are three-sided, irregularly wisted, wrinkled, of a dark-brown colour, in length one-sixth of n inch, and weighing 25 to the grain (*Guy*). The whole plant one of great beauty, from two to six feet high, and having a erminal spike of conspicuous blue flowers. The root has been tally mistaken for horse-radish, an error not easily accounted r, since no similarity exists between them.

§ 81. *Pharmaceutical Preparations of Aconite.*—The preparaons of aconite used in medicine are:—

Aconitine, officinal in all the pharmacopeias.

Aconite liniment (*Linimentum aconiti*), made from the root th spirit, and flavoured with camphor; officinal in the British armacopeia; it may contain about 2·0 per cent. of aconitine.

Aconite tincture, officinal in all the pharmacopeias.

Aconite ointment, 8 grains to the ounce (*i.e.*, 1·66 per cent.); icinal in the British pharmacopeia.

Aconite extract, the juice of the leaves evaporated; officinal most of the pharmacopeias.

Fleming's tincture of aconite is not officinal, but is sold largely in commerce. It is from three to four times stronger than th P.B. tincture.

§ 82. *The Aconite Alkaloids.*—The alkaloids which have been stated to exist in *A. napellus* are—Aconitine napelline, acolyctine, lycoctine, and one or two others. The first is considered t be in combination with aconitic or equisetic acid, $H_3C_6H_3O_6$ the others are probably derivatives from aconitine, produced b the objectionable employment of mineral acids and too high temperature in the process of extraction.

The researches of Dr. Alder Wright on the alkaloids containe in the aconites, although not yet complete, have thrown muc light upon the subject, and are of the greatest importance ; onl a summary of results as obtained by him can, of course, be give here, and the reader is referred to the original papers* for furthe information.

The alkaloids contained in *Aconitum napellus* are by no mean identical with those contained in *Aconitum ferox.*

Aconitum napellus roots yield a crystallised alkaloid, *Aconitin* $C_{33}H_{43}NO_{12}$, of great activity. Some roots, but apparently no all, contain in addition a nearly inert bitter base, termed b Dr. A. Wright *Picraconitine,* $C_{31}H_{45}NO_{10}$. Besides picraconitin and aconitine, there is a third amorphous alkaloid, incapable o yielding crystalline salts, and of lower molecular weight.

Aconitum ferox contains an active alkaloid, to which Dr Wright gives the name of pseudaconitine, and assigns the formula $C_{27}H_{37}NO_5$. From pseudaconitine, apopseudaconitin ($C_{36}H_{47}NO_{11}$), pseudaconine ($C_{27}H_{41}NO_9$), apopseudaconin ($C_{27}H_{39}NO_8$), and other derivatives may be obtained.

Confining our attention to the physiologically-active alkaloids *Aconitine* and *Pseudaconitine*, the points of resemblance and difference between them are as follows :—They are both physiologically active, and both give precipitates with mercuric chlorid potassium mercuro-bromide, potassium mercuriodide, tanni gold chloride, and several other precipitants of the alkaloids.

From aconitine, pseudaconitine differs in its molecular weigh and in its melting point—aconitine melting at 189°C., pseudaconitine at about 104° to 105°C.

Aconitine by saponifying agents breaks up into benzoic aci and a new alkaloid, according to the reaction,

$$C_{33}H_{43}NO_{12} + H_2O = C_7H_6O_2 + C_{26}H_{39}NO_4 \,;$$

while pseudaconitine, treated similarly, gives rise to a new bod (*apopseudaconitine*) and dimethyl-protocatechuic acid,

$$C_{36}H_{49}NO_{12} + H_2O = C_9H_{10}O_4 + C_{27}H_{41}NO_9.$$

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* *Journ. Chem. Society*, i., 1877, p. 143 ; *ib.* i., 1878, p. 151.

Aconitine, again, crystallises anhydrous; pseudaconitine with one atom of water. Aconitine yields well-crystallised salts with facility; pseudaconitine, treated similarly, produces amorphous varnishes, with a few exceptions, *e.g.*, the nitrate.

§ 83. *Separation of the Aconite Alkaloids.*—It would appear certain that in all operations for the separation of aconite alkaloids (whether from the organic matters which make up the plant, or from those constituting animal tissues) mineral acids and a high heat should be avoided. A modification of M. Duquesnel's process of isolation is best—viz., extraction by alcohol acidulated with tartaric acid; evaporation of the extract at temperatures not exceeding 60°C.; re-solution of the extract in water; agitation of the acid liquid with the various solvents described at p. 267, to remove impurities; and, finally, precipitation by sodium bicarbonate. Any precipitate should be crystallised, if possible, several times from ether and petroleum, and lastly, converted into an acid oxalate, and regenerated from the oxalate by re-precipitation with carbonate of soda; or, if the alkaloid sought is derived from *A. ferox*, the purification appears best effected by conversion of the pseudaconitine into nitrate (the nitrate of pseudaconitine is almost insoluble in nitric acid containing 8 to 10 per cent. of HNO_3), and from the nitrate the alkaloid may be regenerated by soda and ether.

In this way it is possible (should any of the preparations of aconite, or the root itself, have been taken) to isolate a more or less minute portion of an alkaloid, which, if derived from the aconites, responds to the reactions given below; and, if applied to the skin, will cause local anæsthesia. If a minute quantity is rubbed on the lip, or placed on the tongue, it will cause tingling and numbness; in order to be personally acquainted with this feeling, the tincture (or the liniment of aconite) can be tried in the same way, and the sensations compared.

Further, if aconitine, or pseudaconitine, in a quantity so small as ·21 mrgm. ($\frac{1}{300}$ grain), is injected subcutaneously into a small animal, a mouse, &c., poisonous symptoms will be developed.

Commercial aconitine is at the present time so variable in its composition that it is hardly safe to generalise from the samples met with. It is usually an amorphous white powder, melting below the temperature of boiling water, and yielding an amorphous sublimate above 150°C.; it dissolves without colour in itric acid, and gives no precipitate with bichloride of platium.

(*a.*) On heating aconitine with phosphoric acid, a violet colour s produced (*Van Hasselt*).

(*b*.) Sulphuric acid produces a brown colour slowly,* passing through different shades of red-brown into violet.

(*c*.) Sugar and sulphuric acid give a red colour (*Schneider*).

§ 84. *Fatal Dose.*—The fatal dose of pure aconitine, or pseudaconitine, is probably about ·64 mgrm. ($\frac{1}{10}$ grain); if in any case so small a quantity should have caused death, it is highly improbable that chemical manipulation would detect it with certainty.

§ 85. *Analysis of Pharmaceutical Preparations of Aconite.*—The yield of total alkaloids from aconite roots is variously stated at from ·03 to ·04 per cent. The approximate strength of tinctures, liniments, &c., may be determined by Mayer's reagent.† Each cc. of this fluid precipitates ·0269 of Duquesnel's aconitine, which (according to the recent researches of Dr. Wright) Duquesnel obtained nearly pure. The titration, according to Dragendorff, must operate upon a fluid containing about one part of the alkaloid in 150 to 200 of water, and a first experiment is necessary in order to ascertain the proper degree of dilution. The reagent is then added from a burette, and by the use of a Beale's filter the point at which a precipitate ceases to be produced is noted.

Extracts of aconite must be treated with acidulated water, and filtered; spirituous preparations must be freed from alcohol, and acidulated. Herr Zinoffsky, operating in this way, found in Russian tinctures ·116 to ·1 per cent. of aconitine. The extracts appear to contain from 4 to 6·5 per cent.

Commercial aconitine may be assayed by the use of saponifying agents, changing aconitine and pseudaconitine respectively into benzoic and dimethyl-protocatechuic acids. The following (from a recent number of the *Pharmaceutical Journal*) is an example of this method:—

0·7895 grain lost at 100° 0·0335, . . . = 4·2 per cent.

2·3040 grain, dissolved in hydrochloric acid, and treated with ether, furnished 0·010 grain of residue, left on spontaneous evaporation of ether, consisting of resinous matter with a little dimethyl-protocatechuic acid, ... = 0·4 „

2·0230 grain, heated to 240 to 250 in a sealed tube for twenty-four hours with water, yielded with hydrochloric acid and ether 0·3660 grain of mixed benzoic and

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* The full violet colour takes twenty-four hours to produce.

† 13·546 grms. of mercuric chloride and 49·8 potassic iodide in a litre of water.

dimethyl-protocatechuic acids, with trace of resin, ... = 18·1 per cent.
On distillation with water, 0·002 grm. of benzoic acid was obtained, melting at 110°C., ... = 0·1 ,,

·1 per cent. of benzoic acid would correspond to 0·6 per cent. of aconitine, since pure aconitine has been found experimentally to yield about one-sixth of its weight of benzoic acid.

Pure pseudaconitine is assumed to yield 25 per cent. of its weight of dimethyl-protocatechuic acid; in other words, the percentage of dimethyl-protocatechuic acid multiplied by 4 (after making corrections for resin, pre-existing acid, and benzoic acid), equals for practical purposes the percentage of pseudaconitine; hence the results of the previous analysis are thus worked out:—

Total dimethyl-protocatechuic and benzoic acids, and resin obtained, ... = 18·1 per cent.
Deduct resin and pre-existing dimethyl-protocatechuic acid, ... = 0·4 ,,

Acids due to pseudaconitine and aconitine present, ... = 17·7 ,,
Benzoic acid due to aconitine, ... = 0·1 ,,

Dimethyl-protocatechuic acid due to pseudaconitine, ... = 17·6 ,,
Percentage of pseudaconitine, = 17·6 × 4 = 70·4 ,,
Ditto of aconitine, . . . = 0·1 × 6 = 0·6 ,,
Water, ... = 4·2 ,,
Pseudaconine and amorphous unnamed base, &c., by difference, ... = 24·8 ,,

XI.—ERGOT OF RYE.

§ 86. Ergot is a peculiar fungus attacking the rye and other graminaceous plants;[*] it has received various names, *Claviceps purpurea*, Tulasne, *Spermœdia clavus*, Fries, *Sclerotium clavus*, D.C., &c. The peculiar train of symptoms arising from the eating of ergotised grain (culminating occasionally in gangrene of the lower limbs), its powerful action on the pregnant uterus, and its styptic effects, are well known.

The very general use of the drug by accoucheurs has, so to

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[*] Some of the *Cyperaceæ* are also attacked.

speak, popularised a knowledge of its action among all classes of society, and its criminal employment as an abortive appears to be on the increase.*

The healthy grain of rye, if examined microscopically in thin sections, is seen to be composed of the seed-coating, made up of two layers, beneath which are the gluten-cells, whilst the great bulk of the seed is composed of cells containing starch. In the ergotised grain, dark (almost black) cells replace the seed-coat and the gluten-cells, whilst the large starch-containing cells are filled with the small cells of the fungus and numerous drops of oil.

§ 87. *The Chemical Constituents of Ergot* are a fixed oil, trimethylamine, certain active principles, and colouring matters.

The *fixed oil* is of a brownish-yellow colour, of aromatic flavour and acrid taste; its specific gravity is 0·924, and it consists chiefly of the glycerides of palmitin and olein; it has no physiological action.

Trimethylamine is always present ready formed in ergot; it can also be produced by the action of potash on ergot.

With regard to the *active principles of ergot* considerable confusion still exists, and no one has hitherto isolated any single substance in such a state of purity as to inspire confidence as to its formula or other chemical characters. They may, however, be briefly described.

C. Tamet (*Compt. Rendus*, xxxi. 896) has separated an alkaloid, which appears identical with Wenzel's *ergotinine*. To obtain this the ergot is extracted by alcohol of 86°, the spirit removed by distillation, and the residue cooled; a resin (which is deposited) and a fatty layer (which floats on the surface) are separated from the extractive liquor and washed with ether; the ethereal solution is filtered and shaken with dilute sulphuric acid, which takes up the alkaloid; the aqueous solution of the sulphate is then filtered, rendered alkaline by KHO, and agitated with chloroform. The ergotinine is now obtained by evaporating the chloroform solution, care being taken to protect it from contact with the air. It gives precipitates with chloride of gold, potassium iodohydrargyrate, phosphomolybdic acid, tannin, bromine water, and the chlorides of gold and platinum. With moderately concentrated SO_4H_2, it gives a yellowish-red coloration, changing to an intense violet, a reaction which does not occur if the alkaloid has been exposed to the air. The composition of the base is represented by the formula $C_{70}H_{40}N_4O_{12}$, and a crystalline sulphate and lactate have been obtained.†

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* The Russian peasantry use the drug for the same purpose. *Vide* Mackenzie Wallace's "Russia," I., p. 117.

† *Comptes Rendus*, April, 1878.

Wenzel's *Ecboline* is prepared by precipitating the cold watery extract of ergot with sugar of lead, throwing out the lead in the usual way by hydric sulphide, concentrating the liquid, and adding mercuric chloride, which only precipitates the ecboline. The mercury salt is now decomposed with hydric sulphide, and after the mercury precipitate has been filtered off, the filtrate is treated with freshly precipitated phosphate of silver, and refiltered; lastly, the liquid is shaken up with milk of lime, again filtered, and the lime thrown out by CO_2. The last filtrate contains ecboline only, and it is obtained by evaporation at a gentle heat. It is an amorphous, feebly bitter substance, with an alkaline reaction, forming only amorphous salts.

The most recent research by Dragendorff on ergot tends to show that Wenzel's alkaloids, ergotinine and ecboline, are inactive. Dragendorff describes also (*a.*) *Scleromucin*, a slimy substance which goes into solution upon extraction of the ergot with water, and which is again precipitated by 40 to 45 per cent. alcohol. It is colloidal and soluble with difficulty in water. It contains nitrogen, but gives no albuminoid reaction, nor any reaction of an alkaloidal or glucosidal body; it yields to analysis—

8·26	per cent.	Water.
26·8	„	Ash.
29·0	„	Carbon.
6·44	„	Hydrogen.
6·41	„	Nitrogen.

(*b.*) *Sclerotic Acid.*—A feebly-acid substance, easily soluble in water and dilute and moderately concentrated alcohol. It passes, in association with other constituents of the ergot extract, into the diffusate, when the extract is submitted to dialysis; but after its separation in a pure state it is, like scleromucin, colloidal. It is precipitated by 85 to 90 per cent. alcohol, together with lime, potash, soda, silica, and manganese; but after maceration with hydrochloric acid, the greater part of the ash constituents can be separated by a fresh precipitation with absolute alcohol. The sample gave 40·0 per cent. of carbon, 5·2 per cent. hydrogen, 4·2 per cent. nitrogen, 50·6 per cent. oxygen, with 3·4 per cent. of ash. Sclerotic acid forms with lime a compound that is not decomposed by carbonic acid, and which upon combustion leaves from 19 to 20 per cent. of calcium carbonate. Both these substances are active, although evidently impure. Sclerotic acid is sold in commerce, and has been employed subcutaneously in midwifery practice in Russia and Germany for some time.

The inert principles of ergot are—1. A red colouring matter, *Sclererythrin*, insoluble in water, but soluble in dilute and stron alcohol, ether, chloroform, dilute solutions of potash, ammonia, & It can be obtained by dissolving in an alkali, neutralising wit an acid, and shaking up with ether. Alcoholic solution of scle erythrin gives with aluminium sulphate, and with zinc chlorid a splendid red mixture ; with salts of calcium, barium, and man of the heavy metals, it gives a blue precipitate ; the yield is onl ·1 to ·05 in a thousand parts.

(2.) Another colouring matter, dissolving in concentrated su phuric acid with the production of a fine blue violet colour, tl discoverer has named *Scleroiodin*. This is not soluble in alcoho ether, chloroform, or water; but dissolves in alkaline solution potash producing a splendid violet colour; yield about 1 to 100

(3, 4.) Two crystalline substances, which may be obtained fro ergot powder, first treated with an aqueous solution of tartar acid, and the colouring matters extracted by ether. One Drage dorff names *Sclerocrystallin*, $C_{10}H_{10}O_4$; it is in colourless needl insoluble in alcohol and water, with difficulty soluble in ethe but dissolving in ammonia and potash solutions. The other cry talline substance is thought to be merely a hydrated compou of sclerocrystallin. Both are without physiological action.

The solid ergot and its preparations are readily recognised l their physical characters, and by the property they possess yielding trimethylamine* on distillation with potash. In tl present state of our knowledge, it is better to trust to the pr duction of this definite, well-known chemical substance, than attempt to isolate the principles which have been described. Wi regard to ergot taken into the stomach, unless the liquid or po der itself remains there for identification, it is hopeless to sear for the *absorbed* drug ; the tests for ergot must be much mo definite than they are at present, before such a search can l successful.

§ 88. *The Detection of Ergot* in flour or meal may be effect by distilling with potash, and examining the distillate f trimethylamine. The liquid (which in any case will conta ammonia) is carefully neutralised with dilute sulphuric aci and evaporated to dryness. On treatment of the dry mass wi ether, the sulphate of trimethylamine is dissolved out of tl ammonium sulphate, the latter being left unacted upon. Tl sulphate of trimethylamine may now be dissolved in a litt water, placed in a retort with freshly-burnt lime, and distille

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* Since trimethylamine is produced from a variety of substances, to fi it would not be sufficient evidence in itself of the presence of ergot; b here, as elsewhere, the judgment is formed not on one isolated fact, but several taken together.

condensing the products in a U tube, which must be cooled by a freezing mixture, or by ice, or in any other suitable manner. Trimethylamine is present if, under such circumstances, a strongly alkaline inflammable liquid, smelling fishy and ammoniacal, is obtained.

Another method is as follows*:—10 grms. are treated twice with 30 grms. of boiling alcohol of 90 per cent. (in which the colouring matter is not soluble), and each time passed through linen. The substance thus purified, is again digested with alcohol, and when filtered off, should be colourless; if not, the extraction must be repeated until it is. The substance is now treated with from 10 to 20 drops of diluted sulphuric acid, shaken up, and then allowed to stand. If the meal is pure, the supernatant fluid should be colourless, or of a pale yellow; but if ergot be present, it will be coloured more or less intensely red. It may be estimated by colorimetric processes, and $\frac{1}{4}$ per cent. of ergot detected in this way.

§ 89. *Pharmaceutical Preparations.*—Ergot itself is officinal in all the pharmacopeias, and occurs in grains from $\frac{1}{3}$ to 1 inch in length, and about the same breadth, triangular, curved, obtuse at the ends, of a purple colour, covered with a bloom, and brittle, exhibiting a pinkish interior, and the microscopical appearances already detailed. Ergot may also occur as a brown powder, possessing the unmistakable odour of the drug. A liquid extract of the B. P. is prepared by exhausting the ergot of fat by ether, digesting the marc in water at 160°F., and evaporating; spirit is then added, and the liquid filtered from the precipitate which is formed. The extract of the Continental pharmacopeias is very similar. It has been found in practice that the addition of a little sulphuric acid aids in preserving the strength of the extract, which will, therefore, be generally found acid, containing from 12 to 14 per cent. of solid matters, and yielding from ·022 to ·028 of albuminoid nitrogen when distilled with alkaline permanganate of potash. A tincture and an infusion are also officinal; the latter is very frequently used, but seldom sold, for it is preferable to prepare it on the spot. The tincture, experience has shown to be far inferior in power to the extract, and it is not much used.

§ 90. *Dose.*—The main difficulties in the statement of the medicinal dose, and of the minimum quantity which will destroy life, are the extreme variability of different samples of ergot and its readiness to decompose. A full medicinal dose of ergot itself, as given to a woman in labour, is 4 grms. (61·7 grains), repeated every half hour. In this way enormous doses may be

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* Jacoby, quoted by Dragendorff—"Beiträge zur Gerichtlichen Chemie." St. Petersburg, 1872.

given in some cases without much effect. On the other ha doses so small as 1 to 4 grms. have caused serious poison symptoms. The extract and the tincture are seldom give larger doses than that of a drachm as a first dose, to ex uterine contraction. In fact, the medical practitioner has many cases to experiment on his patient with the drug, in or to discover not only the individual susceptibility, but activity of the particular preparation used.

XII.—DIGITALIS.

§ 91. The *Digitalis purpurea*, or foxglove, is a plant extrem common in most parts of England, and poisoning may occur fi the accidental use of the root, leaves, or seeds. The seeds very small and pitted; they weigh 1126 to a grain (*Guy*), ar a light brown colour, and in form somewhat egg-shaped. leaves are large, ovate, crenate, narrowed at the base, rug veined, and downy, especially on the under surface. Th colour is a dull green, and they have a faint odour and a bit nauseous taste. The leaf is best examined in section. Its dermis, when fresh, is seen to consist of transparent, hexago colourless cells, beneath which, either singly or in groups, th are round cells of a magenta tint, and beneath these ag a layer of columnar cells, and near the lower surface a lo parenchyma. The hairs are simple, appearing scantily on upper, but profusely on the lower, surface; each is compose from four to five joints or cells, and has as its base a mage coloured cell. The small leaves just below the seed-case, the latter itself, are studded with glandular hairs. The root c sists of numerous long slender fibres.

§ 92. *Chemical Composition.*—It is now generally accep that there exist in the foxglove at least four distinct princip —digitaline ($C_{54}H_{84}O_{27}$), digitonine ($C_{31}H_{52}O_{17}$), digitox ($C_{31}H_{33}O_7$), and digitaleine ($C_{21}H_{46}O_{11}$). These are all proba derivatives of digitaline.

(1.) *Digitaline* ($C_{54}H_{84}O_{27}$), when perfectly pure, forms fi white, glittering, hygroscopic needles, or groups of crystall tufts; it is without smell, but possesses a bitter taste, whic at once of slow development and of long endurance. On wa ing it becomes soft under 100°C., and, above that temperatu is readily decomposed with evolution of white vapours. dissolves but slightly even in boiling water, and is quite insolu in ether and benzole; 12 parts of cold, and 6 of boiling, alco of 90 per cent. dissolve one of digitaline; chloroform dissolves it in all proportions. Dilute hydrochloric or sulphuric acid decompose it into glucose and digitaletine ($C_{42}H_{60}O_{18}$); if the action is prolonged, digitaleretine ($C_{30}H_{50}O_{10}$), and finally dehydrated igitaleretine ($C_{30}H_{42}O_6$) are formed. Concentrated sulphuric acid issolves it with the production of a green colour, which by romine passes into red, but on the addition of water becomes gain green. Hydrochloric acid dissolves it with the production f a greyish-yellow colour, passing gradually into emerald green; water precipitates from this solution a resinous mass.

(2.) *Digitonine* is white, amorphous, and soluble in water in very proportion; its aqueous solution froths. Absolute alcohol issolves it in the cold with difficulty, more easily upon warming, ut the best solvent is a mixture of chloroform and alcohol. It ppears to have somewhat the chemical characters of saponin.

(3.) *Digitoxine*, according to Semiediberg (*Pharm. Journ. Trans.* 3], v. 741–743), is only present in the proportion of one part to very 10,000 of the dried leaves. It may be obtained in crystals y extracting the dry exhausted leaves with alcohol of 50 per ent., precipitating with lead acetate, and washing the precipitate rst with a dilute solution of sodium carbonate (to remove olouring matter), and then with ether, benzine, and carbonic isulphide, in all of which it is insoluble; on decomposing the ad compound, digitoxine may be obtained in colourless scales needle-shaped crystals.

(4.) *Digitaleine* is a colourless, amorphous body, soluble in loroform, alcohol, and water, but insoluble in benzine; its lution has a sharp, bitter taste, and froths on shaking.

The main interest, from a medico-legal point of view, however, ncentrates itself more upon the properties of commercial digi- line, which often consists of an equal mixture of the four bodies d their decomposition products. There are at least two kinds digitaline in commerce; one, the German, containing true gitaline, composed of from 2 to 3 per cent. of digitonine and gitaleine, and soluble in water; the other, the so-called French, luble in water with difficulty, and containing digitaline, gitoxine, and an inactive substance, which has been named *gitine*.

The general behaviour of the four bodies to reagents is as lows:—Concentrated hydrochloric acid colours crystallised gitaline yellow-green; amorphous digitaleine, light yellow; digi- ine, on boiling, garnet to violet-red; digitoxine, yellow-green. ncentrated sulphuric acid dissolves digitaline green-brown; gitaleine, reddish-brown; digitoxine, green to black-brown; gitonine, brown-red. The last is dissolved by dilute sulphuric acid [1 : 3] without colour, and the same remark applies hydrochloric acid; on warming with either of these acids, violet-red colour appears; this reaction thus serves to distinguis digitonine from the three other constituents, as well as fro saponin.

Sulphuric and gallic acids colour the glucosides of digitalin digitaleine, and digitonine, red, but not digitoxine, which ca be identified in this way.

Sulphuric acid and bromine give with digitaline a red, an with digitaleine a violet coloration, which, on the addition water, change respectively into emerald and light green. Thi the most important chemical test we possess, is sometimes calle *Grandeau's test;* it is not of great delicacy, the limit being abou ·1 mgrm.

§ 93. *Pharmaceutical Preparations of Digitaline.*—Digitalin itself is officinal in the French, British, and Austrian pharma copeias. It is prepared in our own by making a strong tinctur of the leaves at 120°F.; the spirit is then evaporated off, and th extract heated with acetic acid, decolorised by animal charcoa and filtered. After neutralisation with ammonia, the digitalin is precipitated with tannic acid, and the tannate of digitalin resolved into tannate of lead and free digitaline, by rubbing i with oxide of lead and spirit.

Digitalis leaf is officinal in most of the pharmacopeias.

Tincture of digitalis is officinal in our own and all the Continental pharmacopeias, and an ethereal tincture is used i France and Germany.

An *Acetum digitalis* is officinal in the Netherlands and Germany an extract and infusion are also used to some extent.

With regard to the nature of the active principle in thes different preparations, according to Dragendorff, digitonine an digitaleine are most plentiful in the acetic and aqueous preparations; whilst in the alcoholic, digitaline, digitoxine, and digitaleine are present.

§ 94. *Fatal Dose.*—It is difficult to say what would be th minimum dose of commercial digitaline, or its equivalent, necessary to destroy life, but it is usually placed at about 4 mgrms. or $\frac{1}{16}$ of a grain.

§ 95. *Detection of the Active Principle in Organic Matters, &c.*— In a case of poisoning by digitaline, or the officinal preparation of digitalis, a remnant undecomposed may be found in th stomach or first portion of the intestines; but any attempt a extraction from the tissues or the blood, if not absolutely hopeless, does not offer much probability of success. The great an essential precaution in searching for digitaline is, never t allow the temperature to exceed 50°C.; if an extract is once heated to 100°C., decomposition and loss may ensue. The contents of the stomach are filtered through linen, pressed, and their bulk, if necessary, reduced, by placing the organic fluid in a large evaporating basin, exposed either to a current of air or to a heat of about 40°C. To this concentrated extract acetic acid is added to the extent of about 50 per cent., and the acid watery extract shaken up with petroleum ether (which removes none of the glucosides, but many impurities), and then with benzine, which may be warm. The benzine thus obtained is best allowed to evaporate spontaneously, and may leave the substances pure enough to respond to tests. Digitaline can be separated from digitaleine by chloroform, which dissolves out the latter, with a little only of the former.

§ 96. *Physiological Tests.*—Before the discovery of the bromine reaction, it was considered that the active principles of the foxglove could only be identified by physiological tests; and although the same necessity does not now exist, yet such tests are still useful.

The local application of digitaline, with its associates, produces irritant effects. If applied to the eye, there is inflammation and slight irritation of the pupil. Hypodermic injections may also excite an erysipelatous inflammation.

Digitaline has a specific and very peculiar action upon the heart, which may be conveniently studied for forensic purposes on a frog. If the experimenter has never witnessed the action of the drug on the heart of the frog, it will be judicious to place two frogs under glass-shades, poisoning the one with commercial digitaline, and using exactly the same weight (or, if impure, a little more) of the unknown substance to the second frog.

Drs. Fagge and Stevenson have shown* that, under the influence of digitaline, there is a peculiar form of irregularity in the beats of the heart in the frog; the ventricle ultimately stops in the white contracted state, the voluntary power being retained for fifteen to twenty minutes afterwards; in very large doses there is, however, at once paralysis.

XIII.—COLCHICUM.

§ 97. The whole of the *Colchicum autumnale*, or common meadow-saffron, is poisonous, owing to the presence of an alkaloid (discovered by Pelletier and Caventou) called *Colchicine.*

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* *Guy's Hospital Reports*, 3d series, vol. xii., p. 37.

According to Johannson's experiments, the dried colchic seeds contain 1·15 per cent. of colchicine; the leaves, 1·459 cent.; the bulbs, from 1·4 to 1·58 per cent.; and the roots, 0·6 per cent. The frequent poisoning of cattle in the autumn colchicum, its use in quack pills for rheumatism, and its suppos occasional presence in beer, give it an analytical importance.

§ 98. *Colchicine*, $C_{17}H_{19}NO_5$, may be extracted from the see &c., in the manner recommended by Hübler:—The seeds a treated, without crushing, by hot 90 per cent. alcohol, and t alcoholic solution evaporated to a syrup, which is diluted wi twenty times its bulk of water and filtered; the liquid is ne treated with acetate of lead, again filtered, and the lead thro out by phosphate of soda. Colchicine is now precipitated a tannate,* the formula of which, according to Hübler, $3C_{17}H_{19}NO_5 2C_{27}H_{22}O_{17}$. The precipitation is best fractional, t first and last portions being rejected as containing impuriti The tannate is decomposed in the usual way with litharge, a extracted by alcohol.

A simpler method is, however, extraction by chloroform fro an aqueous solution, feebly acidified, as recommended by Drage dorff. The parts of the plant are digested in very dilute ac water, and the resulting solution concentrated and shaken with chloroform, which is best done in the flask figured an described at p. 74.

Colchicine is usually obtained as a yellowish-white, gumm or resinous mass, but it is also possible to obtain it in crystalli needles and prisms. It softens at 130°, and at 140° melts; di solves slowly but in every proportion in water; the solutio is neutral. It dissolves easily in spirit. Pure colchicine said by Hübler not to dissolve in ether—a statement contr dicted by Geiger and Hesse, with whom Dragendorff agrees, an adds, that it is also soluble in benzine, amyl alcohol, and chlor form, but not in petroleum ether. Dilute acids and alkalies di solve it, the solution becoming slowly or quickly colour intensely yellow, whilst a decomposition takes place. Boilin with dilute acid, and also the protracted action of baryta wate in closed tubes, forms *colchcieine*. Concentrated potash-lye gives upon heating with it, a brown resinous substance.

Colchiceine crystallises in needles, or in glittering plates, an tastes less bitter than colchicine; it melts at 155°, dissolves bu little in cold, copiously in boiling water; is soluble in chloroform

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* The purest tannic acid must be used. The commercial tannin may be purified by evaporating to dryness with litharge, exhausting the tannate of lead repeatedly with boiling alcohol and water, and, lastly, suspending in water, and separating the lead by SH_2.

methyl and ethyl alcohols, but soluble with difficulty in ether. It appears to be an acid, forming salts with the alkalies; its precipitants are—tannic acid, phosphomolybdic acid, picric acid, chloride of gold, &c.

Colchiceine gives a remarkable series of colours with the inorganic acids, a property which may be utilised as a test either for the presence of colchicine, or, conversely, for the presence of mineral acid in such liquids as vinegar, &c. Concentrated nitric acid of 1·4 specific gravity colours either colchiceine or colchicetine violet-blue, changing into yellow, and lastly passing into green. If the violet solution is diluted with water it becomes yellow, and, on the addition of soda, a beautiful orange-yellow or red. Concentrated sulphuric acid dissolves colchiceine with an intense yellow, and if to this solution a drop of nitric acid be added, a dark brown zone is produced, passing gradually through violet and brown into yellow.

The action of acids is also very distinctive, although slightly different in the case of an acid directly added to an infusion of the seeds. Thus, if a little colchicine be extracted by alcohol and water from a few grains of the seeds, and the yellowish solution diluted until the colour is scarcely perceptible, concentrated sulphuric or nitric acid gives a very pronounced yellow, which a drop of HCl changes to a blue-violet. Nitric acid dropped into another portion of the same solution concentrated, with the addition of a fragment of sodium acetate, develops an orange colour.

The precipitants of colchicine are, chiefly, chloride of gold and phosphomolybdic* and tannic acids; picric acid, potassio-cadmic iodide, and potassio-hydrargyric iodide give no precipitate. Chlorine water causes in a watery solution of colchicine a yellow precipitate, which dissolves in ammonia with an orange colour.

§ 99. *Pharmaceutical Preparations.*—Colchicine itself is officinal in Austria; the wine in the British, French, and Dutch, and the seeds themselves in all the pharmacopeias. The wine of colchicum, officinal in nearly all the pharmacopeias, is made with very different proportions of seeds or bulbs, as the table on next page shows.

The tincture of colchicum is officinal in our own and in all the Continental pharmacopeias; in the British, $2\frac{1}{4}$ oz. of seeds are exhausted by 20 oz. of proof spirit.

A tincture of colchicum seeds, examined by Johannson, contained ·12 per cent. of colchicine, and a tincture prepared from the bulbs ·14 per cent.

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* It is useful to know that the phosphomolybdate of colchicine gives all the colour reactions of pure colchiceine.

	German and Norweg. Ph.	Austrian and Swiss Ph.	Netherland Ph.	British Ph.	French Ph.	
Dry Colchicine corms,	...	...	...	...	6	6
Powdered Seeds, .	10	10	10	10 oz.	...	...
Vin. Hispanii, . .	...	...	80	...	...	...
,, Malaceuse, . .	...	50	...	...	...	...
,, Xereuse, . .	100	...	...	q. s. ad. 50 fld. oz.	100	10
Spirit-rectifical, .	...	...	10	...	...	...

Colchicum vinegar is not officinal in Britain, but one contai ing 5·4 per cent. of acetic acid is so in the Netherlands, German and France; the strength appears to be about ·095 per cent. colchicine.

An extract of colchicum is officinal in Britain and Franc and an acetic extract in Britain; the latter is the most active all the pharmaceutical preparations of colchicum.

Lastly, an oxymel of colchicum is in use in Germany, Franc and the Netherlands.

Quack and Patent Medicines.—In all specifics for gout th analyst will naturally search for colchicum. Most gout pill contain the extracts; and liquids, such as "Reynolds' gou specific," the wine or the tincture variously flavoured an disguised.

§ 100. *Fatal Dose.*—The probable poisonous dose of colchicu may be fairly predicted from the cases detailed in *Archiv. fu Pharmacie*, Bd. 131, p. 1.; Husemann's "Toxicologie," an Taylor's "Principles of Medical Jurisprudence." In the latte work is mentioned an instance in which 3½ drachms of colchicu wine, taken in divided doses, caused death on the fourth day The quantity of the active principle in the colchicum wine, a found by Johannson (*Dragendorff*) being 0·18 per cent., i follows that ·378 of a grain (or ·0244 grm.) was fatal, though not given as one dose. In any medico-legal case, the analyst should, if material is at hand, endeavour to ascertain the strength of the preparation administered.

§ 101. *Separation of Colchicine from Organic Matters.*—The solution of colchicine from the stomach, or tissues of the body is best effected by extraction with alcohol, filtration, and concentration of the resulting filtrate by evaporation. When cool it is acidified and shaken up several times with petroleum ether, which will not dissolve the colchicine, but will remove some of the impurities. After separation of the petroleum ether, the solution is shaken up with chloroform, the latter removed in the usual way, agitated with pure water once or twice, again separated, and lastly evaporated to dryness. The colchicine, probably mixed with colchicetine, will now be in a pure enough state to admit of the successful application of tests.

In cases of poisoning by colchicum at Berlin, Wittstock used the following process:—The contents of the stomach were mixed with a large amount of alcohol, a few drops of HCl added, and the whole well shaken; the fluid was then filtered, and the filtrate evaporated to a syrupy consistence at 37°C. The resulting residue was dissolved in distilled water, the fat, &c., filtered off, and the liquid carefully evaporated. From the extract foreign matter was again separated by treatment with alcohol and filtration, and the last filtrate was evaporated to a syrupy consistence. The syrupy fluid was taken up by distilled water, filtered, evaporated to 30 grms., and 2 grms. of calcined magnesia with 90 grms. of ether were added. After a time, the ether was removed, and allowed to evaporate spontaneously. The residue was once more taken up with water, filtered from fat, &c., and evaporated. This final residue gave all the reactions of colchicine. In medico-legal researches, it must be remembered that colchicine is absorbed but slowly, a not insignificant portion remaining in the bowels, and being excreted with the fæces.

The quantitative estimation of colchicine may be made gravimetrically by evaporating to dryness its solution in chloroform; or, with certain precautions, pharmaceutical products may be titrated with Mayer's reagent. For the precipitation by the latter to be complete, it is absolutely necessary to acidify with sulphuric acid, and to do so in a proper proportion, and with the liquid to be tested of a certain concentration. Dragendorff recommends one part of colchicine in 600, to contain 7 to 10 per cent. of dilute sulphuric acid. Wine, tincture, and vinegar of colchicum require evaporation to dryness, extraction with water, and lastly, the addition of the sulphuric acid. 1 cc. of Mayer's reagent = ·0317 grm. of colchicine.

XIV.—BIBIRINE.

§ 102. *Bibirine* (also named *Buxin*, *Pelosin*, *Beberia*) is a alkaloid found in the bark of the *Buxus sempervirens*, the *Necta dra Rodiæi*, Schomb., the root of the *Pareira brava*, and the bark o the *Cissampelos pareira*.

The general principles of extraction are : treatment with acidulated water, neutralisation with lime, and to the filtered solution the addition of ammonia, which throws down an impure bibirine. The alkaloid is afterwards purified by the ordinary methods.

Pareira bark is said to be used occasionally for the purpose o bittering beer; and in such cases, provided sufficient beer b taken, the separation of bibirine may be possible, but the percentage of the alkaloid found in the bark is very small. Flückiger only isolated ·5 per cent. ; the root contains more, viz., from to 5 per cent. (*Wiggers.*)

Pure bibirine ($C_{18}H_{21}NO_3$) is a white, light, amorphous powder becoming electric by rubbing at 100°C. ; it loses 8·2 per cent. o water, corresponding to one and a half H_2O ; at about 145° t 148°C. it melts. Its taste is bitter, and it has a strong alkaline reaction ; it is very little soluble in cold or hot water (6600 parts cold, 1500 to 1800 parts boiling), requires five parts of absolute alcohol and thirteen parts of ether for solution, and dissolves easily in chloroform, aceton, amyl alcohol, benzole, and bisulphide of carbon.

Bibirine unites with acids, but forms uncrystallisable compounds only. The sulphate is found in commerce, and is used to a small extent in medicine ; it occurs in dark-brown, thin, translucent scales, yellow when powdered, and having a strong bitter taste.

Solutions of the salts, such as the acetate, give white amorphous precipitates with phosphate of soda, nitrate of potash, nitric acid, iodide of potash, mercuric potassic iodide, and corrosive sublimate. The platinocyanurate of potash gives a precipitate, which after a little time becomes crystalline. Chlorides of gold and platinum, ferro and ferridcyanides of potash, sulphocyanide of potash, and picric acid, all give coloured precipitates. Phosphomolybdic acid, in a strong acid solution, gives a yellowish precipitate, which dissolves in an aqueous solution of ammonia with production of a blue colour.

XV.—LABURNUM.

§ 103. The laburnum tree, *Cytisus laburnum*, so common in shrubberies, is intensely poisonous. The flowers, bark, wood, seeds, and the root have all caused very serious symptoms.* The only active principle hitherto discovered is an alkaloid termed *Cytisin*, which may be extracted from the plant by water acidulated with sulphuric acid, neutralisation with lime, subsequent treatment of the filtrate with acetate of lead, and precipitation by tannic acid. To obtain the alkaloid pure, it is finally crystallised as a nitrate.

§ 104. *Cytisin*, $C_{20}H_{27}N_3O$, is in white radiating crystals, of a bitter, weakly caustic taste, and without odour. It has a strong alkaline reaction, is soluble in every proportion in water, and is also very soluble in spirit. It scarcely dissolves in anhydrous ether, chloroform, benzole, and bisulphide of carbon. It may be sublimed at 154·5°C. in hydrogen, in the form of very long needles and small leaflets; at higher temperatures it melts to a yellow oily fluid, again becoming crystalline on cooling. Cytisin is one of the strongest bases existing in plants; it precipitates the earths and oxides of the heavy metals from solutions of the chlorides, and even in the cold expels ammonia from its combinations.

The nitrate of cytisin ($C_{20}H_{27}N_3O2NHO_3 + 2H_2O$) forms large, thick, transparent monoclinic prisms, losing the water of crystallisation at 100° to 110°, and becoming opaque; it has an acid reaction. It is insoluble in ether, and almost so in absolute alcohol; but soluble in water and weak spirit. The rest of the salts are easily decomposed. A hydrochlorate ($C_{20}H_{27}N_3O4HCl + 3H_2O$), a platinum salt of an orange-yellow colour ($C_{20}H_{27}N_3O2HCl, 2PtCl_2$), a gold salt, at first yellow and flocculent, but later changing into needles ($C_{20}H_{27}N_3O2HCl,2AuCl_3$), a mercury salt ($C_{20}H_{27}N_3O4HgCl$), and many others can be obtained.

Concentrated sulphuric acid dissolves cytisin without colour; if to the solution is added a drop of nitric acid, it becomes orange yellow, and on addition of a crystal of potassic bichromate, first yellow, then dirty brown, and lastly green. Concentrated nitric acid dissolves the base in the cold without colour, but on warming it becomes orange-yellow. Picric, tannic, and phosphomolybdic

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* The symptoms induced by all parts of the plant, save the root, are those of an irritant poison. On the other hand (in a case lately detailed by Dr. Vallance, *Brit. Med. Journ.*) fifty-eight boys in an industrial school, who had chewed the root of an old laburnum tree, all showed narcotic symptoms, with unequally dilated pupils; hence we may infer the existence of a different substance in the root.

acids, potass. mercuric and potass. cadmium iodides, and iodine with iodide of potash, all give precipitates. The carbonates of the alkalies, the caustic alkalies, and chlorine water, with chromate of potash, give no precipitate.*

Fatal Dose.—1 to 3 centigrammes (·15 to ·46 grain) act fatally in dogs and cats.† Persian insect powder is said to be prepared from laburnum.

XVI. OXALIC ACID, BINOXALATE OF POTASH, &c.

§ 105. Oxalic acid and binoxalate of potash, from their extensive use in the arts and their cheapness,‡ frequently come under the notice of the analyst as poisons.

Oxalic Acid, $H_2C_2O_42H_2O$ (90 + 36); specific gravity, 1·64; (anhydrous, $C_2H_2O_4$), occurs in commerce in prismatic crystals, very similar to, and liable to be mistaken for, either magnesic or zincic sulphates. The crystals are intensely acid, easily soluble in water (one part requiring at 14·5°C. 10·46 parts of water), soluble also in 2½ parts of cold, and readily in boiling alcohol.

An aqueous solution, if kept at 100°C., loses acid; further, the subliming temperature is below 100°C.; consequently, all heating or evaporating operations must not be allowed to exceed 98°C., or there will be some loss. At 100°C. the sublimation is very slow, but rapid and complete at 150°C., especially if aided by a current of air. The best way to obtain the anhydride pure for analytical purposes is to put a sufficient quantity of the acid in a strong flask, clamp it (by means of a caoutchouc cork, &c.) to a Sprengel pump, and sublime in vacuo; in this way a sufficient quantity may be rapidly sublimed at 100° to 110°C.

The effect of heat is first to drive off water, then, if continued up to about 190°C., there is decomposition into carbonic oxide, dioxide, water, and formic acid, the two reactions occurring simultaneously:—

$$C_2H_2O_4 = CO_2 + CO + H_2O$$
$$C_2H_2O_4 = CO_2 + CH_2O_2.$$

Heated with oil of vitriol to 110°C., the following decomposition takes place:—

$$H_2C_2O_4 = H_2O + CO_2 + CO.$$

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* Husemann, Die Pflanzenstoffe, p. 67.

† W. Marmé, *Jahresber. d. Natur. Gesell.* Graub (1869), xiv. 219.

‡ The present price of oxalic acid is 5d. per lb.

Oxalic acid decomposes fluor spar, the phosphates of iron, silver, zinc, copper, and the arseniates of iron, silver, and copper. It may be used to separate the sulphides of iron and manganese from the sulphides of zinc, cadmium, uranium, cobalt, mercury, and copper—dissolving the former, not the latter. Many minerals and other substances are also attacked by this acid.

If a solution of oxalic acid in water is boiled with ammonio or sodio terchloride of gold (avoiding direct exposure to light) the gold is precipitated—

$$2AuCl_3 + 3H_2C_2O_4 = 6CO_2 + 6HCl + Au_2.$$

When black oxide of manganese (free from carbonate) is mixed with an oxalate, and treated with dilute sulphuric acid, the oxalic acid is decomposed, and carbon dioxide evolved—

$$MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2H_2O + 2CO_2.$$

A similar reaction occurs with permanganate of potash.

If to a solution of oxalic acid (which may be neutralised by an alkali, or may contain free acetic acid), a solution of acetate of lime be added, oxalate of lime is thrown down. This salt, important in an analytical point of view, it will be well to describe.

§ 106. *Oxalate of Lime* ($CaC_2O_4H_2O$), one part = 1·0678 crystallised oxalic acid, or ·7457 of C_2O_4. This is the salt which the analyst obtains for the quantitative estimation of lime or oxalic acid ; it is not identical with that occurring in the vegetable kingdom, the latter containing $3H_2O$. Oxalate of lime cannot be precipitated for quantitative purposes from solutions containing chromium, aluminium, or ferric iron, since somewhat soluble salts are formed. It dissolves in solutions of magnesium and manganese,* and citrate of soda, and is also decomposed by boiling with solutions of copper, silver, lead, cadmium, zinc, nickel, cobalt, strontium, or barium. It is insoluble in solutions of chlorides of the alkalies and alkaline earths, and in water, in alkaline solutions, or in acetic acid ; and is soluble in mineral acid only when the acid is strong and in considerable excess. It is unalterable in the air, and at 100°C. When carefully and slowly ignited it may be wholly converted into carbonate of lime ; if the heat is not properly managed (that is, if excessive), caustic lime may be formed in greater or smaller quantity.

§ 107. *Use in the Arts.*—Oxalic acid is chiefly used by dyers and calico-printers, but also by curriers and harness-makers for cleaning leather, by marble masons for removing iron stains, by

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* But it is reprecipitated unaltered by excess of alkaline oxalate.

workers in straw for bleaching; and it is applied to variou household purposes, such as the whitening of boards, the removing of iron mould from linen, &c. The binoxalate of potash i used for scouring metals, and for removing ink stains from linen

§ 108. *Fatal Dose.*—The smallest dose of oxalic acid known t have destroyed life is, according to Dr. Taylor, 60 grains (3·8 grms.); but recovery has taken place, on prompt administration o remedies, after eight times this quantity had been swallowed.

With regard to oxalate of soda, or binoxalate of potash, hal an ounce (14·2 grms.) has been taken without fatal result, although the symptoms were very serious; and it may be held that about that quantity would usually cause death. Oxalic acid is not used in medicine.

§ 109. *Binoxalate of Potash*, KHC_2O_4 (H_2O), has been mistaken for cream of tartar, and in this way caused death. When heated in platinum foil, it leaves carbonate of potash, which may be recognised by the usual tests. On solution it is acid in reaction, and it gives a precipitate of oxalate of lime with a solution of the sulphate or acetate of lime; it is insoluble in alcohol. The above reactions are quite sufficient to distinguish it from oxalic acid.

§ 110. *Oxalic Acid in the Vegetable and Animal Kingdoms.*—Oxalic acid is very widely distributed, both in the free state and in combination with bases, through the vegetable kingdom. In combination with potash it is found in the *Geranium acetosum*, L., *Spinacia oleraceæ*, L., *Phytolacca decandra*, L., *Rheum palmatum*, L., *Rumex acetos*, *Atropa belladonna*, and several others; in combination with soda, in different species of *Salsola* and *Salicornia;* and in combination with lime, in most plants, especially in the roots and bark. Many lichens contain half their weight of oxalate of lime; and oxalic acid, either free or combined (according to the observations of Hamlet and Plowright*), is present in all mature, non-microscopic fungi. Oxalate of lime may be frequently seen by the aid of the microscope in the cells of plants. According to Schmidt,† this crystallisation only takes place in the fully mature cell, for in actively-growing cells the oxalate of lime is entirely dissolved by the albumen of the plant.

In the animal kingdom, oxalic acid has only been found combined with lime; the allontoic liquor of the cow, the urine of man, swine, horses, and cats,‡ may be mentioned as fluids in

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* *Chem. News*, vol. xxxvj. 93.

† *Ann. Chem. Pharm.*, lxi. 297.

‡ Oxalic acid is said to be always present in the intestinal contents of the caterpillar.

which oxalate of lime is nearly always present. With regard to human urine, the presence or absence of oxalate of lime greatly depends upon the diet, and also upon the individual, some persons almost invariably secreting oxalates, whatever the food may be.

§ 111. *Oxalic Acid as a Poison.*—Oxalic acid destroys life with great rapidity, if given in large doses; the acid oxalate of potash, the oxalate of soda, and, in fact, so far as is known, all soluble oxalates are poisonous. Should the oxalate of soda, a neutral, tasteless salt, be given for a long time in moderate doses, it would probably cause death, and there would be great difficulty in obtaining satisfactory evidence by chemical means.*

In all chemico-legal investigations the question will be asked of the analyst, whether or not the oxalic acid found could be naturally introduced in articles of food, such as sorrel, rhubarb, vegetables, &c. The answer to this will partly depend upon the quantity found, and the history of the particular case, whilst the diagnosis of poisoning by oxalic acid, or an oxalate, must turn in great part upon the pathological changes after death, and the symptoms during life. As a rule, it will be found that—no matter how corroded the state of the stomach—if the gullet should be healthy, oxalic acid will not be present, for, in nearly all recorded cases, the mucous membrane of the gullet has been more or less extensively destroyed or changed. The same remark applies to salt of sorrel (binoxalate of potash). On the other hand, when the fatal dose has been small, or a succession of small doses has brought about a fatal result, the gullet may be perfectly normal, and this valuable indication thus wanting. It will then be necessary to examine the blood by the spectroscope; for in Eulenberg's experiments the blood of the animals poisoned invariably gave the spectrum of *acid hematin.*

The urine, if possible, should also be examined for oxalates, since it is certain that if oxalic acid (free or in combination) is taken into the system, the main, perhaps the only, channel of excretion is through the kidneys.

The external application of oxalic acid does not appear to cause illness; workmen engaged in trades requiring the constant

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* Mohr says very truly—"Oxalic acid is the more dangerous, because its neutral alkali salts (especially oxalate of soda) are colourless and tasteless; in a mixture of fluids the whiteness of the latter would disappear, and it would gradually dissolve. The action of small doses is cumulative. The skilled poisoners, Bocarmé, Dr. Palmer, la Pommerais, Dr. Trumpi, gave themselves great trouble to render difficult the discovery of poison by the expert, in using nicotine, strychnine, and digitalis, whilst oxalate of soda, a poison at once more difficult to discover and easier to administer, was at hand."—"Chemische Toxicologie," p. 107.

use of the acid often have the nails white, opaque, and brittl but no direct injury to health is on record.

Eulenberg has experimented by pigeons on the action of oxa acid when breathed. In one of his experiments, ·75 grm. of t acid was volatilised into a glass shade, in which a pigeon h been placed; after this had been done five times in two minut there was uneasiness, shaking of the head, and cough, wi increased mucous secretion of the nasal membrane. On cc tinuing the transmission of the vapour, after eight minutes the was again restlessness, shaking of the head, and cough; aft eleven minutes the bird fell, and was convulsed. On disco tinuing the sublimation it got up, and moved freely, but show respiratory irritation. On the second day after the experimer it was observed that the bird's note was hoarse, on the four day there was slowness of the heart's action and refusal of foc and on the sixth day the bird was found dead. Examinati after death showed slight injection of the cerebral membrane the cellular tissue in the neighbourhood of the trachea contain in certain places extravasations of blood, varying from the si of a pea to that of a penny; the mucous membrane of the laryr and trachea was swollen and covered with a thick croupo layer; the lungs were partially hepatised, and the pleu thickened; the crop as well as the true intestines still containe some food.*

§ 112. *Separation from Organic Matters*, &c.—When oxal acid has been taken into the stomach, it will invariably be foun partly in combination with lime, soda, ammonia, &c., and partl free; or if such antidotes as chalk have been administered, it ma be wholly combined. Vomiting is nearly always present, an valuable evidence of oxalic acid may be obtained from stains o sheets, carpets, &c. In a recent case of probably suicidal poisor ing, the writer found no oxalic acid in the contents of th stomach, but some was detected in the copious vomit which ha stained the bedclothes. The urine also contained a great exces of oxalate of lime—a circumstance of little value taken by itsel but confirmatory with other evidence. If a liquid is strongl acid, oxalic acid may be separated by dialysis from organi matters, and the clear fluid thus obtained precipitated by su phate of lime, the oxalate of lime being identified by its micrc scopic form and its other characters.†

The usual general method for the separation of oxalic aci from organic substances or mixtures is the following:—Extrac

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* Eulenberg, "Gewerbe Hygiène," p. 423.

† Occasionally the solubility of oxalic acid in alcohol may be take advantage of.

with boiling water, filter (which in some cases must be difficult or even impossible), and then precipitate with acetate of lead. The lead precipitate may contain, besides oxalate of lead, phosphate, chloride, sulphate, and various organic substances and acids. This is to be decomposed by sulphuretted hydrogen, and in filtering off the sulphide of lead, oxalic acid is to be tested for in the filtrate. This process, however, can only be adopted with advantage in a few cases, and is by no means to be recommended as generally applicable. The best general method, and one which ensures the separation of oxalic acid, whether present as a free acid, as an alkaline, or a calcic oxalate, is perhaps the following: —The substance or fluid under examination is digested with hydrochloric acid until a fluid capable of filtration is obtained; the free acid is neutralised by ammonia in very slight excess, and permitted to deposit, and the fluid is then carefully decanted, and the deposit thrown on a filter. The filtrate is added to the decanted fluid, and precipitated with a slight excess of acetate of lime, this precipitate, like the first, being collected on a filter. The first precipitate contains all the oxalic acid which was in combination with lime; the second, all that which was in the free condition. Both precipitates should be washed with acetic acid.

The next step is to identify the precipitate, which is supposed to be oxalate of lime. The precipitate is washed into a beaker, and dissolved with the aid of heat by adding, drop by drop, pure hydrochloric acid; it is then reprecipitated by ammonia, and allowed to subside completely, which may take some time. The supernatant fluid is decanted, and the precipitate washed by subsidence; it is lastly dried over the water-bath in a tared porcelain dish, and its weight taken. The substance is then identified by testing the dried powder as follows:—

(*a*.) It is whitish in colour, and on ignition in a platinum dish leaves a grey carbonate of lime. All other organic salts of lime—viz., citrate, tartrate, &c.—on ignition become coal-black.

(*b*.) A portion suspended in water, to which is added some sulphuric acid, destroys the colour of permanganate of potash—

$$\begin{aligned}&2KMnO_4 + 5CaH_2O_4 + 8H_2SO_4\\ &= K_2SO_4 + 2MnSO_4 + 5CaSO_4 + 8H_2O\end{aligned}$$

reaction by which, as is well known, oxalic acid or an oxalate may e conveniently titrated. This reaction is so peculiar to oxalic cid, that there is no substance with which it can be confounded. t is true that uric acid in an acid solution equally decolorises ermanganate, but it does so in a different way; the reaction between oxalic acid and permanganate being at first slow, a afterwards rapid, while the reaction with uric acid is just t reverse—at first quick, and towards the end of the proc extremely slow.

(*c.*) A portion placed in a test-tube, and warmed with c centrated sulphuric acid, develops on warming carbonic ox and carbonic dioxide; the presence of the latter is easily sho by adapting a cork and bent tube to the test-tube, and leadi the evolved gases through baryta water.

§ 113. *Oxalate of Lime in the Urine.*—This well-known urin sediment occurs chiefly as octahedra, but hour-glass, contracted dumb-bell-like bodies, compound octahedra, and small, flatten bright discs, not unlike blood discs, are frequently seen. may be usually identified under the field of the microscope its insolubility in acetic acid, whilst the ammonio mag. phospha as well as the carbonate of lime, are both soluble in that ac From urates it is distinguished by its insolubility in warm wat A chemical method of separation is as follows:—The deposit freed by subsidence as much as possible from urine, washed wi hot water, and then dissolved in hydrochloric acid and filtere to the filtrate ammonia is added in excess. The precipitate m contain phosphates of iron, magnesia, lime, and oxalate of lim On treatment of the precipitate by acetic acid, the phosphates the alkaline earths (if present) dissolve, the insoluble porti will be either phosphate of iron, or oxalate of lime, or bo On igniting the residue in a platinum dish, any oxalate will changed to carbonate, and the carbonate of lime may be titrat with d. n. HCl acid and cochineal solution, and from the data th obtained the oxalate estimated. The iron can be tested qua tatively in the acid solution by ferrocyanide of potash, or can be determined by the ordinary methods. If the qualitati detection of oxalate of lime in the deposit is alone required, it quite sufficient evidence should the portion insoluble in acet acid, on ignition in a platinum dish, give a residue effervesci on the addition of an acid.

§ 114. *Estimation of Oxalic Acid.*—Oxalic acid is estimated the free state by direct weighing, or by titration either wi alkali or by potassic permanganate, the latter being standardis by oxalic acid. If (as is commonly the case) oxalic acid is pr cipitated as oxalate of lime, the oxalate may be—

(*a.*) Dried at 100°C. and weighed directly, having the pr perties already described.

(*b.*) Titrated with dilute sulphuric acid and permanganate.

(*c.*) Ignited, and the resulting carbonate of lime weighed; dissolved in standard acid and titrated back—one part of calc rbonate corresponds to 1·26 part of crystallised oxalic acid, or 8 part of C_2O_4; similarly, 1 cc. of standard acid equals 50 of lcic carbonate (or 63 of crystallised oxalic acid).

(*d.*) The oxalate may be dissolved in the smallest possible mount of hydrochloric acid, and boiled with ammonio chloride f gold, avoiding exposure to light; every part of gold precipitated orresponds to ·957 part of crystallised oxalic acid, or ·4456 art of oxalic acid.

(*e.*) The oxalate may be placed in Geissler's carbonic acid pparatus, with peroxide of manganese and diluted sulphuric cid. The weight of the gas which at the end of the operation as escaped, will have a definite relation to that of the oxalate, nd if multiplied by 1·4318 will give the amount of crystallised xalic acid.

PART IV.

ANIMAL POISONS: CANTHARIDES — PUTRI ANIMAL MATTERS — COBRA VENOM.

I.—CANTHARIDES.

§ 115. Commercial cantharides is either the dried entire, the dried and powdered blister beetle, or Spanish fly (*Cantha vesicatoria*). The most common appearance is that of a greyi brown powder, containing shining green particles, from wh cantharidine is readily extracted by exhausting with chlorofor driving off the chloroform by distillation or evaporation, a subsequently treating the extract with bisulphide of carb which dissolves the fatty matters only. Finally, the cantha dine may be recrystallised from chloroform; the yield be about 4 per cent.

§ 116. *Cantharidine* ($C_5H_{12}O_2$) has two crystalline forms—(Right-angled four-sided columns with four surfaces, each surf being beset with needles; and, (2.) flat tables. 100 parts alcohol (99 per cent.) dissolve at 18°C. 0·125 part; 100 bisulphide of carbon, at the same temperature, 0·06 pa ether, ·11 part; chloroform, 1·2 part; and benzine, ·2 pa it is almost completely insoluble in water. Cantharidine c be completely sublimed, if placed in the subliming cell (descri at p. 284), floating on mercury; a scanty sublimate of cryst may be obtained at so low a temperature as 82·5°C.; at 85° and above, the sublimation is rapid. If the cantharidine suddenly heated it melts, but this is not the case if the tempe ture is raised gradually. Chromate of potash with sulphu acid decomposes cantharidine with the production of the gre oxide of chromium. An alkaline solution of permanganate potash, iodic acid, and sodium amalgam, are all without influe on an alcoholic solution of cantharidine.

§ 117. *Pharmaceutical Preparations of Cantharides.*—The P. preparations of cantharides are—*Acetum cantharides,* or vine of cantharides, containing about ·04 per cent. of cantharidine ;

Tincture of cantharides, containing about ·005 per cent. of antharidine;

A solution of cantharides for blistering purposes, *Liquor epis- asticus*, a strong solution of the active principle in ether and cetic acid, containing about ·16 per cent. of cantharidine.

There are also—An ointment; a blistering paper, *Charta epis- atica;* a blistering plaster, *Emplastrum cantharides;* and a warm laster, *Emplastrum calefaciens.*

§ 118. *Fatal Dose.*—It is difficult to state the fatal dose of antharidine, the unassayed powder or tincture having mostly een taken. A young woman died from 1·62 grm. (25 grains) of he powder, which is perhaps equivalent to 6·4 mgrms. (1 grain) f cantharidine, whilst the smallest dose of the tincture known o have been fatal is (according to Taylor) an ounce. This ould be generally equivalent to 15 mgrms. (·24 grain). Hence he fatal dose of cantharidine may be approximately stated as om 6 mgrms. upwards. But, on the other hand, recovery has ken place from very large doses.

§ 119. *Tests for Cantharidine, and its Detection in the Tissues, c.*—The tests for cantharidine are—(1.) Its form, (2.) its action the subliming cell, and, (3.) its power of raising a blister.

The most convenient method of testing its vesicating proper- es, is to allow a chloroformic solution of the substance supposed be cantharidine to evaporate to dryness, to add to this a drop olive oil (or almond oil), and to take the drop up on the nallest possible quantity of cotton wool, and apply the wool to e inside of the arm, covering it with good oilskin, and strap- ng the whole on by the aid of sticking-plaster. In about an our or more the effect is examined. The thin skin of the lips far more easily blistered than that of the arm, but the applica- on there is inconvenient.

Dragendorff has ascertained that cantharidine is not present the contents of a blister raised by a cantharides plaster, hough it has been found in the urine of a person treated by e; and Pettenkoffer has also discovered cantharidine in the ood of a boy to whose spine a blister had been applied.

The great insolubility of cantharidine in water has led to rious hypotheses as to its absorption into the system. Dra- ndorff considers it as the anhydride of an acid, which is erably easily dissolved by potash, soda, and ammonia solution, d is also taken up in small proportion by sulphuric, phosphoric, d lactic acids. The resulting compounds quickly diffuse them- ves through animal membranes. Even the salts, with lime, gnesia, alumina, and the heavy metals, are not quite insoluble. solution of salt with cantharidine, put in a dialysing apparatus, separates in twenty-four hours enough cantharidine to rais blister.

Cantharidine has actually been discovered in the heart, br muscles, contents of the stomach, intestines, and fæces (as w as in the blood and urine) of animals poisoned by the substan A urine containing cantharidine is alkaline and albumino Cantharidine, although readily decomposed by chemical agen is so permanent in the body that it has been detected in corpse of a cat eighty-four days after death.

In any forensic case, the defence will not improbably be up that some animal (*e.g.*, a fowl poisoned by cantharides) been eaten and caused the toxic symptoms, for cantharides is interesting example of a substance which, for certain anim (such as rabbits, dogs, cats, and ducks), is a strong pois whilst in others (*e.g.*, hedgehogs, fowls, turkeys, and fro although absorbed and excreted, it appears inert. Experim has shown that a cat may be readily poisoned by a fowl satura with cantharides; and in Algeria the military surgeons m with cystitis among the soldiers, caused by eating frogs in months of May and June, the frogs living in these months alm exclusively on a species of cantharides.

Dragendorff recommends the following process:—The fin pulped substance is boiled in a porcelain dish with potash- (1 part of potash and 12 to 18 of water) until the fluid is o uniform consistence. The fluid, after cooling, is (if necessa diluted with an equal bulk of water, for it must not be too thic then shaken with chloroform in order to remove impurities; a after separation of the chloroform, strongly acidified with s phuric acid, and mixed with about four times its volume alcohol of 90 to 95 per cent. The mixture is kept for some ti at a boiling temperature, filtered hot, and the alcohol distill from the filtrate. The watery fluid is now again treated wi chloroform, as above described. The chloroform extract is wash with water, the residue taken up on some hot almond oil, and blistering properties investigated. The mass, heated with pota in the above way, can also be submitted to dialysis, the dif sate supersaturated with sulphuric acid, and shaken up wi chloroform.

In order to test further for cantharidine, it can be dissolved the least possible potash or soda-lye. The solution, on evapo tion in the water-bath, leaves crystals of a salt not easily solu in alcohol, and the watery solution of which gives, with chlori of calcium and baryta, a white precipitate; with sulphate copper and sulphate of protoxide of nickel, a green; with coba ous sulphate, a red; with sugar of lead, mercury chloride, a argentic nitrate, a white crystalline precipitate. With palladium chloride there occurs a yellow, hair-like crystalline precipitate; later crystals are isomorphous with nickel and copper salts.

If the tincture of cantharides has been used in considerable quantity, the urine may be examined; in such a case there will collect on the surface drops of a green oil, which may be extracted by petroleum ether; this oil is not blister-raising. Cantharidine in powder may, of course, be detected by its appearance.

To the question whether the method proposed would extract any other blister-producing substance, the answer is negative, since ethereal oil of mustard would be decomposed, and the active constituents of the *Euphorbias* do not withstand the treatment with KHO. Oils of anemone and anemonin are dissolved by KHO, and again separated out of their solutions, but their blistering property is destroyed. They are volatile, and found in anemone and some of the *Ranunculaceæ.* In the *Aqua pulsatilla* there is an oil of anemone, which may be obtained by shaking with ether; but this oil is not permanent, and if the *Aqua pulsatilla* stand for a little time, it splits up into anemonic acid and anemonin, and then cannot be re-obtained. A blistering substance, obtained from the *Anacardia orientalia* and the fruit of the *Anacardium occidentale* and *Semecarpus anacardium*, is not quite destroyed by a short action with potash, but is by one of long duration; this substance, however, cannot be confused with cantharidine, for it is oily, yellow, easily soluble in alcohol and ether, and differs in other respects.

II.—PUTRID ANIMAL AND OTHER MATTERS.

§ 120. Cases of poisoning from time to time occur in which he active agent producing the symptoms is highly obscure—*e.g.*, he death, recorded by Crzaut,[*] of thirty-two persons from eating he putrid brains of a walrus, the now numerous instances of ausage-poisoning, and the curious case which recently occurred t Barnsley from eating a bread pudding.[†] In a few instances t is possible that some well-known poison may have been present, ut escaped detection through error in the process employed;

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[*] "History of Greenland."

[†] Eight persons partook of a bread pudding, two of whom died with arcotico-irritant symptoms of poisoning, and all were ill. Mr. Allen, after prolonged and careful examination of the remnant of the pudding and her matters, was unable to detect any known poison; although he appears have isolated some substance allied to Ergot. The case is detailed in the *nalyst*, Nov., 1878.

for when there is no clue, it is not always a simple matter frame a method so entirely satisfactory that it shall infallib detect every probable poison ; in others it would seem a feasib explanation, that an unknown poison was developed during tl process of putrefaction.

We know now that at least three substances giving the rea tions of alkaloids have been separated from decomposing anim matter—(1.) A non-crystalline alkaloid, discovered by Selmi which yields a violet-red colour with sulphuric acid; (2.) a simil (perhaps identical) substance, separated by Schwanery[†] fro decomposing human livers, spleens, &c., by the Stas-Otto proce the ultimate extraction being by ether acting on an *alkali* solution; and (3.) Rörsch and Fassbender[‡] describe an analogo product from livers, spleens, and kidneys, but obtained from a *acid* liquid.

In a third class of cases, again, it is possible that the food w really the bearer of a zymotic poison, which would, of cours escape detection by any chemical or other means of investigatio known. Thus in India, in 1871, a dinner of rice distinctl propagated cholera to seventy-three cases.[§] Recent investig tions also on summer diarrhœa[||] in this country have shown i extremely contagious character ; and one can well imagine th if, from uncleanliness or other cause, any article of food shou be contaminated by specific excreta, a most complete imitati of irritant-poisoning would be produced.

III.—THE POISON OF THE COBRA.

§ 121. The poison excreted from the salivary glands of the co di capello is the most deadly animal fluid known. When fir ejected, it is an amber-coloured, rather syrupy, frothy liquid, specific gravity 1·046, and of feeble acid reaction ; it dries rapidl on exposure to air to a yellow film, which readily breaks up int brilliant yellow granules, closely imitating crystals. The yello powder is very acrid and pungent to the nostrils, and excites painful (though transitory) inflammation, if applied to the muco

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[*] F. Selmi, *Deut. Chem. Ges. Ber.*, vi. 142.

[†] W. Schwanery, *ib.*, vii., 1332 ; *Journ. Chem. Soc.*, vol. xiii., 187 p. 293.

[‡] Börsch and Fassbender, *Deut. Chem. Ges. Bericht.*, vii. 1064.

[§] See the author's "Dict. of Hygiène," Art. Cholera, p. 131.

[||] See a Paper by Dr. Wm. Johnstone, on "Summer Diarrhœa," *Lance* Sept. 21 and 28, 1878. Dr. Johnstone, in his prolonged microscopical inve tigation of the excreta, acquired the disease himself no less than five times.

membrane of the eye; the taste is bitter, and it raises little blisters on the tongue. It is perfectly stable, and preserves its activity for an indefinite time. Some at present in the writer's possession, although two years old, is as active as when first obtained from the snake. The dried poison as described is perfectly soluble in water, and if the water is added in proper proportions, the original fluid is without doubt reproduced, the solution usually depositing a sediment of epithelial debris, and often containing little white shreds.

The poison has been examined by several chemists, but until lately with a negative result. The writer was, however, fortunate enough, after a prolonged investigation, to isolate a crystalline principle, which appears to be the sole active ingredient; the yellow granules were dissolved in water, the albumen which the venom so copiously contains coagulated by alcohol, and separated by filtration; the alcohol was then driven off at a gentle heat, the liquid concentrated to a small bulk, and precipitated with basic acetate of lead. The precipitate was separated, washed, and decomposed in the usual way by SH_2, and on removing the ead sulphide, crystals having a marked acid reaction and toxic properties were obtained. To this substance the name of *cobric acid* has been provisionally applied.

Further details will be found in the writer's original communiation in the *Analyst*, Feb. 28, 1877.

PART V.

INORGANIC POISONS:

(I.) PRECIPITATED FROM A HYDROCHLORIC ACID SOLUTION BY HYDRIC SULPHIDE, PRECIPITAT YELLOW OR ORANGE:

ARSENIC—ANTIMONY—CADMIUM.

I.—ARSENIC.

§ 122. Arsenic causes so many deaths both in men and cattle, th it comes under the notice of the chemist more frequently than an other poison. It will therefore be necessary to notice it at som length.

Metallic Arsenic, at. wt. 75, specific gravity of solid 5·62 to 5·9 sublimes without fusion in small quantities at 110°C. (230 F.) *Gu* It occurs in commerce in whitish-grey, somewhat brittle, crysta line masses, and is obtained by subjecting arsenical pyrites t sublimation in earthen retorts, the arsenic being deposited i suitable receivers in sheet iron. In the course of analysis, ho ever, it is usually seen as a film on copper, a stain on porcelai or a metallic ring in the interior of glass tubes: the distincti marks of these stains are described p. 385. Metallic arseni whether as a solid* or as a vapour, is poisonous.†

§ 123. *Arsenious Anhydride—Arsenious Acid—White Arsenic— Arsenic*, $As_2O_3 = 198$; specific gravity of vapour, 13·85; specif gravity of opaque variety, 3·699; specific gravity of transpare variety, 3·7385. Composition in 100 parts, As 75·75, O 24·2 therefore one part of arsenic equals 1·32 of As_2O_3.

In analysis it is obtained in brilliant octahedral crystals as sublimate on discs of glass, or within tubes, the result of heatin a film of metallic arsenic with access of air. It is obtained i commerce on a very large scale from the roasting of arsenic

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* Orfila.

† Eulenberg, "Handbuch der Gewerbe Hygiène."

pyrites. As thus derived, it is usually in the form of a white cake, the arsenious acid existing in two forms—an amorphous and a crystalline—the cake being generally opaque externally, whilst in the centre it is transparent. According to Kruger, this change from the crystalline to the amorphous condition is dependent upon the absorption of moisture, no alteration taking place in dry air. Both varieties of arsenious anhydride are acid to test paper.

The solubility of arsenious acid is often a question involving chemical legal matters of great moment. Unfortunately, however, no precisely definite statement can be made on this point, the reason being that the two varieties of arsenic occur in very different proportions in different samples. Both the amorphous and crystalline varieties having very unequal solubilities, every experimenter in succession has given a different series of figures, the only agreement amid the general discrepancy being that arsenic is very sparingly soluble in water.

The statement of Taylor may, however, be accepted as very near the truth—viz., that an ounce of cold water dissolves from half a grain to a grain. According to M. L. A. Buchner,[*] one part of crystalline arsenious acid dissolves after twenty-four hours digestion in 355 parts of water at 15°C.; and the amorphous, under the same condition, in 108 of water. A boiling solution of the rystalline acid, left to stand for twenty-four hours, retains one art of acid in 46 of water; a similar solution of the amorphous etains one of arsenic in 30 parts of water—*i.e.*, 100 parts of water issolve from 104 to 208 parts of As_2O_3.

Boiling water poured on the powdered substance retains in ooling a grain and a quarter to the ounce; in other words, 100 arts of water retain ·26. Lastly, arsenious acid boiled in water r an hour is dissolved in the proportion of 12 grains to the unce—*i.e.*, 100 parts of water retain 2·5.

§ 124. *Arseniuretted Hydrogen Arsine*, H_3As.—Mol. weight, 8; vol. weight, 39; specific gravity, 2·702; weight of a litre, 4944; percentage composition, 95·69 As, 4·31 H; volumetric mposition, 2 vol. H_3As = half vol. As + 3 vol. H. A colourss inflammable gas, of a fœtid alliaceous odour, coercible into a npid colourless liquid at a temperature of from 30°C. to 40°C. e products of the combustion of arseniuretted hydrogen are ter and arsenious acid; thus, $2H_3As + 6O = 3H_2O + As_2O_3$. supplied with air in insufficient quantity, if the flame itself be led by (for example) a cold porcelain plate, or if the gas pass rough a tube, any portion of which is heated to redness, the s is decomposed and the metal separated. Such a decomposi-

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[*] *Bull. de la Société Chem. de Paris*, t. xx., 10, 1873.

tion may be compared to the deposit of carbon from ordina flames, when made to play upon a cooled surface. The g burns with a blue-white flame, which is very characteristic, a was first observed by Wackenroder. It cannot, however, properly seen by using the ordinary apparatus of Marsh, the flame is always coloured from the glass; but if the gas made to stream through a platinum jet, and then ignited, t characters mentioned are very noteworthy.

Oxygen or air, and arseniuretted hydrogen, make an explosi mixture. Chlorine decomposes the gas with great energy, co bining with the hydrogen, and setting free arsenic as a bro cloud; any excess of chlorine combines with the arsenic as chloride. Sulphur, submitted to arseniuretted hydrogen, for sulphuretted hydrogen, whilst first arsenic and then sulphide arsenic separate. Phosphorus acts in a similar way. Arse uretted and sulphuretted hydrogen may be evolved at ordina temperatures without decomposition; at the boiling point mercury (350°C.) they are decomposed, sulphide of arsenic a hydrogen being formed; thus, $3H_2S + 2AsH_3 = As_2S_3 + 6H_2$, reaction which is of some importance from a practical point of vie Many metals have also the property of decomposing the gas high temperatures, and setting hydrogen free. Metallic oxid again, in like manner, combine with arsenic, and set water fr *e.g.*, $3CuO + 2H_3As = Cu_3As_2 + 3H_2O$.

Arseniuretted hydrogen acts on solutions of the noble met like phosphuretted hydrogen, precipitating the noble metal a setting free arsenious acid; for example, nitrate of silver decomposed thus—

$$12AgNO_3 + 2H_3As + 3H_2OAs_2O_3 + 12HNO_3 + 12Ag.$$

This reaction admits of valuable practical application to estimation of arsenic; for the precipitated silver is perfec arsenic-free; the excess of nitrate of silver is easily got rid of a chloride of sodium solution, and the absorption and decomp tion of the gas are complete.

In cases of poisoning by arseniuretted hydrogen, the blo when examined by the spectroscope (a process the analyst sho never omit where it is possible), is of a peculiar inky colour, a the bands between D and C are melted together, and h almost vanished. Such blood, exposed to oxygen, rema unaltered.

§ 125. *Arseniuretted Hydrogen in the Arts,* &c.—In the bro ing of brass, in the desilverising of lead by zinc, and subsequ treatment of the silver zinc with hydrochloric acid, in the tinning of sheet iron, and similar processes, either from the use of acids containing arsenic as an impurity, or from the application of arsenic itself, arseniuretted hydrogen is evolved. Of late years, moreover, this gas has been recognised as a source of disease, by being emanated from wall papers which had been strongly impregnated with arsenic, the gas resulting from the contact of arsenious acid with organic matter.*

The researches of Fleck, ridiculed by L. Krahmer,† are confirmed by Sonnenschein,‡ who, by the aid of an aspirator, drew the air of a room first through water, and then through a red-hot glass tube, and obtained a distinct arsenical ring. They are further attested by Hamberg,§ who, in a similar manner, caused the air of a room, the wall-paper of which was arsenical, to pass through a solution of nitrate of silver, and obtained in the solution arsenious acid, together with some sulphide of silver ;|| very few solid particles being detected. That arseniuretted hydrogen is evolved from wall-papers, excites no surprise in those who have ever quantitatively estimated the arsenic in various pigments and papers. The writer analysed a very sober drab-coloured paper a short time ago, and found arsenic equivalent to 2 per cent. of its weight of arsenious acid.

Poisoning from arseniuretted hydrogen¶ has been scarcely described in English works, an omission principally to be attributed to want of material. Two cases are detailed by Dr. Valette in Tardieu's "Etude."** A mistake occurred in a laboratory, by which a solution of arsenic (instead of sulphuric acid) was poured on zinc to develop hydrogen. Of the two sufferers, the one recovered after an illness of about a week or ten days, the other died at the end of twenty-eight days. The main symptoms were yellowness of skin, vomiting, bloody urine, great depression, slight diarrhœa, headache, and in the fatal case a morbilliform eruption. In a case recorded in the *British Medical Journal*, November 4, 1876, there were none of the

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* Fleck, *Zeitschr. für Biologie*, Bd. viii., p. 445.

† "Handbuch der Staats Arzneikunde," ii. 455.

‡ Sonnenschein, "Handbuch der Gerichtlichen Chemie."

§ *Pharm. Journ. Trans.* [3], 81-83.

|| The unpleasant odour often possessed by Schweinfurt green papers ppears to be due to the decomposition of the acetic acid by moisture and ould, with the formation as a principal product of propionic acid.

¶ The discoverer of the gas, Gehlen, died in eight days through inhaling ; in order to discover a flaw in his apparatus, he smelt strongly at the ints.

** Ambroise Tardieu, "Etude medico-légale sur l'empoisonnement," *bserv.*, xxv., p. 449.

usual symptoms of gastric irritation, but loss of memory of recen acts, drowsiness, and giddiness.*

§ 126. *The Sulphides of Arsenic.*—Of the sulphides of arseni two only, realgar and orpiment, are of any practical importanc *Realgar*, $As_2S_2 = 214$; specific gravity, 3·356; composition i 100 parts, As 70·01, S 29·91; average composition of commerci product, As 75, S 25. Realgar is found native in ruby-re crystals, and is also prepared artificially by heating together 9 par of arsenic and 4 of sulphur, or 198 parts of arsenious anhydric with 112 parts of sulphur, $2As_2O_3 + 7S = 2As_2S_2 + 3SO_2$. It insoluble in water and in hydrochloric acid, but is readily di solved by potassic disulphide, by nitric acid, and by aqua regi It is decomposed by caustic potash, leaving undissolved a brow sediment ($As_{12}S$), which contains 96·5 per cent. of arsenic.

§ 127. *Orpiment, or Arsenic Trisulphide.*—$As_2S_3 = 246$; specif gravity, 3·48; composition in 100 parts, As 60·98, S 39·0 found native in crystals, presents itself in the laboratory usual as a brilliant yellow amorphous powder, on passing sulphurett hydrogen through an acid solution of arsenious acid or a arsenite. It is very insoluble in water (about one in a millio *Fresenius*), scarcely soluble in boiling concentrated hydrochlor acid, and insoluble generally in dilute acids. Red fumin nitric acid dissolves it, converting it into arsenic and sulphur acids; ammonia and other alkaline sulphides, the alkalies ther selves, alkaline carbonates, bisulphite of potash, and aqua regi all dissolve it readily. In the arts it is used as King's yello (see p. 378). Tanners also formerly employed a mixture of 9 parts of orpiment and 10 of quicklime, under the name *Rusma*, as a depilatory; but the alkaline sulphides from ga works are replacing this to a great extent.

§ 128. *Haloid Arsenical Compounds.*—*The Chloride of Arsen* $AsCl_3 = 181·5$; specific gravity, liquid, 0°C. 3·205; boiling poin 134°C. (273·2°F.), is a heavy, colourless, oily liquid, which h been used as an escharotic in cancerous affections (principal by quacks). In one process of detecting and estimati arsenic, the properties of this substance are utilised (see p. 39 It is immediately decomposed by water into arsenious and hyd chloric acids.

The Iodide of Arsenic (AsI_3) is used occasionally in sk

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* *See also*—Trost: "Vergiftung durch Arsenwasserstoff bei der tech schen Gewinnung des Silbers," *Vierteljahrsschrift f. Geric Med.*, xviii., Bd. s. 269, 1873.

Chevers.—"Manual of Jurisprudence for India," *Appendix*, p. 833.

Husemann.—*Jahresbericht der Toxicologie*, 1871, p. 522.

Eulenberg.—"Handbuch der Gewerbe Hygiène," p. 286.

diseases, but is of little interest to the analyst; it is commonly seen in the form of brick-red brilliant flakes.

§ 129. *Arsenic in the Arts.*—The metal is used in various alloys; for example, speculum metal is made of tin, copper, and a little arsenic; white copper is an alloy of copper and arsenic; shot is composed of 1000 parts of lead mixed with 3 of arsenic; the common Britannia metal used for tea-pots, spoons, &c., often contains arsenic; and brass is bronzed with a thin film of arsenic. It was formerly much employed in the manufacture of glass, but is being gradually superseded. It is also now used to some extent in the reduction of indigo blue, and in that of nitrobenzole in the manufacture of aniline.

In cases of suspected poisoning, therefore, and the finding of arsenic in the stomach, or elsewhere, it may be set up as a defence that the arsenic was derived from shot used in the cleansing of bottles, from the bottles themselves, or from metal vessels, such as tea-pots, &c.

The arsenic in all these alloys being extremely insoluble, any solution to a poisonous extent is in the highest degree improbable. It may, however, be necessary to treat the vessels with the fluid or fluids which have been supposed to exert this prejudicial action, and test them for arsenic. The treatment should, of course, be of a severe and exhaustive character, and the fluids should be allowed to stand cold in the vessels for twenty-four hours; then the effect of a gentle heat should be studied, and, lastly, that of boiling temperatures. The analysis of the alloy itself, or of the glass, it would seldom be of value to undertake, for the crushed and finely divided substance is in a condition very different from that of the article when entire, and inferences drawn from such analytical data would be fallacious. It does not matter one iota to us that the vessels out of which we drink are made of metallic arsenic, provided that under all possible domestic conditions the arsenic is insoluble.

Arsenious anhydride is also used for the preservation of wood, and is thrown occasionally into the holds of vessels in large quantities to prevent vegetable decomposition. In India, again, a solution of arsenic is applied to the walls as a wash, in order to prevent the attacks of insects.

§ 130. *Pharmaceutical, Non-officinal, and other Preparations of Arsenic.*

(1.) *Pharmaceutical Preparations.* — The *Liquor Arsenicalis* Fowler's solution), or solution of arsenic of the pharmacopeia, is omposed of—

Carbonate of potash, . .	80 grains (2·78 grms.)
Arsenious acid, . . .	80 „ (2·78 „)
Lavender, ...	5 drachms (21·2 cc.)

dissolved in 1 pint (567·9 cc.) of water; every ounce, therefore contains 4 grains of arsenious acid (or 100 cc. = ·9As_2O_3).

The *hydrochloric solution of arsenic* is simply arsenious aci dissolved in hydrochloric acid; its strength should be exactly th same as that of Fowler's solution.

A solution of *arseniate of soda*[*] contains the *anhydrous* salt i the proportion of 4 grains to the ounce (·9 in 100 cc.) of water.

Donovan's Solution of Arsenic.—This is not officinal, but i used to some extent in skin diseases; it appears to be a solutio of the iodides of mercury and arsenic; 100 cc. contain about ·15 grm. of metallic arsenic, or each fluid drachm contains ·08 grain.

Arseniate of Iron, $Fe_3As_2O_8$, is an amorphous green powde used to some extent in medicine. It should contain 33·6 pe cent. of metallic arsenic.

(2.) *Veterinary Arsenical Medicine.*—Common veterinary pr parations containing arsenic are:—A ball for worms, containin in parts—

Calomel, ...	1·3 per cent.
Arsenious acid, . . .	1·3 „
Tin filings, ...	77·9 „
Venice turpentine,[†] . .	19·5 „

A common tonic ball:[‡]—

Arsenic, . .	5 to 10 grains	(·324 to ·648 grms.)
Aniseed, . .	½ oz.	(14·1744 grms.)
Opium, . .	30 grains	(1·94 „)
Treacle, . .	q. s.	

An arsenical ball, often given by grooms to horses for th purpose of improving their coats, contains in 100 parts—

Arsenic, ...	2·5 per cent.
Pimento, ...	19·2 „
Extract of gentian, . .	78·3 „

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[*] The formula for arseniate of soda is $Na_2HAsO_47H_2O$, but it sometim contains more water.

[†] The Venice turpentine is rarely found in ordinary commerce, what i sold under that name consisting of black resin and oil of turpentine.

[‡] A similar preparation in common use has the addition of sulpha of zinc.

Another ball in use is composed of arsenic and verdigris (acetate of copper), of each 8 grains (·518 grm.); cupric sulphate, 20 grains (1·3 grm.); q. s. of linseed meal and treacle.

(3.) *Rat and Fly Poisons*, &c.—An arsenical paste sold for rats has the following composition:—

Arsenious acid, . . .	5·8	per cent.
Lampblack, ...	·6	,,
Wheat-flour, ...	46·3	,,
Suet, ...	46·3	,,
Oil of aniseed, a small quantity.		

Another rat poison is composed as follows:—

White arsenic, . . .	46·8	per cent.
Carbonate of baryta, . .	46·8	,,
Rose-pink,*	5·8	,,
Oil of aniseed, . . .	·2	,,
Oil of rhodium, . . .	·2	,,

Various arsenical preparations are used to kill flies; the active principle of the brown "*papier moure*" is arsenious acid. A dark grey powder, which used to be sold under the name of fly-powder, consisted of metallic arsenic that had been exposed some time to the air.

Fly-water is a strong solution of arsenic of uncertain strength, sweetened with sugar, treacle, or honey. Another fly-poison consists of a mixture of arsenious acid, tersulphide of arsenic, treacle, and honey.

(4.) *Quack Nostrums.*—The analyst may meet with several quack preparations for external use in cancer. A celebrated arsenical paste for this purpose is composed of—

Arsenious acid, ...	8	per cent.
Cinnabar, ...	70	,,
Dragon's blood, ...	22	,,

A pill, used by unprofessional persons as a preventive for hydrophobia (!) is composed of $\frac{1}{16}$ to $\frac{1}{12}$ (4 to 5·4 mgrms.) of a grain of arsenic and a grain of common pepper. A similar pill is much used in the East Indies.

The tasteless "*ague drops*" used in the fen countries are simply a solution of arsenite of potash.

Davidson's Cancer Remedy consists, according to Dr. Paris, of equal parts of arsenious acid and powdered hemlock.

In India, arsenic given as a medicine by native practitioners,

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* Alum and carbonate of lead coloured with Brazil and peach woods.

or administered as a poison, may be found coloured and impure, from having been mixed either with cow's urine, or with the juice of leaves, &c.*

Arsenious acid is used by dentists to destroy the nervous pulp of decayed and painful teeth, about the twenty-fifth of a grain (2·5 mgrms.) being placed in the cavity. There is no record of any accident having resulted from this practice hitherto; but since the dentist seldom weighs the arsenic, it is not altogether free from danger.

(5.) *Pigments, &c.—King's yellow* should be As_2S_3, the trisulphide of arsenic or orpiment. It is frequently adulterated with 80 to 90 per cent. of arsenious acid, and in such a case is, of course, more poisonous. King's yellow, if pure, yields to water nothing which gives any arsenical reaction.

A blue pigment, termed *mineral blue*, consists of about equal parts of arsenite of copper and potash, and should contain 38·7 per cent. of metallic arsenic (= to 51·084 As_2O_3H), and 15·6 of copper.

Schweinfurt green (Syn. *Emerald green*), $(CuAs_2O_4)_3Cu(C_2H_3O_2)_2$, is a cupric arsenite and acetate, and should contain 25 per cent. of copper and 58·4 per cent. of arsenious acid. In analysis the copper in this compound is readily separated from the arsenic by first oxidising with nitric acid, and then adding to the nitric acid solution ammonia, until the blue colour remains undissolved. At this point ammonium oxalate is added in excess, the solution is first acidified by hydrochloric or nitric acid, and, on standing, the copper separates completely (or almost so) as oxalate, the arsenic remaining in solution.

Scheele's green ($CuHAsO_3$) is a hydrocupric arsenite, and contains 52·8 per cent. of arsenious anhydride and 33·8 per cent. of copper.

(6.) *External Applications of Arsenic for Sheep, &c.*—Many of these are simply solutions of arsenic, the solution being made by the farmer. Most of the yellow sheep-dipping compounds of commerce are made up either of impure carbonate of potash, or of soda ash, arsenic, soft soap, and sulphur. The French *bain de tersier* is composed of—

Arsenious acid, . . .	1·00	kgrms.
Ferrous sulphate, . . .	10·00	,,
Peroxide of iron, . . .	0·40	,,
Gentian powder, . . .	0·20	,,

This is to be added to 100 kgrms. of water. Another common

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[*] Chever's "Med. Jurisprudence for India," p. 116.

application consists of alum and arsenic (10 or 12 to 1), dissolved in two or three hundred parts of water.

(7.) *Arsenical Soaps*, &c.—Arsenic is used in preserving the skins of animals. One of the compounds for this purpose, known under the name of *Bécoeur's arsenical soap*, has the following composition :—

Camphor,	3·4 per cent.
Arsenic,	20·2 ,,
Carbonate of potash,	56·2 ,,
Lime,*	20·2 ,,

(8.) *Arsenical compounds* used in pyrotechny :—

		Parts.
Blue fires — (1.)	Realgar,	2
	Charcoal,	3
	Potassic chlorate,	5
	Sulphur,	13
	Nitrate of baryta,	77
(2.)	Sulphur,	40·9
	Nitre,	36·8
	Sulphide of antimony,	12·3
	,, arsenic,	5
	Charcoal,	5
Green fires —	Metallic arsenic,	2
	Charcoal,	3
	Chlorate of potash,	5
	Sulphur,	13
	Nitrate of baryta,	7
Light green fire—	Charcoal,	1·75
	Sulphide of arsenic,	1·75
	Sulphur,	10·50
	Chlorate of potash,	23·25
	Nitrate of baryta,	62·50
White fire — (1.)	Arsenious acid,	·76
	Charcoal,	1·63
	Sulphide of antimony,	12·27
	Nitrate of potash,	36·59
	Sulphur,	48·75
(2.)	Realgar,	6·1
	Sulphur,	21·2
	Nitrate of potash,	72·7

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[*] The dust from the preserved skins of animals has caused, at least, one case of poisoning. *Ann. d'Hyg. Pub. et de Méd. Lég.*, 2 ser., 1870, t. xxxiii., p. 314.

(9.) *Arsenical Violet Powder.*—Public attention has recently been directed to the fact that violet powder has been found adulterated with arsenic, either accidentally or by design. Two deaths from this cause have been established by coroners' inquests.* Dr. Tidy found the violet powders used in the two cases to have the following composition :—

	1. Per cent.	2. Per cent.
Arsenious acid, . . .	38·5	38·3
Starch (potato), . . .	54·8	55·4
Magnesia, &c., . . .	6·7	6·3†

Although the children were poisoned by absorption through the skin (unless it is allowed that some may have found its way in the form of arsenical dust into the throat, or, what is still more probable, that the infants may from time to time have seized the puff-ball and *sucked* it), the large quantity of 6·5 grains of arsenious acid was separated in the one case, and 3 grains in the other. In these cases arose the question which is sure to recur in legal inquiries into poisoning by absorption—viz., whether the poison lying on the surface and folds of the skin could not have been mixed during the *post-mortem* examination with the organs of the body ? In these particular cases special care appears to have been taken, and the answer was satisfactory. It is not amiss, however, to call attention to the extreme precautions which such instances necessitate.

By the 14th of Vict. c. 12, every person selling arsenic is bound to keep a written record of every particular relative to each transaction, such as the name, abode, and calling of the purchaser, the purpose for which the poison is required, and the quantity sold, &c. These particulars are to be signed also by the

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* "Gleanings in Toxicology," by C. Meymott Tidy, M.B.—*Lancet*, August 21, 1878.

† Two recipes were handed in at the coroner's inquest which pretty fairly represent the composition of commercial violet-powder :—

First Quality, sold at 7s. per gross.

Starch Powder, ...	28 lbs.
Magnesia, ...	1½ lb.
Orris-root, ...	1 lb.
Violet Perfume, ...	1 oz.
Essence of Roses, ...	5 drops.

Second Quality, sold at 6s. per gross.

Terra Alba (Sulphate of Lime), ...	14 lbs.
Potato Starch, ...	21 lbs.
Magnesia, ...	3 lbs.
Orris-root, ...	1½ lb.
Violet Perfume, ...	1½ oz.
Essence of Roses, ...	5 drops.

purchaser. No person (sec. 2) is allowed to sell arsenic to any one unknown to the seller, unless in the presence of a witness, whom the seller is acquainted with. The arsenic sold (sec. 3) is to be mixed with soot or indigo in the proportion of half an ounce of indigo to a pound of arsenic. It, therefore, follows that the coloured substance should not contain more than 70 per cent. of arsenious acid. The Act applies to all the colourless preparations of arsenic: but it is not to affect chemists in making up prescriptions for medical men, or in supplying medical men; nor is it to affect the wholesale dealers in supplying arsenic to retail shops, &c. The penalty for conviction is £20, or less. Commercial arsenic is often much adulterated, especially with gypsum, chalk, &c. These are most readily detected by subliming the arsenic. The sublimed arsenic itself may not be entirely pure, sometimes containing arsenical sulphides and antimonious oxide.

§ 131. *Dose.*—The smallest dose of arsenic known to have proved fatal to a human being is 2½ grains (16 grms.). Farriers and grooms are in the habit of giving as much as 20 grains a day to a horse, so that the poisonous dose for this animal must be very large.*

The maximum dose for the horned cattle appears to be from 5 to 6 grains; that for a dog is a quarter of a grain, and even this may, in the smaller kinds, cause illness.

The following may be considered as *dangerous doses* of arsenic:—2 grains for an adult, 30 for a horse, 10 for a cow, and half a grain to a grain for a dog.

§ 132. *Detection of Arsenic.*—The analyst may have to identify arsenic in substance, in solution, in alloys, in wall-papers, in earth, and in various animal, fatty, resinous, or other organic matters.

Arsenious Acid in Substance.—The general characters of arsenious acid have been already described, and are themselves so marked as to be unmistakable. The following are the most conclusive tests:—

(1.) A small fragment placed in the subliming cell (p. 284), and heated to about the temperature of 137·7°C. (286°F.), at once sublimes in the form of an amorphous powder, if the upper glass disc is cool; but if heated (as it should be) to nearly the same temperature as the lower, characteristic crystals are obtained, remarkable for their brilliance and permanency, and almost always distinct and separate. The prevailing form is the regular octahedron, but the rhombic dodecahedron, the rectangular prism, superimposed crystals, half crystals, deep triangular

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* In cases of horse-poisoning which have come under the writer's notice, over 30 grains of arsenious acid have been separated.

plates like tetrahedra, and irregular and confused forms, all occasionally occur.

(2.) A beautiful and well-known test is that of Berzelius:—A small hard-glass tube is taken, and the closed end drawn out to the size of a knitting needle. Within the extreme point of this fine part is placed the fragment (which may be no more than a milligramme), and a splinter of charcoal, fine enough to enter freely the narrow part, as shown in the figure. The portion of the tube containing the charcoal (*e*) is first heated until it glows, and then the extreme end; if arsenic is present, a mirror-like coating is easily obtained in the broader portion of the tube (*d*). That this coating is really arsenical can be established by the behaviour of metallic crusts of arsenic towards solvents (as given at p. 385). The portion of the tube containing the crust may also be broken up, put in a very short, wide test-tube (the mouth of which is occupied by a circle of thin microscopic glass) and heated, when the arsenic will sublime on to the glass disc, partly as a metal and partly as crystalline arsenious acid.

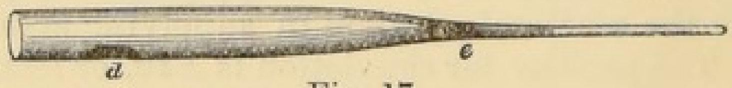

Fig. 17.

(3.) Arsenious acid, itself inodorous, when heated on coal, after mixing it with moist oxalate of potash, evolves a peculiar garlic-like odour. To this test oxide of antimony adulterated with arsenic will respond, if there is only a thousandth part present. Simply projecting arsenious acid on either red-hot charcoal or iron produces the same odour.

(4.) A little bit of arsenious acid heated in a matrass with two or three times its weight of acetate of potash, evolves the unsupportable odour of kakodyl.

Arsenites and Arseniates, mixed with oxalate of soda and heated in a matrass, afford distinct mirrors, especially the arsenites of the earths and silver; those of copper and iron are rather less distinct.

Sulphides of Arsenic are reduced by any of the processes described at p. 396.

In Solution.—An acid solution of arsenious acid gives, when treated with SH_2, a canary-yellow precipitate, soluble in ammonia, carbonate of ammonia, and bisulphite of potash (see p. 374), and also a metallic sublimate when heated in a tube with the reducing agents in the manner described at p. 397. By these properties the sulphide is distinguished and, indeed, separated from antimony, tin, and cadmium.

The sulphides of tin and cadmium are certainly also yellow, but the latter is quite insoluble in ammonia, while the former gives no metallic sublimate when heated with reducing substances.

The sulphide of antimony, again, is orange, and quite insoluble in potassic bisulphite, and scarcely dissolves in ammonia.

A small piece of sodium amalgam placed in a test-tube or flask containing an arsenic-holding liquid, produces in a short time arseniuretted hydrogen, which will blacken a piece of paper soaked in nitrate of silver, and inserted in the mouth of the flask. —(*Dr. Ed. Davy.*) This is certainly the most convenient test for arsenic. If the liquid be previously made alkaline, no antimoniuretted hydrogen (*stibine*) is given off.

Marsh's Original Test for Arsenic consisted in evolving nascent hydrogen by zinc and sulphuric acid, and then adding the liquid to be tested. The apparatus for Marsh's test, in its simplest form, consists of a flask provided with a cork conveying two tubes, one a funnel reaching nearly to the bottom of the flask, the other a delivery tube, which is of some length, is provided with a chloride of calcium bulb,* and towards the end is turned up at right angles, the end being narrowed. By evolving hydrogen from zinc and sulphuric acid, and then adding portions of the liquid through the funnel, arseniuretted hydrogen in a dry state is driven along the leading tube, can be ignited on its issue, and on depressing a piece of cold porcelain, a dark metallic spot of arsenic is obtained.† Or, if any portion of the tube be made red-hot, the metal is deposited in the same way as a ring. The apparatus admits of much complication and variety. One of the most useful additions is, perhaps, the interposition of a small gasometer. This consists of a cylindrical glass vessel with entrance and exit tubes, open at the bottom, immersed in water in a larger vessel, and counterpoised by weights and rollers, exactly like the large gasometers used at gasworks; the exit tube must have a stopcock, and the gas must pass through sulphuric acid in order to dry it thoroughly.

M. Blondlot has observed‡ that if pure zinc, a weak solution

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* Otto recommends the first half of the drying tube connected with the development flask to be filled with caustic potash, the latter half with chloride of calcium (*Ausmittelung der Gifte*). Dragendorff approves of this, but remarks that it should be used when arsenic alone is searched for, since caustic potash decomposes stibine. The potash fixes SH_2, and prevents the formation of chloride of arsenic.

† For identification of arsenical films, see p. 385.

‡ Blondlot: "Transformation de l'arsenic en hydrure solide par l'hydrogène naissant sous l'influence des composés nitreux."—*Jour. de Pharm. et de Chim.*, 3e ser., t. xliv., p. 486.

of arsenious acid, and a sulphuric acid containing nitric acid o nitrous compounds, be mixed together, the arsenic passes int a solid hydrate, which is deposited on the surface of the zinc Certain organic substances (such as sugar, gum, &c.) preven this formation of solid hydrate. Thus, in two ways, the analys may be deceived—under the above conditions, the zinc may b arsenical, and yet pure hydrogen be evolved until the ver moment in which the liquid to be tested is added; or, on th other hand, if the liquid to be tested and the acid itself contai nitrous compounds, no arsenic may come off, although arseni be actually present. The formation of the solid hydrate in th original testing may always be prevented by the addition of little pure cane sugar; but in operating on liquids of unknow composition, Blondlot's observation shows clearly, that if n result is obtained from Marsh's test as ordinarily applied, arseni may yet be present. This objection does not hold good in th evolution of hydrogen by galvanism, nor, so far as is known when sodium amalgam is used.

The precautions to be observed in Marsh's test are—

1. Absolute freedom of the reagents used from arsenic, antimony,* and other impurities.
2. The sulphuric acid should be diluted with five times it weight of water, and if freshly prepared should be cooled befor use. Strong acid must not be employed.†
3. The fluid to be tested should be poured in little by little.
4. Nitrous compounds, nitric acid, hydrochloric acid, chlorides are all more or less prejudicial.
5. The gas should come off regularly in not too strong stream, nor out of too small an opening.
6. The gas should pass through the red-hot tube at least on hour, if no stain is at once detected.
7. A little pure bichloride of platinum solution may be adde without injury, to the zinc if the gas comes off too slowly.‡

The characteristics of the metallic stains which may occu either on glass or porcelain in the use of Marsh's test, may b noted as under:—

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* With regard to purity of reagents, Sonnenschein states that he has onc found chlorate of potash contaminated with arsenic. — Sonnenschein *Gericht. Chemie*, p. 139.

† M. A. Gautier uses sulphuric acid diluted with five times its weight o water; when the hydrogen has displaced the air, he adds to the arsenica matter 45 grms. of this acid and 5 grms. of pure sulphuric acid.—*Bull. d la Société Chim. de Paris*, 1875, t. xxiv.

‡ A solution of sulphate of copper has been recommended; according t Gautier, two-thirds of the arsenic in such a case are retained.

MIRROR OR CRUST OF ARSENIC	MIRROR OR CRUST OF ANTIMONY
Is deposited at a little distance from the flame.	Is deposited close to the flame, and on both sides of it, and is therefore notched.
An arsenical stain is in two portions, the one brownish, the other a glittering black.	The stain is tolerably homogeneous, and usually has a tin-like lustre.
On heating, it is rapidly volatilised as arsenious acid.	Volatilisation very slow ; no crystalline sublimate obtainable.
On transmission of a stream of SH_2, whilst immediately behind the stain a gentle heat is applied, the arsenic is changed to yellow sulphide;* if dry ClH is now transmitted, the arsenical sulphide is unchanged.	The same process applied in the case of antimony produces the orange or black sulphide ; and on passing dry ClH, chloride of antimony volatilises without the application of heat.
Chloride of lime dissolves the arsenic completely.	Antimony not affected.
Protochloride of tin has no action on metallic arsenic.	Dissolves slowly but completely the antimony stain.
The arsenic stain, dissolved in aqua regia, or ClH and chlorate of potash, and then treated with tartaric acid, ammonia, and magnesia mixture, gives a precipitate of ammonia magnesian arseniate.†	No precipitate with antimony.

Reinsch's Test is a simple electrolytic method of depositing arsenic on copper :—A piece of pure bright copper foil or gauze is

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[*] It is desirable to dissolve away the free sulphur often deposited with the arsenical sulphide by bisulphide of carbon.

[†] Schönbein has proposed ozone as an oxidiser of arsenical stains. The substance containing the stain, together with a piece of moist phosphorus, is placed under a shade, and left there for some time ; the oxidisation product is, of course, coloured yellow by SH_2 if it is arsenious acid, orange if antimony. The vapour of iodine colours metallic arsenic pale yellow, and later a brownish hue ; on exposure to the air it loses its colour. Iodine, on the other hand, gives with antimony a carmelite brown, changing to orange.

An arsenical ring may be also treated as follows :—Precipitated zinc sulphide is made into a paste with a little water, and introduced into the end of the tube ; the same end is then plunged into dilute sulphuric acid, and the ring heated, when the arsenical sulphide will be produced.

attached to a platinum wire, and the copper immersed in the liquid to be tested, which is then boiled. The liquid must be distinctly acid, and should be contained in a flask, the mouth of which is conveniently partially closed by a funnel, the free end of the wire reaching well out of the flask, so that the copper may be from time to time examined. The boiling in very dilute solutions should be prolonged, but it need not be violent—a gentle simmering is all that is required. The copper, if a very minute quantity of arsenic is present, will have a greyish stain upon it; with larger quantities a somewhat glistening black-lead appearance is produced. Mercury, sulphur, selenium, and antimony, all stain copper.

On heating the stained copper in the subliming cell (p. 284) or in a tube, if mercury is present it will sublime in microscopic globules. Sulphide of copper can be rubbed off with the fingers, but the arsenical stain, on the contrary, is a true alloy, consisting, according to Lippert,* of one atom of arsenic and five of copper. The arsenical stain, again, dissolves in caustic ammonia; the sulphide of copper does not do so. The arsenical stain also dissolves in a mixture of equal parts of water and HCl with development of hydrogen, an action which does not take place with sulphide of copper.

The arsenical stain, when heated in the tube or cell, gives a crystalline sublimate of arsenious acid; while the antimonial stain is much bluer, and gives no crystalline sublimate. Moreover, the antimony can readily be converted into antimoniate of potash, by warming the copper in water made alkaline by potash and first reddened by potassic permanganate; heated in this way it, of course, dissolves; and on filtering off the manganese, acidifying with HCl, and testing with SH_2, the orange sulphide is obtained.

Some of the foregoing tests may be applied if there is sufficient material, but if not, it is better at once to pass to Bloxam's method (p. 390), which will give positive results without interfering with subsequent tests.

§ 133. *Arsenic in Organic Matters.*—Animal matters are dealt with as described (pp. 244, 398), and saccharine substances, such as treacle, in the same way. Resinous matters may be first extracted by alcohol, and the residue dissolved in boiling water containing hydrochloric acid, condensing the steam by a vertical condenser; the alcoholic solution may be tested by electrolysis, to see whether any arsenic has been dissolved, and if this is the case, it may be freed from the resin by the addition of water and filtration.

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* *Journ. f. Pract. Chemie,* 13, 68, p. 168.

From ordinary pills, quack extracts, and similar preparations, drying, powdering, and exhaustion with boiling dilute HCl, will remove the whole of the arsenic, if in a soluble state; if not, *aqua regia* must be employed.

Oils and matters consisting almost entirely of fat, suspected of containing arsenic, are gently heated, and allowed to deposit any insoluble matter they may contain; the oil is then decanted, and, if necessary, filtered from any deposit; saponified by alcoholic potash, the soap decomposed by HCl, the fatty acids separated as described (p. 74), and the arsenic looked for both in the first deposit and in the solution, now fairly free from fat and easy to treat.

In searching for arsenic in the fluids or tissues of the body, the analyst is generally at the mercy of the pathologist, and sometimes the work of the chemist leads to a negative result, solely from not having the proper organs sent to him.*

In all cases the chemist should have portions of the brain, spinal cord, liver, lungs, and muscular tissue, as well as the stomach and its contents.†

We have very decided evidence that where investigation is made for the *absorbed* metal, search should preferably be directed to the nervous tissue, the amount (according to the experiments of Scolosuboff)‡ being generally greatest in the marrow, then in the brain, next in the liver, and least in the muscles. The following may be taken as a fairly accurate statement of the relative proportion in which arsenic is likely to be found in the body, 100 grms. being taken of each :—

Muscles,	1
Liver,	10·8
Brain,	36·5
Spinal Marrow,	37·3

With regard to the preliminary treatment of the stomach and fluids submitted to the analyst, the careful noting of appearances, the decantation, washing, and examination (microscopical and chemical) of any deposit, are precautions so obviously dictated by

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* For example, in cases of poisoning by external application, more than once merely the empty stomach and a piece of intestine have been forwarded to the writer.

† Caspar recently found arsenic in the hair of an exhumed corpse. The possibility of this has been often denied, but it may now be looked upon as a very rare, though occasional occurrence.—Caspar's "Gerichtliche Medicin," Bd. ii. 4, 25.

‡ *Bull. Soc. Chim.* [2], xxiv. 124.

common sense, that they need only be alluded to in passing. Of some considerable moment is the question which may be put to the analyst in court, in reference to the possible entrance of arsenic into the body, while living, by accidental and, so to speak, *subtle* means. Such are the inhaling of the fumes from the burning of arsenical candles,* and of emanations from papers (see p. 373),† as well as the possible entrance of arsenic into the body after death from various sources, such as arsenical earth, &c.‡

The arguments which are likely to be used in favour of a corpse having become arsenical may be gathered from a case related by Sonnenschein :—Certain bodies were exhumed in two churchyards ; the evidence went to show that they had been poisoned by arsenic, and this substance was actually found in the bodies, while at the same time it was discovered to exist also in traces in the earth of the churchyard. The theory for the defence was, that although the arsenic in the earth was in an insoluble state, yet that it might combine with lime as an arsenite of lime ; this arsenite would become soluble by the action of carbonic acid set free by vegetation, and filter down to the corpse. Sonnenschein suspended a quantity of this earth in water, and passed CO_2 through it for twelve hours ; on filtering, the liquid gave no evidence of arsenic. A similar result was obtained when an artificial mixture of 1 grm. of arsenious acid and 1 pound of earth were submitted to the same process.

The fact would appear to stand thus : oxide of iron in ordinary earth retains arsenic, and requires treatment with a concentrated acid to dissolve it. It therefore follows, that if a defence of arsenical earth is likely to be set up, and the analyst finds that by mere extraction of the tissues by *water* he can detect arsenic, the defence is in all probability unsound. The expert should of

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* See a case of poisoning (non-fatal) of a lady by the use of arsenical candles, *Med. Times and Gazette*, iii., 1876, 467.

† To solve this question, it has been at times considered necessary to analyse an extraordinary number of things. In the "affaire Danval" (*Journ. d'Hygiène*, 2e ser., No. 108, July, 1878), more than sixty different articles, comprising drugs, drinks, perfumes, bed-curtains, wall-paper, and other matters, were submitted to the experts.

‡ The following important case is related by Sonnenschein :—

Nicholas Nobel and his wife Jerome were buried two metres from each other in the churchyard at Spinal, the earth of which notoriously contained arsenic. A suspicion of poisoning arose. The bodies were exhumed, and arsenic was found in the stomach and intestines of Nobel, but not the slightest trace in the corpse of the wife. The remains of the bodies were re-interred, and after six months, on a fresh suspicion of poisoning arising, again exhumed. The corpse of the woman had been put naked in the moist earth during a heavy shower, but this time also no arsenic was detected in it.

course deal with this question on its merits, and without prejudice. According to Eulenberg,* in arsenical earth—if after having been crushed and washed, it lies for some time exposed to the disintegrating action of the air—soluble arsenical salts are formed, which may find their way into brooks and supplies of drinking water. We may infer that it is hardly probable (except under very peculiar circumstances) for a corpse to be contaminated internally with an estimable quantity of arsenic from the traces of arsenic met with in a few churchyards.

It occasionally happens that an exhumation is ordered a very long time after death, when no organs or parts (save the bones) are to be distinguished. In the case of a man long dead, the widow confessing that she had administered poison, the bones were analysed by Sonnenschein, and a small quantity of arsenic found. Conièrbe and Orfila have both asserted that arsenic is a normal constituent of the bones—a statement which has been repeatedly disproved. Sonnenschein relates:—† "I procured the remnants of a body of a person killed twenty-five years previously, from a churchyard of this place (Berlin), and investigated several others in a similar way, without finding the least trace of arsenic. Similar experiments in great number were repeated in my laboratory, but in no case was arsenic recognised." The opinion of the expert, should he find arsenic in the bones, must be formed from the amount discovered, and other circumstances.

§ 134. *Analysis of Wall-paper for Arsenic.*—The separation of arsenic from paper is extremely easy, and admits of great variety of manipulation. A very quick special method is as follows:—The paper is saturated with chlorate of potash solution, dried, set on fire in a suitable plate, and instantly covered with a bell-glass. The ash is collected, pulverised, and exhausted with cold water, which has previously thoroughly cleansed the plate and bell-glass; the arsenic in combination with the potash is dissolved, whilst oxides of chromium, copper, aluminium, tin, and lead, remain in the insoluble portion.‡

On investigating the air of a room or chamber suspected of being impregnated with arsenic, it is important to know whether it is caused by arsenical dust or by AsH_3. In the case of a child dying with symptoms of arsenical poisoning in a room papered with a pigment containing Scheele's green, Sonnenschein § placed a perfectly clean table in the room, which was kept

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* "Gewerbe Hygiène," p. 284.

† *Gerichtlich. Chemie*, p. 122.

‡ Kapferschlaeger: *Rev. Universelle des Mines*, 1876.

§ "Handbuch der Gericht. Chemie." p. 153.

closed for eight days. At the end of that time he examined the dust of the table by the microscope and chemically; the former revealed green particles, the latter arsenic. It would, however, appear both a more rapid and convenient method to draw a large number of litres of air through a solution of nitrate of silver, and filter the air through cotton wool; at the termination of the experiment examining the wool for arsenical dust, and the nitrate of silver for arsenious acid. A convenient aspirator for such a purpose is an ordinary ale cask, filled with water; a bit of brass tubing is screwed through a hole in the bung, and connected with the absorption apparatus, the water being allowed to trickle away slowly through a tap placed in the usual position.*

§ 135. *Elimination of Arsenic from the Body.*—Orfila and Geoghegan consider that arsenic is entirely eliminated from the body in from twelve to fifteen days. Husemann detected arsenic in the urine of a hound seventeen days after administering the poison, and Sonnenschein found it in the fæces of a man ten days after the poison had been taken. Some experiments of Flandin and Danger showed that in one case elimination was complete in three days, whilst in another traces could be found as late as the thirty-fifth day. The latter case, however, appears to be quite exceptional, and there is unanimity of opinion among toxicologists as to the elimination of arsenic being relatively rapid. If a person should live a few days after taking a poisonous dose of arsenic, it is not probable that the poison would be discovered in the body.

§ 136. *Estimation of Arsenic.*—Most of the methods for the quantitative determination of arsenic are also excellent tests for its presence. It may be regarded, indeed, as an axiom in legal chemistry, that the precise amount of every substance detected, if it can be weighed or estimated by any process whatever, should be accurately stated. Indefinite expressions, such as "a small quantity was found," "traces were detected," &c., are most objectionable. The more perfect of the methods of evolving arsenic can be made quantitative. For example, the galvanic process introduced by Bloxam may be utilised as follows:—A fractional part of the arsenical solution is taken for the experiment; the bottom of a narrow-necked bottle of about 100 cc. capacity is removed, and replaced by a piece of vegetable

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* The investigation of emanations supposed to be arsenical from manu factories, &c., must be conducted on the same principles. It would appear that arsenical fumes are evolved in the action of impure sulphuric acid on coprolites, a fact not before observed.—"On the Presence of Arsenic in the Vapour of Bone Manure," by J. Adams.

parchment. The neck of the bottle carries a cork, which is pierced by (1.) a platinum wire, which is attached to a platinum electrode; (2.) a short tube, bent at right angles, and connected by piping with a longer tube which has also a rectangular bend, and dips into a solution of silver nitrate; (3.) an ordinary funnel-tube, reaching nearly to the bottom. The bottle is placed in a beaker of such a size as to leave a small interval between the two, and the whole apparatus stands in a large vessel of cold water. Dilute sulphuric acid is now put into the bottle, and also into the beaker, so that the fluid reaches exactly the same level in each. The positive platinum electrode of a battery of six of Grove's cells, or other efficient combination, is immersed in the liquid outside the bottle, connection with the negative plate is established, and hydrogen very soon comes off, and passes over into the nitrate of silver solution. When all the air is expelled, a portion of the rectangular tube is heated to redness, and if there is no stain nor any reduction of the silver, the acid is pure. If the gas is passed for a long time into the silver solution, the silver will be reduced to some extent by the hydrogen, although arsenic-free;* so that it is better to rely upon the metallic ring or stain, which is certain to be formed on heating a portion of the tube red-hot, and keeping it at that temperature for *at least ten minutes.* The liquid is then passed through the funnel in successive portions; if arsenic is present there will be a decided metallic ring on heating the tube as before, and if antimony is present there will also be a stain; the distinctions between these stains have been described at p. 385.

The tube is kept red-hot until the stain is very distinct; then the source of heat is removed, and the gas allowed to bubble through the argentic nitrate solution, which it decomposes, as before detailed (p. 372). This process is continued until, on placing the delivery tube in a sample of clear nitrate of silver solution, there is no darkening of colour. In certain cases this may take a long time, but the apparatus once set to work, requires little superintendence. At the conclusion, the whole of the arsenic is separated,—part is in the silver solution as arsenious acid, part in the tube as a ring of metallic arsenic. The portion of the tube containing the metallic arsenic should be cut off with a file and weighed, the arsenic then removed and re-weighed; the loss is the metal approximately. It is also possible to estimate the amount of arsenic in a metallic ring

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* Nitrate of silver solution is reduced by H_2, CH_3, PH_3, and SbH_3; hence it is absolutely necessary in any qualitative examination to prove that arsenious acid has actually been produced in the silver solution.

by having a set of similar deposits of known weights or quantities, in tubes exactly corresponding to those used in the analysis, and comparing or matching them.

In cases where a very small quantity of arsenic only is present, it will be better to continue the heating of the tube until the end of the operation, so as to obtain all the arsenic present in the metallic state; the nitrate of silver solution can in such a case be omitted. M. Cromydis * has given some analyses in support of this simple and easy quantitative and qualitative process, and it is with due care exact, but very tedious if certain organic liquids are operated upon.

The arsenious acid in the nitrate of silver may be dealt with in several ways. The equation given p. 372, shows clearly that pure arsine passed into nitrate of silver solution decomposes it in such a manner that, if either the silver deposited or the free acid is estimated, the quantity of arsenic can from such data be deduced. In operating on organic liquids, ammonia and other products may be given off, rendering either of the indirect processes inadvisable. A very convenient method, applicable in many cases, is to throw out the silver by hydrochloric acid, alkalise the filtrate by bicarbonate of soda, and titrate with iodine solution. The latter is made by dissolving exactly 12·7 grms. of pure dry iodine, by the aid of 18 grms. of potassic iodide in one litre of water, observing that the solution must take place in the cold, without the application of heat. The principle of the titration is, that arsenious acid, in the presence of water and free alkali, is converted into arsenic acid—

$$As_2O_3 + 4I = 2Na_2O + As_2O_5 + 4NaI.$$

The end of the reaction is known by adding a little starch-paste to the solution; as soon as a blue colour appears, the process is finished.

Another convenient way by which (in very dilute solutions of arsenious acid) the arsenic may be determined, is a colorimetric method, which depends on the fact that sulphuretted hydrogen, when arsenious acid is present in small quantity, produces no precipitate at first, but a yellow colour, proportionate to the amount of arsenic present. The silver solution containing arsenious acid is freed from silver by hydrochloric acid; a measured quantity of saturated SH_2 water is added to a fractional and, if necessary, diluted portion, in a Nessler cylinder or colorimetric apparatus, and the colour produced exactly imitated,

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* *Bull. Soc. Chim.* [2], xxv. 348, 349.

by the aid of a dilute solution of arsenious acid, added from a burette to a similar quantity of SH_2 water in another cylinder. The fluid must of course be acidified with HCl.

The arsenious acid may also be precipitated as tersulphide, and the tersulphide dissolved by ammonia; in this case also the silver should be removed from the solution first.

The electrotype method of evolving nascent hydrogen is without doubt almost perfect; but Davy's method, already alluded to (p. 383), is decidedly more convenient, and of great delicacy. The only objection to its use is, that it introduces mercury into the liquid to be tested, which is therefore rendered unfit for subsequent search for that metal; it, however, but rarely happens that the material operated upon is so scanty that the chemist cannot afford a carefully weighed or measured portion to be used only for the detection or exclusion of arsenic.

The method has been very prominently brought forward by Dr. E. Davy, * and is simply the evolution of nascent hydrogen by sodium amalgam. In the original paper the author proposes it as a qualitative test only, and uses paper soaked in argentic nitrate solution as an indicator. It is, however, obvious that the arsenic evolved may be absorbed by argentic nitrate solution, or arsenic deposited as a metallic coating in the tube. A sodium amalgam is prepared by adding 1 part of sodium to 10 parts of mercury; if any quantity of this amalgam is required, the sodium may be melted under paraffin, and poured in a thin stream on to the mercury, † which becomes solid sooner than the paraffin, and the latter may be poured off, finally cleansing the amalgam by petroleum ether. This amalgam will contain no arsenic; but in a medico-legal investigation it should be nevertheless tested, by evolving hydrogen from water with it, and passing the gas for an hour through argentic nitrate solution. A little silver may be precipitated, giving the solution a slightly smoky colour; but on freeing the solution from silver by HCl, no arsenic should be detected by hydric sulphide or other tests.

The quantitative analysis by Davy's test is made by placing in a flask a fractional part of the liquid to be examined, adding a few pieces of the amalgam, and conducting the evolved gas into a 4 per cent. argentic nitrate solution. The flask may be conveniently fitted up with an india-rubber cork pierced by two tubes, the one a thistle funnel-tube, reaching nearly to the bottom, the other commencing at the lower end of the cork, and eading in the usual way into the silver solution. When bubbles

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* *Chem. News*, xxxiii. 58.

† *Ibid.*, xxxiii. 94.

cease to come off, heat should be applied, and the last trace of arsine driven over by boiling. After boiling, the liquid should be cooled, some fresh amalgam added, and the process repeated until no arsine is evolved. In personal experiments upon this method (using solutions of arsenious acid in beer, wine, spirits, urine, &c.) the writer has found it accurate, although often taking considerable time.

Despite the advantages of the processes described, which are (to a certain extent) new, easy, and accurate, not a few chemists still prefer the old method of precipitation with hydric sulphide SH_2, because, although tedious, it has stood the test of experience If this be used, it is well in most cases to pass sulphurous anhydride through the liquid until it smells strongly of the gas, for by this means any arsenic acid present is reduced, the sulphurous anhydride is quickly got rid of by a current o carbonic anhydride, and then the liquid is saturated with hydric sulphide. In the ordinary way, much time is often wasted in saturating the liquid with this gas. Those, however who have large laboratories, and daily employ hydric sulphide possess (or should possess) a water saturated with the gas under pressure; such a liquid, added in equal volume to an arsenica solution, is able to convert the whole of the arsenic into sulphide in a very few minutes. Those who do not possess this hydric sulphide water can saturate in an hour the liquid to be tested by passing the gas in under pressure. A convenient method is to evolve SH_2 from sulphide of antimony and HCl; the gas passes first into a wash-bottle, and then into a strong flask containing the solution under trial. This flask is furnished with a safety-valve, proportioned to the strength of the apparatus the two tubes dipping into the wash-bottle and the last flask are provided with Bunsen's valves, which only allow the gas to pass in one direction. The hydric sulphide is then driven over by heat, and when sufficient gas has in this way passed into the liquid, the flame is withdrawn, and the apparatus allowed to stand for some hours, the valves preventing any backward flow of the liquid or gas. When the precipitate has settled to the bottom, the supernatant fluid is carefully passed through a filter, and the precipitate washed by decantation i the flask, without transference to the filter, if it can b avoided.

The sulphide thus obtained is the trisulphide of arsenic, mixed with sulphur, and, in most medico-legal inquiries, contaminated by organic matter. It is therefore too impure to be directly weighed, and there are several methods of purification open t the analyst.

(*a.*) *Solution in Ammonia and Estimation by Iodine.*[*]—The filter is pierced, the sulphide washed into a flask by ammonia water (which need not be concentrated), and dissolved by warming with ammonia water, filtered from any insoluble matter, neutralised by ammonia, and estimated by iodine and starch (p. 392).

(*b.*) *Drying the Purified Precipitate at a high temperature, and then directly weighing.*[†]—The sulphide is dissolved as before in ammonia, filtered, and evaporated to dryness in a porcelain dish, which is placed with its contents on a sand-bath, and heated carefully. With attention it is easy to evaporate off in this way any free sulphur,[‡] and to carbonise the traces of organic matter, without any volatilisation of the sulphide of arsenic. The black mass is once more dissolved in ammonia, filtered, and the filtrate evaporated in a tared porcelain dish to dryness, and finally weighed as sulphide of arsenic.

(*c.*) *Oxidation of the Sulphide and Precipitation as Ammonia Magnesian Arseniate, or Magnesia pyroarseniate.*—The tersulphide, as before, is dissolved in ammonia (not omitting the filter paper, which should be soaked in this reagent), the solution filtered, and evaporated to dryness. The dry residue is now oxidised by fuming nitric acid, taking care to protect the dish with a large watch-glass (or other cover) during the first violent action; the dish is then heated in the water-bath until all the sulphur has disappeared, and only a small bulk of the liquid remains; it is then diluted and precipitated by "magnesia mixture."[§] The fluid must stand for several hours, and if the arsenic is to be determined as the usual ammoniacal salt, it must be passed through a weighed filter, and washed with a little ammoniacal water (1 : 3). The solubility of the precipitate is considerable, and for every 16 cc. of the filtrate (not the washings) 1 mgrm. must be allowed. The precipitate dried at 100°C., $2(NH_4MgAsO_4)H_2O$ represents 39·47 per cent. metallic arsenic.

The solubility of the magnesium arseniate itself, and the general dislike which chemists have to weighing in such hygroscopic material as a filter are, perhaps, the main reasons for the variation of this old method, which has lately come

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[*] P. Champion and H. Pellet, *Bull. Soc. Chim.* [2], xxvj. 541-544.

[†] F. Mohr, "Chemische Toxicologie," p. 56.

[‡] Ammonia always dissolves some free sulphur.

[§] Magnesia mixture :

Sulphate of magnesia,	1
Chloride of ammonium,	1
Solution of ammonia,	4
Water,	8

issolve; then allow to stand for several days; finally filter, and keep for use.

into notice. Rose proposed some time ago the conversio of the double salt into the pyroarseniate, a method condemne by Fresenius and Parnell, but examined and pronounce a practicable and accurate process by Remol, Rammelsber Thorpe, Fuller, Wittstein, Emerson, Macivor, Wood, an Brauner. The modification of Rose's process, recommende by Wood,* and still further improved by Brauner,† may b accepted.

The precipitation is effected by magnesia mixture, with th addition of half its bulk of alcohol. The solution is allowed t stand for several hours, until it is possible to decant the clea liquid from the precipitate ; the latter is now dissolved in HC reprecipitated as before, thrown on a small filter, and washe with a mixture of one volume of ammonia, two volumes of alcoho and three of water. The precipitate is now dried, and tran ferred as completely as possible from the filter into a sma porcelain crucible, included in a larger one made of platinum moistened with nitric acid, covered and heated at first gentl lastly to a bright redness ; the filter is then treated similarly, an the crucible with its contents weighed. Pyroarseniate of arsen ($Mg_2As_2O_7$) contains 48·29 per cent. of metallic arsenic.

(*d.*) *Conversion of the Trisulphide of Arsenic into the Arsenom lybdate of Ammonia.*—The purified sulphide is oxidised by nitr acid, the acid solution is rendered alkaline by ammonia, and the precipitated by a molybdenum solution, made as follows :—1 grms. of molybdic acid are dissolved in 150 cc. of ordinar ammonia and 80 of water; this solution is poured drop by dro into 500 cc. of pure nitric acid and 300 cc. of water ; it is allowe to settle, and, if necessary, filtered. The molybdic solution mu be mixed in excess with the liquid under treatment, the temper ture raised to 70° or 80°, and nitric acid added in excess until yellow coloration appears ; the liquid is then passed through tared filter, and dried at 100°C. It contains 5·1 per cent. arsenic acid [3·3 As].‡

(*e.*) *Conversion of the Sulphide into Metallic Arsenic.*—If the should be any doubt as to the nature of the precipitated su stances, the very best way of resolving this doubt is to redu the sulphide to metal. The original process of Fresenius was mix the sulphide with carbonate of soda and cyanide of pota sium, and place the mixture in the wide part of a tube of har German glass, drawn out at one end to a capillary fineness. Ca bonic anhydride, properly dried, was passed through the tub

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* *Zeitschrift für Anal. Chem.*, xiv. 356.

† *Ibid.*, xvj. 57, 58.

‡ Champion and Pellet, *Bull. Soc. Chim.*, Jan. 7, 1877.

and the portion containing the mixture heated to redness; in this way the arsenical sulphide was reduced, and the metal condensed in the capillary portion, where the smallest quantity could be recognised. A more elaborate and accurate process, based on the same principles, has been advocated by Mohr:—*

A convenient quantity of carbonate of soda is added to the sulphide, and the whole mixed with a very little water, and gently warmed. The yellow precipitate is soon dissolved, and then the whole is evaporated carefully, until it is in a granular, somewhat moist, adhesive state. It is now transferred to a glass tube, open at top and bottom, but the top widened into a funnel; this tube is firmly held perpendicularly on a glass plate, and the prepared sulphide hammered into a compact cylinder by the aid of a glass rod, which just fits the tube. The cylinder is now dried over a flame, until no more moisture is to be detected, and then transferred into a glass tube four or five inches long, and with one end drawn to a point (the weight of this tube should be first accurately taken). The tube is connected with the following series:—(1.) A chloride of calcium tube; (2.) a small bottle containing nitrate of silver; (3.) a hydrogen-generating bottle containing zinc and sulphuric acid. The hydrogen goes through the argentic nitrate solution, leaving behind any sulphur and arsenic it may contain; it is then dried by chloride of calcium, and streams in a pure dry state over the cylinder of prepared sulphide. When it is certain that pure hydrogen, unmixed with air, is being evolved, the portion of the tube in which the cylinder rests is heated slowly to redness, and the metallic arsenic sublimes at a little distance from the source of heat. No error with regard to impurities in the gas is likely to occur; but in rigid inquiries it is advisable to heat a portion of the tube, previous to the insertion of the cylinder, for some time, in order to *prove* the absence of any external arsenical source. Loss is inevitable f the tube is too short, or the stream of hydrogen too powerful. The tube after the operation is divided, the portion soiled by he soda thoroughly cleansed, and then both parts weighed; he difference between the weight of the empty tube and the ube + arsenic gives the metallic arsenic.

This is the process as recommended by Mohr; it may, howver, be pointed out that the glass tube itself loses weight when any portion of it is kept red-hot for some little time; nd therefore, unless the crust is required in the original ube, it is better to divide it, carefully weigh the arsenical ortion, remove the crust, and then reweigh. The method nearly but not perfectly accurate; for if the white alkaline

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* Mohr's "Toxicologie," p. 57.

residue be examined, arsenic will be detected in it, the reas being that the arsenical sulphide generally contains pent sulphide of arsenic as well as free sulphur. Now the pentasu phide does not give up metallic arsenic when treated as befo detailed; nor, indeed, does the trisulphide, if mixed with mu sulphur, yield an arsenical crust. It is, therefore, of gre moment to free the precipitate as much as possible from sulph before attempting the reduction.

The development of a reducing gas from a special and som what complicated apparatus is not absolutely necessary. T whole process of reduction, from beginning to end, may take pla in a single tube by any of the following processes:—(1.) T sulphide is mixed with oxalate of soda (a salt which contains water of crystallisation), and the dry mixture is transferr to a suitable tube, sealed at one end. An arsenical mirror readily obtained, and if the heat is continued long enough, arsenic remains behind—an excellent and easy method, in whi the reducing gas is carbonic oxide, in an atmosphere of carbon anhydride. (2.) The sulphide is oxidised by aqua regia, and t solution evaporated to complete dryness. The residue is th dissolved in a few drops of water, with the addition of so largish grains of good wood charcoal (which absorb most of t solution), and the whole carefully dried. The mass is no transferred to a tube closed at one end, a little charcoal add in the form of an upper layer, and heat applied first to this upp layer, so as to replace the air with CO_2, and then to bring the who tube gradually to redness from above downwards. In this ca also the whole of the arsenic sublimes as a metallic mirror.

There are various other modifications, but the above a trustworthy, and quite sufficient. Brugelmann's method determining arsenic, elsewhere described, would appear to po sess some advantages, and to promise well; but the writer h had no personal experience of it with regard to arsenic.

(*f.*) *Conversion of Arsenic into Arsenious Chloride*, $AsCl_3$.—Th process, first employed by Schneider and Fyfe, and afterwar modified by Taylor, differs from all the preceding, since a attempt is made to separate by one operation volatile metall chlorides, and to destroy the organic matter, and thus obtain tw liquids—one a distillate—tolerably clear and free from soli particles, whilst the mass in the retort retains such metals copper, and is in every way easy to deal with.

Schneider and Fyfe employed sulphuric acid and common salt but Taylor recommends hydrochloric acid, which is in every respe preferable. As recommended by Taylor, all matters, organic otherwise, are to be completely desiccated before their reductio into a retort, and on these dried substances sufficient pure hydrochloric acid poured, and the distillation pushed to dryness. Every one is well aware how tedious is the attempt to dry perfectly the organs of the body (such as liver, &c.) at any temperature low enough to ensure against volatilisation of such a substance as, *e.g.*, calomel. This drying has, therefore, been the great stumblingblock which has prevented the general application of the process. It will be found, however, that drying in the ordinary way is by no means necessary. The writer cuts up the solid organ (such as liver, brain, &c.) with scissors into small pieces, and transfers them to a retort fitted by an air-tight joint to a Liebig condenser; the condenser in its turn being connected with a flask by a tube passing through an india-rubber stopper. Another tube from the same flask is connected with india-rubber piping, which terminates ultimately, by an iron tube, in an open fire, furnace chimney, or other place convenient for conveying off the very offensive vapours from the laboratory. The distillation is now carried on to carbonisation; on cooling, a second quantity of hydrochloric acid is added, and the last fraction of the distillate examined for arsenic. If any is found, a third distillation is necessary. At the termination of the operation the retort is washed with water, the solution filtered, and this solution and the distillate are each separately examined for arsenic. If properly performed, however, the second distillation brings over the whole of the arsenical chloride,* and none will be found in the retort. With good management there is no odour, nor is there any loss of substance. In the distillate the arsenic can hardly be in the form of arsenious chloride, but rather arsenious acid and hydrochloric acid; for the chloride easily splits up in the presence of water into these substances. However that may be, it is in a condition to be very easily dealt with. It is perhaps best to convert it into the trisulphide. Taylor † recommends evolving arsine in the usual way, and passing the arsine (AsH_3) into solution of silver nitrate, finally estimating it as an arseniate of silver. Objections with regard to the impurity of reagents should be met by blank experiments. Kaiser ‡ has proposed and practised a modification of this method, which essentially consists in the use of sulphuric acid and sodic chloride (as in Schneider and Fyfe's original process), and in passing the distillate first

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Dragendorff asserts to the contrary; but we may quote the authority f Taylor, who has made several experiments, in which he obtained all he arsenic as chloride. The writer has performed the process many times, nd each time carefully testing the mass in the retort for arsenic; but he result proved that it had entirely passed over.

† "Principles of Medical Jurisprudence," I. 267.

‡ *Zeitschr. f. Anal. Chem.*, xiv. 250–281.

into a flask containing a crystal or two of potassium chlorat and thence into an absorption bulb; in the latter most of th arsenic is found in the form of arsenic acid, the chloride havin been oxidised in its passage. The apparatus is, however, con plicated in this way without a corresponding advantage.

§ 137. *The Action of Arsenical Fumes on Plants.*—The actio of fumes of arsenic on plants occasionally becomes a leg question. Vapours containing arsenic evolved from works ar seldom, perhaps never, simply arsenical, but mixed with othe objectionable gases,* so that an accurate estimation of th damage and danger done by arsenic alone is perhaps hardl possible. The present state of knowledge with regard to th action of simply arsenious acid fumes seems to be, that if th fumes are not in great excess, but little alteration is observed.†

Arsenic in sufficient quantity to affect plants produces she ding of the leaves and rapid withering; the action is mos intense on grass and corn fields; trees are less susceptible.

Poultry, bees, &c., are often poisoned in the neighbourhood arsenical works from absorption of the dust.‡

Superphosphate of manure is frequently rich in arsenic. D Edmund Davy asserts that plants to which such manure i applied take up arsenic in their tissues, and M. Andouard ha made a similar statement. Tuson§ has also undertaken som experiments, which confirm Andouard and Davy's researche The bearing of this with relation to the detection of arsenic i the stomachs of the herbivora needs no comment.

II.—ANTIMONY.

§ 138. *Metallic Antimony.*—Atomic weight, 122; specif gravity, 6·715; fusing point, about 621°C. (1150°F.) In the cours of analysis, metallic antimony may be seen as a black powd thrown down from solutions; as a film deposited on copper platinum; and lastly, as a ring on the inside of a tube from th decomposition of stibine. At a bright-red heat it is volatilise slowly, even when hydrogen is passed over it; chlorine, bromin and iodine combine with it directly. It may be boiled in con centrated HCl without solution; but aqua regia, sulphides potassium and sodium readily dissolve it. The distinctio

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* 3 *Rep. Local Gov. Board.*

† *Ibid.*

‡ Eulenberg: "Gewerbe Hygiène."

§ Cooley's Dictionary, Art. *Arsenic.*

between thin films of this metal and of arsenic on copper and glass are pointed out at p. 385. It is chiefly used in the arts for purposes of alloy, and enters to a small extent into the composition of fireworks (*vide* p. 405).

§ 139. *Antimonious Sulphide.*—Sulphide of antimony = 340; composition in 100 parts, Sb 71·76, S 28·24. The commercial article, known under the name of black antimony, is the native sulphide, freed from siliceous matter by fusion, and afterwards pulverised. It is a crystalline metallic-looking powder, of a steel-grey colour, and is often much contaminated with iron, lead, copper, and arsenic.

The amorphous sulphide (as obtained by saturating a solution of tartar emetic with SH_2) is an orange-red powder, soluble in potash, ammonic, sodic, and potassic sulphides; and dissolving also in concentrated hydrochloric acid with evolution of SH_2. It is insoluble in water and dilute acid, scarcely dissolves in carbonate of ammonia, and is quite insoluble in bisulphite of potash. If ignited gently in a stream of carbonic acid gas, the weight remains constant. To render it anhydrous a heat of 200°C. is required.

The recognition of arsenic in the commercial sulphide is most easily effected by placing 2 grms. or more in a suitable retort (with condenser), adding hydrochloric acid, and distilling. The chloride of arsenic passes over before the chloride of antimony; and by not raising the heat too high, very little antimony will come over, even if the distillation be carried almost to dryness. The arsenic is detected in the distillate by the ordinary methods.

Several lamentable accidents have happened recently through mistaking the sulphide of antimony for oxide of manganese, and using it with chlorate of potash for the production of oxygen. The addition of a drop of hydrochloric acid, it is scarcely necessary to say, will distinguish between the two.

Antimony is frequently estimated as sulphide. An amorphous ersulphide of mercury, containing a small admixture of antimonious oxide and sulphide of potassium, is known under the name of *Kermes mineral*, and has lately been employed in the ulcanising of india-rubber. Prepared in this way, the latter may be used for various purposes, and thus become a source f danger. It behoves the analyst, therefore, in searching for ntimony, to take special care not to use any india-rubber fittings hich might contain the preparation.

A *pentasulphide of antimony* (from the decomposition of chleppe's salt [$Na_3S_6S_4 + 9H_2O$], when heated with an acid) is sed in calico-printing.

§ 140. *Tartarated Antimony, Tartrate of Potash and Antimony, or Tartar emetic*, is, in a medico-legal sense, the most important of the antimonial salts. Its formula is $KSbC_4H_4O_7H_2O$, and 100 parts, theoretically, should contain 38·2 per cent. of antimony. According to the B.P., 20 grains (1·296 grm.) dissolve without residue in an ounce (28·396 cc.) of water; and the solution gives with sulphuretted hydrogen an orange precipitate, which, when weighed and dried at 100°C. (212°F.), weighs 9·91 grains [·641 grm.] Tartar emetic occurs in commerce in colourless, transparent, rhombic, octahedral crystals, slightly efflorescing in dry air.

A crystal placed in the subliming cell (p. 284) decrepitates at 193·3°C. (380°F.), sublimes at 248·8°C. (480°F.) very slowly and scantily, and chars at a still higher temperature, 287·7°C. (550°F.) On evaporating a few drops of a solution of tartar emetic, and examining the residue by the microscope, the crystals are either tetrahedra, cubes, or branched figures. 100 parts of cold water dissolve 5 of tartar emetic, whilst the same quantity of boiling water dissolves ten times as much, viz., 50. The watery solution decomposes readily with the formation of algæ; it gives no precipitate with ferrocyanide of potassium, chloride of barium, or nitrate of silver, unless concentrated.

§ 141. *Metantimonic Acid*, so familiar to the practical chemist from its insoluble sodium salt, is technically applied in the painting of glass, porcelain, and enamels; and in an impure condition, as antimony ash, to the glazing of earthenware.

§ 142. *Pharmaceutical, Veterinary, and Quack Preparations of Antimony.*[*]

(1.) *Pharmaceutical Preparations*:—

Oxide of Antimony, Sb_2O_3, is a white powder, fusible at a low red heat, and soluble without effervescence in hydrochloric acid, the solution responding to the ordinary tests for antimony. Arsenic may be present in it as an impurity; the readiest means of detection is to throw small portions at a time on glowing charcoal when very small quantities of arsenic will, under such conditions, emit the peculiar odour. Carbonate of lime appears also to have been found in the oxide of commerce.

Antimonial Powder is composed of one part of oxide of anti

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[*] The history of antimony as a drug is curious. Its use was prohibited in France in 1566, because it was considered poisonous, one Besnier being actually expelled from the faculty for transgressing the law on this point. The edict was repealed in 1650; but in 1668 there was a fresh enactment confining its use to the doctors of the faculty.

mony and two parts of phosphate of lime; in other words, it ought to give 33·3 per cent. of Sb_2O_3.

Tartar Emetic itself has been already described. The preparations used in medicine are—

The Wine of Antimony (*Vinum antimoniale*), which is a solution of tartar emetic in sherry-wine, and should contain 10 grains of the salt in each ounce of the wine (2·27 grains in 100 cc.)

Antimony Ointment (*Unguentum antimonii tartarati*) is a mechanical mixture of tartar emetic and lard, or simple ointment;* strength 20 per cent.

There is no recorded case of conviction for the adulteration of tartar emetic; cream of tartar is the only probable addition. In such a case the mixture is less soluble than tartar emetic itself, and on adding a small quantity of carbonate of soda to a boiling solution of the suspected salt, the precipitated oxide, at first thrown down, becomes redissolved.

Solution of Chloride of Antimony is a solution of the terchloride in hydrochloric acid; it is a heavy liquid of a yellowish-red colour, powerfully escharotic; its specific gravity is 1·47. One drachm (3·549 cc.) mixed with 4 ounces (112 cc.) of a solution of tartaric acid (·25 : 4), gives a precipitate with SH_2, which weighs *at least* 22 grains (1·425 grm.) This liquid is used on very rare occasions as an outward application by medical men; farriers sometimes employ it in the foot-rot of sheep.

Sulphurated Antimony (*Antimonium sulphuratum*) is a mixture of sulphide of antimony, Sb_2S_3, with a small and variable amount of oxide, Sb_2O_3. The P. B. states that 60 grains (3·888 grms.) dissolved in HCl, and poured into water, should give a white precipitate of oxychloride of antimony, which (properly washed and dried) weighs about 53 grains (3·444 grms.) The officinal compound-pill of subchloride of mercury (*Pilula hydrargyri subchloridi composita*) contains 1 grain (·0648 grm.) of sulphurated antimony in every 5 grains (·324 grm.), *i.e.*, 20 per cent.

(2.) *Patent and Quack Pills* :—

Dr. J. Johnson's Pills. From the formula each pill should contain,—

	Grains.	Grms.
Compound Extract of Colocynth,	2·5	·162
Calomel, ...	·62	·016
Tartar Emetic, ...	·04	·002
Oil of Cassia, ...	·12	·007
	3·28	·187

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* Simple ointment is composed of white wax 2, lard 3, almond oil 3.

The oil of cassia can be extracted by petroleum ether; the calomel sublimed and identified by the methods given in the article on *Mercury;* the antimony deposited in the metallic state on platinum or tin; and the colocynth identified as under article *Beer*.

Mitchell's Pills contain in each pill—

	Grains.	Grms.
Aloes,	1·1	·070
Rhubarb,	1·6	·103
Calomel,	·16	·010
Tartar Emetic,	·05	·003
	2·91	·186

The mineral substances in this are easy of detection by the methods already given; the aloes by the formation of chrysammic acid, and the rhubarb by its microscopical characters.

Dixon's Pills probably contain the following in each pill:—

	Grains.	Grms.
Compound Extract of Colocynth,	2·0	·1296
Rhubarb,	1·0	·0648
Tartar Emetic,	·06	·0038
	3·06	·1982

(3.) *Antimonial Medicines, chiefly Veterinary.*[*]

Liver of Antimony is a preparation formerly much used by farriers. It is a mixture of antimonious oxide, sulphide of potassium, carbonate of potassium, and undecomposed trisulphide of antimony (and may also contain sulphate of potassium), all in very undetermined proportions. When deprived of the soluble potash salts, it becomes the *washed saffron of antimony* of the old pharmacists. A receipt for a grease-ball, in a modern veterinary work, gives, with liver of antimony, cream of tartar and guiacum as ingredients.

Hind's Sweating-ball is composed of 60 grains (3·888 grms.) of tartar emetic and an equal portion of assafœtida, made up into a

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[*] There has long prevailed an idea (the truth of which is doubtful) that antimony, given to animals, improves their condition; thus, the *Encyclop. Brit.*, 5th ed., Art. "Antimony"—"A horse that is lean and scrubby, and not to be fatted by any means, will become fat on taking a dose of antimony every morning for two months together. A boar fed for brawn, and having an ounce of antimony given him every morning, will become fat a fortnight sooner than others put into the stye at the same time, and fed in the same manner, but without the antimony." Probably the writer means by the term *antimony* the impure sulphide.

ball with liquorice powder and syrup. The assafœtida will be readily detected by the odour, and the antimony by the methods already recommended.

Ethiops of Antimony, very rarely used now, is the mechanical mixture of the sulphides of antimony and mercury,—proportions, 3 of the former to 2 of the latter.

The Flowers of Antimony is an impure oxysulphide of antimony, with variable proportions of trioxide and undecomposed trisulphide.

Diaphoretic Antimony (*calcined antimony*) is simply antimoniate of potash.

Glass of Antimony is a mixture of sulphide and oxide of antimony, contaminated with a small quantity of silica and iron. A quack pill, by name *Ward's Red Pill*, is said to contain glass of antimony and dragon's blood.

Antimonial Compounds used in Pyrotechny—

Blue fire :—

Antimonious Sulphide,	1
Sulphur,	2
Nitre,	6

This composition is used for the blue or Bengal signal-light at sea. Bisulphide of carbon and water are solvents which will easily separate the powder into its three constituents.

Crimson fire :—

Potassic Chlorate,	17·25
Alder or Willow Charcoal,	4·5
Sulphur,	18·
Nitrate of Strontia,	55·
Antimonious Sulphide,	5·5

The spectroscope will readily detect strontia and potassium, and the analysis presents no difficulty. In addition to these a very great number of other pyrotechnical preparations contain antimony.

§ 143. *Alloys.*—Antimony is much used in alloys. The ancient *Pocula emetica*, or everlasting emetic cups, were made of antimony, and with wine standing in them for a day or two they acquired emetic properties. The principal antimonial alloys are Britannia and type metal, the composition of which is as follows :—

		Tin, per cent.	Copper, per cent.	Antimony, per cent.
Britannia Metal,	Best,	92·0	1·8	6·2
	Common,	92·1	2·0	5·9
	For Castings,	92·9	1·8	5·3
	For Lamps,	94·0	1·3	4·7

		Tea Lead, per cent.	Antimony, per cent.	Block Tin, per cent.
Type metal,	(1.)	75	20	5
	(2.)	70	25	5
Metal for Stereotype,	.	84·2	13·5	2·3

There is also antimony in brass, concave mirrors, bell-metal, &c.

§ 144. *Pigments.*—Cassella and Naples Yellow are principally composed of the antimoniate of lead.

Antimony Yellow is a mixture of antimoniate of lead with basic chloride of lead.

§ 145. *Dose.*—A medicinal dose of a soluble antimonial salt should not exceed a grain and a half (·0648 grm.) With circumstances favouring its action, a dose of 2 grains (·1296 grm.) has proved fatal;[*] but this is quite exceptional, and few medical men would consider so small a quantity dangerous for a healthy adult, especially since most posological tables prescribe tartar emetic as an emetic in doses from 1 to 3 grains (·0648 to ·1924 grm.). The smallest dose which has killed a child appears to be $\frac{3}{4}$ of a grain (·048 grm.).[†] The dose of tartar emetic for horses and cattle is very large, as much as 90 grains (5·832 grms.) being often given to a horse in his gruel three times a day. 60 grains (3·8 grms.) are considered a full, but not an excessive, dose for cattle; 6 grains are used as an emetic for pigs, and half this quantity for dogs.

§ 146. *Detection of Antimony in Organic Matters.*—In acute poisoning by tartar emetic it is not impossible to find a mere trace only in the stomach, the greater part having been expelled by vomiting, which nearly always occurs early, so that the most certain method is, where possible, to analyse the vomit. In cases of slow poisoning the brain and spinal cord should always be examined: for, like arsenic, antimony accumulates in the nervous tissues.[‡] If it should be suspected that a living person is being slowly poisoned by antimony, it must be remembered that the poison is mainly excreted by the kidneys, and the urine should afford some indication. The readiest way to test is to collect a considerable quantity of the urine (if necessary, two or three days' excretion), concentrate by evaporation, acidify, and then transfer the liquid to a platinum dish, in which is placed a slip of zinc. The whole of the antimony is in time deposited on the platinum dish, and being thus concentrated, may be subsequently identified in any way thought fit.

Organic liquids are boiled with hydrochloric acid; organic solids are extracted with the same acid in the manner described,

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[*] Taylor: *Guy's Hospital Reports*, Oct., 1857.

[†] *Op. cit.*

[‡] Millon et Reiset. *Ann. de Chimie,* 1845, 787.

p. 244; or, if the distillation process given at p. 399 be employed, the antimony may be found partly in the distillate, and partly in the retort. In any case, antimony in solution may be readily detected in a variety of ways, one of the most convenient being to concentrate on tin or platinum, to dissolve off the antimonial film by sulphide of ammonium, and thus produce the very characteristic orange sulphide.

If a slip of pure tinfoil be suspended for six hours in a solution, which should not contain more than one-tenth of its bulk of HCl, and exhibit no stain or deposit, it is certain that antimony cannot be present. Antimony may also conveniently be deposited on a platinum dish,* by filling the same with the liquid properly acidulated, and inserting a rod of zinc; the metallic antimony can afterwards be washed, dried, and weighed.

Reinsch's and Marsh's tests have been already described (pp. 383, 385), and require no further notice. There is, however, a very beautiful and delicate means of detecting antimony, which should not be omitted. It is based upon the action of stibine (SbH_3) on sulphur.† When this gas is passed over sulphur, it is decomposed according to the equation, $2SbH_3 + 6S = Sb_2S_3 + 3SH_2$, the action taking place slowly in diffused daylight, but very rapidly in sunshine. An ordinary flask for the evolution of hydrogen (either by galvanic processes or from zinc and sulphuric acid), with its funnel and drying-tubes, is connected with a narrow tube having a few fragments of sulphur, kept in place by plugs of cotton wool. The whole apparatus is placed in sunshine; if no orange colour is produced when the hydrogen has been passing for some time, the liquid to be tested is poured in gradually through the funnel, and if antimony should be present, the sulphur acquires a deep orange colour. This is distinct even when so small a quantity as ·0001 grain has been added through the funnel. The sulphide of antimony thus mixed with sulphur can, if it is thought necessary, be freed from the sulphur by repeated exhaustion with bisulphide of carbon. The stibine does not, however, represent all the antimony introduced, a very large proportion remaining in the evolution flask;‡ hence it

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* According to Fresenius (*Zeitschr. f. Ann. Chem.*, i. 445), a solution which contains $\frac{1}{10000}$ of its weight of antimony, treated in this way, gives in two minutes a brown stain, and in ten a very notable and strong dark-brown film. When in the proportion of 1 to 20,000, the reaction begins to be certain after a quarter of an hour; with greater dilution it requires longer time, 1 to 40,000 giving a doubtful reaction, and 1 to 50,000 not responding at all to this test.

† See Ernest Jones on Stibine, *Journ. Chem. Soc.*, i., 1876.

‡ Rieckher: *Jahresbericht*, 1865, p. 255.

cannot be employed for quantitative purposes. Moreover, the test can, of course, only be conveniently applied on sunny days, and is therefore in England more adapted for summer.* Often, however, as mentioned elsewhere, when the analyst has no clue whatever to the nature of the poison, it is convenient to pass SH_2 in the liquid to saturation.† In such a case, if antimony is present (either alone or in combination with other sulphides), it remains on the filter, and must be separated and identified as follows :—The sulphides are first treated with a solution of carbonate of ammonia, which will dissolve arsenic, if present, and next saturated *in situ* with pure sulphide of sodium, which will dissolve out sulphide of antimony, if present. The sulphide of antimony will present the chemical characters already described, more particularly—

(1.) It will evolve SH_2 when treated with HCl, and at the same time pass into solution.‡

(2.) The solution evaporated to get rid of free HCl gives with water a thick cheesy precipitate of basic chloride of antimony. This may be seen if only a drop or two of the solution is taken and tested in a watch-glass.

(3.) If tartaric acid be added to the solution, this precipitation does not occur.

(4.) The solution from (3.) gives an orange precipitate with SH_2.

Such a substance can only be sulphide of antimony. With regard to (2.), bismuth would act similarly, but under the circumstances could not be present, for the sulphide of bismuth is insoluble in sodic sulphide.

§ 147. *Quantitative Estimation.*—The quantitative estimation of antimony is best made by some volumetric process—*e.g.*, the sulphide can be dissolved in HCl, some tartrate of soda added, and then carbonate of soda to weak alkaline reaction. The strength of the solution of tartarised antimony thus obtained can now be estimated by a decinormal solution of iodine,

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* The action of salts of caesium with chloride of antimony might be used as a test for the latter. A salt of caesium gives a white precipitate with chloride of antimony in concentrated ClH; it contains 30·531 per cent. of antimony, and corresponds to the formula $SbCl_3CsCl$. Chloride of tin acts similarly.—E. Godeffroy: *Berichte der Deutschen Gesellschaft.* Berlin, 1874.

† The solution must not be too acid.

‡ By adding chloride of tin to a solution of chloride of antimony in sufficient quantity, and passing SO_2 through the liquid, the whole of the antimony can be thrown down as sulphide, whilst the tin remains in solution. Thus,—

$$9SnCl_2 + 2SbCl_3 + 3SO_2 + 12ClH = Sb_2S_3 + 9SnCl_4 + 6OH_2.$$

—Federow: *Zeitschrift für Chemie*, 1869, 16.

the end reaction being indicated by the previous addition of a little starch solution, or by a solution of permanganate of potash, either of which should be standardised by the aid of a solution of tartar emetic of known strength.

III.—CADMIUM.

§ 148. *Cadmium*, Cd = 112; specific gravity, 8·6 to 8·69; fusing point, 227·8°C. (442°F.); boiling point, 860°C. (1580°F.)—Cadmium in analysis is seldom separated as a metal, but is estimated either as oxide or sulphide.

§ 149. *Cadmium Oxide*, CdO = 128—cadmium 87·5 per cent., oxygen 12·5 per cent.—is a yellowish or reddish-brown powder, non-volatile even at a white heat; insoluble in water, but dissolving in acids. Ignited on charcoal, it is reduced to metal, which volatilises, and is then deposited again as oxide, giving to the coal a distinct coat of an orange-yellow colour in very thin layers —in thicker layers, brown.

§ 150. *Cadmium Sulphide*, CdS = 144—Cd 77 to 78 per cent., S 22 to 23 per cent.—known as a mineral termed Greenockite. When prepared in the wet way it is a lemon-yellow powder, which cannot be ignited in hydrogen without loss, and is insoluble in water, dilute acids, alkalies, alkaline sulphides, sulphate of soda, and cyanide of potassium. The solution must not contain too much hydrochloric acid, for the sulphide is readily soluble with separation of sulphur in concentrated hydrochloric acid. It may be dried in the ordinary way at 100°C. without suffering any decomposition.

§ 151. *Medical Preparations.—The Iodide of Cadmium* (CdI_2) occurs in white flat micaceous crystals, melting at about 315·5°C. (600°F.), and at a dull red heat giving off violet vapour. In solution the salt gives the reactions of iodine and cadmium. The B. P. states that 10 grains dissolved in water give a precipitate, which, after being washed with water, and then with half an ounce of solution of ammonium, and dried, weighs 12·5 grains (or 1 grm. gives a silver precipitate weighing 1·25 grm.) The ointment of iodide of cadmium (*Unguentum cadmii iodidi*) contains the iodide in the proportion of 62 grains to the ounce, or 2·9 per cent.

Cadmium Sulphate is officinal in the German and French pharmacopeias.

§ 152. *Cadmium in the Arts*, &c.—Cadmium is used in various lloys. The sulphide is found as a colouring ingredient in certain toilet-soaps, and it is much valued by artists as a pigment. The iodide of cadmium is employed in photography and an amalgam of metallic cadmium to some extent in dentistry

§ 153. *Fatal Dose of Cadmium.*—Although no deaths from cadmium appear to have as yet occurred, its growing use in photography, &c., may lead to accidents. There can be no question about the poisonous action of cadmium, for Marmé * in his experiments with it on animals observed giddiness, vomiting, syncope, difficulty in respiration, loss of consciousness, and cramps. The amount necessary to destroy life can only be gathered from the experiments on animals: a strong hound died after the injection of ·03 grm. (·462 grain) subcutaneously of a salt of cadmium; kittens are poisoned if from ·30 to ·6 grain (·0194 to ·0388 grm.) are introduced into the stomach. A watery solution of ·5 grm. (7·5 grains) of the bromide administered to a dove caused instant death, without convulsion; the same dose of the chloride killed a second dove in six minutes. ·25 grm (3·85 grains) of sulphite of cadmium administered to a pigeon excited vomiting, and after two hours diarrhœa; it died in eight days. Another pigeon died from a similar dose in fourteen days, and cadmium, on analysis, was separated from the liver. From the above cases it would seem probable that a drachm would be a *dangerous dose* of a soluble salt of cadmium and that in a case of chronic poisoning it would most probably be found in the liver.

§ 154. *Separation and Detection of Cadmium.*—If cadmium be in solution, and the solution is not too acid, on the addition of SH_2 there is precipitated a yellow sulphide, which is distinguished from antimony and arsenical sulphides by its insolubility in ammonia and alkaline sulphides. Should all three sulphides be on the filter (an occurrence which will seldom, perhaps never, happen), the sulphide of arsenic can be dissolved out by ammonia, the antimony by sulphide of sodium, leaving the sulphide of cadmium as the residue.†

The further tests of the sulphide are :—

(1.) It dissolves in dilute nitric acid to a colourless fluid, with separation of sulphur.

(2.) The solution filtered and freed from excess of nitric acid by evaporation, gives a white precipitate of carbonate of cadmium insoluble in excess. This distinguishes it from zinc which gives a similar white precipitate, but is soluble in excess of the precipitant.

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* *Zeitschr. f. Rationelle Med.*, xxix. 1. 1867.

† It is unnecessary to state that absence of sulphur is supposed.

(3.) The carbonate thus obtained, treated in platinum foil, is changed into the brown-red non-volatile oxide.

(4.) The oxide behaves in charcoal as already detailed.

(5.) A metallic portion can be obtained by melting the oxide with cyanide of potash; it is between zinc and tin in brilliancy, and makes a mark on paper like lead, but not so readily. There are many other tests, but the above are conclusive.

If cadmium in any case be specially searched for in the organs or tissues, the latter should be boiled with nitric acid. The acid solution is filtered, saturated with caustic potash, evaporated to dryness, and ignited; the residue is dissolved in dilute hydrochloric acid, and treated after filtration with SH_2. Cadmium may also be estimated volumetrically by digesting the sulphide in a stoppered flask with ferric chloride and hydrochloric acid; the resulting ferrous compound is titrated with permanganate, each cc. of a d.n. solution of permanganate = ·0056 grm. of cadmium.

(II.) PRECIPITATE BY HYDRIC SULPHIDE IN HYDROCHLORIC ACID SOLUTION—BLACK.

LEAD—COPPER—BISMUTH—SILVER—MERCURY.

I. LEAD.

§ 155. *Lead and its Oxides.*—Lead is a well-known bluish-hite, soft metal; fusing point, 325°C.; specific gravity, 11·36.

Oxides of Lead.—The two oxides of lead necessary to notice ere briefly are—litharge and minium.

Litharge, or Oxide of Lead, $PbO = 223$; specific gravity, 9·2 to ·5—Pb 92·82 per cent., O 7·18—is either in crystalline scales, fused mass, or a powder, varying in colour (according to its ode of preparation) from yellow to reddish-yellow or orange. hen prepared below the temperature of fusion it is called *massicot.*" It may be fused without alteration in weight; in state of fusion it dissolves silica acid and silicates of the earths. must not be fused in platinum vessels.

Minium, or Red Lead, $2PbO,PbO_2$; specific gravity 9·08, is a mpound of protoxide of lead with the dioxide. It is of a brilliant red colour, much used in the arts, and especially in th preparation of flint-glass.

§ 156. *Sulphide of Lead*, PbS = 239; Pb 86·61 per cent., 13·39 per cent., occurring in the usual way, is a black precipitat insoluble in water, dilute acids, alkalies, and alkaline sulphide It dissolves in strong nitric acid with separation of sulphu in strong hydrochloric acid with evolution of SH_2. Fumin nitric acid does not separate sulphur, but converts the sulphid into sulphate.

§ 157. *Sulphate of Lead*, $PbSO_4$ = 303; specific gravity, 6·3 PbO 73·61 per cent., SO_2 26·39 per cent.—when produced arti ficially is a heavy white powder, of great insolubility in wate 22,800 parts of cold water dissolving only one of lead sulphate and if the water contains sulphuric acid, no less than 36,500 part of water are required. The salts of ammonia (especially th acetate and tartrate) dissolve the sulphate, and it is also solubl in hyposulphite of soda. The sulphate can be readily change into the carbonate of lead, by boiling it with solutions of th alkaline carbonates. The sulphate of lead, fused with cyanid of potassium, yields metallic lead; it may be also reduced o charcoal, and alone it may be fused without decomposition provided reducing gases are excluded.

§ 158. *Acetate of Lead, Sugar of Lead*, $Pb(C_2H_3O_2)_2 3OH_2$, is found in commerce in white spongy masses composed of acicula crystals. It may, however, be obtained in flat four-sided prisms It has a sweet metallic taste, is soluble in water, and respond to the usual tests for lead. The P.B. directs that 38 grms. dissolved in water, require, for complete precipitation, 200 grai measures of the volumetric solution of oxalic acid, correspondin to 22·3 grms. of oxide of lead.

§ 159. *Chloride of Lead*, $PbCl_2$ = 278; specific gravity, 5·8— Pb 74·48 per cent., Cl 25·52 per cent.—is in the form o brilliant crystalline needles. It is very insoluble in cold wate containing hydrochloric or nitric acids. According to Bischof 1635 parts of water containing nitric acid dissolve one part onl of chloride of lead. It is insoluble in absolute alcohol, an sparingly in alcohol of 70 to 80 per cent. It fuses below re heat without losing weight; at higher temperatures it may b decomposed.

§ 160. *Carbonate of Lead.*—The commercial carbonate of lea (according to the recent very exhaustive researches of Wigne and Harland*) is composed of a mixture of neutral carbonate o

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* On the Composition of Commercial Samples of White Lead, by G. W. Wigner and R. H. Harland.—*Analyst*, 1877, p. 208.

lead and hydrate of lead; the best mixture being 25 per cent. of hydrate, corresponding to an actual percentage of 12·3 per cent. carbonic acid. The nearer the mixture approximates to this composition the better the paint; whilst samples containing as much as 16·33 per cent., or as little as 10·39 per cent., of CO_2 are practically useless.

§ 161. *Preparations of Lead used in Medicine, the Arts, &c.*

(1.) *Pharmaceutical:—*

Lead Plaster (*Emplastrum plumbi*) is simply a lead soap, in which the lead is combined with oleic and margaric acids.

Lead Iodide, PbI_2, is contained in the *Emplastrum plumbi iodidi,* to the extent of 20 per cent., and in the *Unguentum plumbi iodidi* to the extent of about 11·4 per cent.

Acetate of Lead is contained in a pill, a suppository, and an ointment. The pill, *Pilula plumbic opio,* contains 74 per cent. of lead acetate, and 12·5 per cent. of opium, the rest confection of roses. The suppository (*Suppositoria plumbi composita*) contains 20 per cent. of acetate of lead, and 10 per cent. of opium, mixed with oil of theobroma, white wax, and benzoated lard. The ointment (*Unguentum plumbi acetatis*) contains 24 per cent. of lead acetate, mixed with benzoated lard.

The solution of subacetate of lead (*Liquor plumbi subacetatis*) is the subacetate, $Pb(C_2H_3O_2)_2PbO$, dissolved in water. The P.B. states that 413·3 grains by weight (6 fluid drachms) require for perfect precipitation 810 grain measures of the volumetric solution of oxalic acid, corresponding to about 30 grains of lead. In other words, the solution must contain at least 8·1 per cent. of oxide of lead.

A dilute solution of the stronger, under the name of *Liquor plumbi subacetatis dilutus,* and commonly called Goulard water, is prepared by mixing 1·25 part (by volume) of the solution, and 1·25 part of spirit, and making up to 100 parts with distilled water.

There is an ointment, called the *Compound Ointment,* of subacetate of lead, which contains the subacetate in about the proportion of 2 per cent of the oxide, the other constituents being amphor, white wax, and almond oil.

Carbonate of Lead.—The ointment (*Unguentum plumbi caronatis*) should contain about 11·4 per cent of the carbonate, and he rest simple ointment.

(2.) *Quack Nostrums,* &c. :—

The quack medicines composed of lead are not very numerous.

Liebert's *Cosmetique Infaillible* is said to have for its bas nitrate of lead.

One of "*Ali Ahmed's Treasures of the Desert,*" viz., the autosept malagma, is a plaster made up of lead plaster 37·5 per cent gum thus 25 per cent., salad oil 25 per cent., beeswax 12·5 p cent.

Lewis' Silver Cream contains white precipitate and a salt lead.

Goulard's Balsam is made by triturating acetate of lead wit hot oil of turpentine.

There are various ointments in use made up of litharg Some herbalists in the country (from cases that have come und the writer's own knowledge) apply to cancerous ulcers, &c., a lin ment of linseed and other common oils mixed with litharg and acetate of lead.

Acetate of lead may be also found as a constituent of variou eye-waters.

(3.) *Preparations of Lead used in the Arts, &c.*:—

Ledoyen's Disinfecting Fluid has for its basis nitrate of lead.

In various hair-dyes, the following are all used:—Litharg lime, and starch; lime and carbonate of lead; lime and acetat of lead; litharge, lime, and potassic bicarbonate. The dete tion of lead in the hair thus treated is extremely easy; it ma be dissolved out by dilute nitric acid.

Lead Pigments.—The principal pigments of lead are whit yellow, and red.

White Pigments:—

White Lead, Flake White, Ceruse, Mineral White, are so man different names for the carbonate of lead already described.

Newcastle White is white lead made with molasses vinegar.

Nottingham White.—White lead made with alegar (sour ale often, however, replaced by permanent white, *i.e.*, sulphate baryta.

Miniature Painters' White, White Precipitate of Lead, is simpl lead sulphate.

Pattison's White is an oxychloride of lead, $PbCl_2PbO$.

Yellow Pigments:—

Chrome Yellow may be a fairly pure chromate of lead, or it ma be mixed with sulphates of lead, barium, and calcium. Th pigment known as Cologne yellow consists of 25 parts of lea chromate, 15 of lead sulphate, and 60 of calcic sulphate. Th easiest method of analysing chrome yellow is to extract wit boiling hydrochloric acid in the presence of alcohol, which di solves the chromium as chloride, and leaves undissolved chlorid of lead, sulphate of lead, and other substances insoluble in ClH

Every grain of chromate of lead should yield 0·24 grain of oxide of chromium, and 0·4 grain of chloride of lead.

Turner's Yellow, Cassella Yellow, Patent Yellow, is an oxychloride of lead ($PbCl_27PbO$) extremely fusible.

Dutch Pink sometimes contains white lead.

Red Pigments:—

Chrome Red is a bichromate of lead.

Red Lead or *Minium,* is the red oxide of lead.

Orange Red is an oxide prepared by calcining the carbonate.

The chief preparations of lead which may be met with in the arts, in addition to the oxides and the carbonate, are—

The *Nitrate of Lead,* much used in calico-printing.

The *Pyrolignite of Lead,* which is an impure acetate used in dyeing; and

The *Sulphate of Lead* is a by-product in the preparation of acetate of aluminium for dyeing.

The alloys containing lead are extremely numerous; but, according to the experiments of Knapp,[*] the small quantity of lead in those used for household purposes has no hygienic importance.

§ 162. *Lead as a Poison.*—All the compounds of lead are said to be poisonous; but this statement cannot be regarded as entirely correct, for the sulphocyanide has been proved by experiment not to be so,[†] and the sulphide is also probably inactive. In the treatment of cases of lead poisoning, however, the flowers of sulphur given internally appears to be successful.[‡]

Lead poisoning, either in its obscure form (producing uric acid in the blood, and, as a consequence, indigestion and other evils), or in the acute form (as lead colic and various nervous affections), is most frequent among those who are habitually exposed to the influence of the metal in its different preparations, viz.—workers of lead, house-painters, artists, gilders, workers of arsenic, workers of gold, calico-printers, colourists, type-founders, type-setters, shot-founders, potters, faience makers, braziers, and many others.[§]

Lead, again, has been found by the analyst in most of the ordinary foods, such as flour, bread, beer, cider, wines, spirits, tea, vinegar, sugar, confectionery, &c., as well as in numerous drugs, especially those manufactured by the aid of sulphuric acid (the

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[*] *Dingl. Polyt. Journ.*, ccxx. 446–453.

[†] Eulenberg, "Gewerbe Hygiène," p. 712.

[‡] "Mohr's Toxicologie," 78.

[§] The attention which the use of lead in the arts has always excited is evident from the fact that one of the oldest works on Trade Hygiène (by Stockhausen) is entitled, "De lithargyrii fumo noxio, morbifico ejusque metallico frequentiori morbo, vulgo dicto *hüttenkatze*," Goslar, 1556.

latter nearly always containing lead), and those salts or chemica products which (like citric and tartaric acids) are crystallised i leaden pans. Hence it follows that in almost everything eate or drunk the analyst, as a matter of routine, tests for lead. Th channels through which it may enter into the system are, however, so perfectly familiar to practical chemists, that a few *unusu* instances of lead-poisoning only need be quoted here.

A cabman suffered from lead colic, traced to his taking the firs glass of beer every morning at a certain public-house; the bee standing in the pipes all night, as proved by analysis, was strongl impregnated with lead.[*]

The employment of red lead for repairing the joints of stea pipes has before now caused poisonous symptoms from volatilisation of lead. [†] The use of old painted wood in a baker's ove and subsequent adherence of the oxide of lead to the outside the loaves, has recently caused the illness of sixty-six people. [‡]

Seven persons became affected with lead-poisoning throug horse-hair coloured with lead.[§]

The manufacture of *American overland cloth* creates a whit lead dust, which has caused serious symptoms among th workmen (*Dr. G. Johnson*). The cleaning of pewter pots, [||] th handling of vulcanised rubber,[¶] the wrapping up of variou foods in tinfoil, [**] have all caused accidents in man.

Cattle are also more or less frequently poisoned by lead. I one case under the writer's notice, a field had been manure with the refuse of a plumber's yard; the young cattle, attracte by the linseed oil, greedily ate the lumps of paint scattered abou the field, with a fatal result in many instances.[††] Casks repaire with old lead have been used in the mashing of malt; th malt subsequently given to cattle has caused death. [‡‡] Taylo also relates the curious instance of the death of cattle fro eating grass covered with the splashes of lead coming from butts. [§§]

The lead in glass, though in the form of an insoluble silicat is said to have been dissolved by vinegar and other acid fluids t a dangerous extent. This, however, is hardly well established. [||||]

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[*] *Chem. News.*

[†] Eulenberg, *op. cit.*, 708.

[‡] *Annales d'Hygiène.*

[§] Hitzig, "Studien über Bleivergiftung."

[||] *Med. Gazette*, xlviij. 1047.

[¶] *Pharm. Journ.*, 1870, 426.

[**] Taylor, "Prin. Med. Jurisprudence," I.

[††] The symptoms in these cattle were those of uraemic poisoning; in on there was blindness (*Retinitis albuminuria*), and the kidneys were degene rated precisely as in Bright's disease.

[‡‡] Eulenberg, *op. cit.*, 707.

[§§] Taylor, *op. cit.*

[||||] See *Aertzl. Intelligenzblatt. f. Baiern.*, Jahr., 1869; *Buchner's Rep.* *Pharm.* Bd. 19, p. 1; *Med. Centrbl.*, Jahr., 1869, p. 40.

Localisation of Lead in the Human Body.—According to Henbel,* the osseous tissues take up most lead, then the kidneys and liver, the brain and spinal cord, and, lastly, the muscles, heart, and lungs; the latter organs standing last. It is of no value to search the blood for lead; for although Tiedemann, Gmelin, Lassaigne, Chevallier, and others have frequently done so, only traces have been found. It nevertheless is taken up by the blood, and forms with organic bodies compounds soluble with difficulty.

Without going so far as to say that lead is a natural constituent of the body, it is certain that it may be frequently met with in persons who have been apparently perfectly healthy, and quite free from all symptoms of lead poisoning. Legrip found in the liver and spleen of a healthy person, 5·4 mgrms. of lead oxide in every kilogram; Oidtmann, in the liver of a man 56 years of age, 1 mgrm. of lead oxide per kilogram, and in the spleen 3 mgrms. per kilogram. Hence the analyst in searching for poison must be very careful in his conclusions. Grave and serious errors may also arise from complications; suppose, *e.g.*, that a deceased person previous to death had partaken of game, and inadvertently swallowed a shot—if the analyst had not carefully searched the contents of the stomach for *solid* bodies, but merely treated them at once with acid solvents, he would naturally get very decided lead reactions, and would possibly conclude, and give evidence to the effect, that a poisonous soluble salt of lead had been administered shortly before death.

§ 163. *Detection and Estimation of Lead.*—A great number of fluids (such as beer, wines, vinegar, water, &c.), if they contain anything like the amount of one-tenth of a milligramme in 100 cc. will give a very marked dark colour with SH_2. It is, however, usually safest in the first place to concentrate the liquid, to add an acid, and deposit the lead on platinum, in the way to be shortly described. Nearly all the lead from oils and fatty matter may be dissolved out by shaking up the fat with dilute nitric acid; if necessary, the fat should previously be melted.

If (in the usual course of routine research) a hydrochloric acid solution is obtained from the treatment or destruction of organic substances by that agent, and lead sulphide (mixed possibly with other sulphides) is filtered off, any arsenical sulphide may irst be extracted from the filter by ammonia, and any antimonious sulphide by sodic sulphide; then the sulphide may be extracted by warm hydrochloric acid, which will leave undisolved such sulphides as those of copper and mercury. On

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* "Pathogenese u. Symptomatologie der chron. Bleivergiftung." Berlin, 871, p. 66.

diluting the liquid, and filtration at a boiling temperatur crystals of lead chloride will be deposited on cooling.

If, however, organic matters are *specially* searched for lea hydrochloric acid is not the best solvent, but nitric should alwa be preferred; and if there is reason to think that the lead exis in the form of sulphate, then the proper solvent is either tl acetate or the tartrate of ammonia; but in either case the soluti should contain an excess of ammonia. It must, however, remembered that organic matters retain lead with great tenacit and that in all cases where it can with any convenience effected, the substances should be not only carbonised, but bur to an ash; for Boucher has shown * that carbon retains lead, an that the lead in carbon resists to a considerable extent the actio of solvents.

In the case of sulphate of lead, which may be always produc in an ash from organic substances by previous treatment wi sufficient sulphuric acid, a very excellent method of identific tion is to convert it into sugar of lead. To do this, it is mere necessary to boil it with carbonate of ammonia, which changes into carbonate of lead; treatment with acetic acid will now gi the acetate; the solution may (if the lead is in very small qua tity) be concentrated in a watch-glass, a drop evaporated dryness on a circle of thin microscopic glass, and the cryst examined by the microscope; the same film next exposed to t fumes of HS_2, which will blacken it; and lastly, the soluti (which should be sweet) tasted. A crystalline substance, p sessing a sweet taste and blackening when exposed to SH_2, ca under the circumstances, be none other than acetate of lead.

If the analyst does not care for this method, there is room f choice. A solution containing lead can be converted into su phide; in this case it is, however, absolutely necessary that the should be no great excess of acid, since as little as 2·5 p cent. of free hydrochloric acid will prevent all the lead goi down. On obtaining the sulphide, the latter, as alrea described, can be converted into chloride by hydrochloric aci and the crystalline chloride is extremely characteristic.

From the solution of the chloride, the metal may be obtain in a solid state by inserting a piece of zinc in the solution co tained in a crucible; the lead will be deposited gradually, an can be then collected, washed, and finally fused into a litt globule on charcoal. A lead bead flattens easily when hit with hammer, and makes a mark on paper. Solutions of the chlori also give a heavy precipitate of lead sulphate, when treated wi a solution of sodic sulphate.

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* *Ann. d'Hygiène*, t. xli.

When lead is in very minute quantity, an electrolytic method is generally preferable; the lead is precipitated on platinum by using a similar apparatus to that in Bloxam's test, described at p. 391; the liquid to be tested being placed in the inner cell, on identification of the lead film, it may be dissolved in nitric acid, and estimated by a colorimetric process. For the estimation of the minute fractions of a grain by a colour method, it is merely necessary to have a very dilute solution of acetate of lead, to add a known volume of SH_2 water to the liquid to be tested in a Nessler cylinder, noting the colour, and add to another a known quantity of the standard lead solution and the same quantity of SH_2 as was added to the first.

The process has an advantage which is great, viz., that it either detects copper or proves its absence at the same time; and there are few cases in which the analyst does not look for copper as well as for lead. Lead, if in sufficient quantity, may be most conveniently estimated as oxide, sulphate, or chloride; the chief properties of these substances have been already described.

II.—COPPER.

§ 164. *Copper*, $Cu = 63·5$; specific gravity, from 8·921 to 8·952; fusing point, 1091°C. (1996 °F.) Copper in analysis occurs either as a film or coating on such metals as platinum, iron, &c., or in a state of fine division; or, finally, as a bead. In thin films, copper has a yellowish or a yellowish-red colour; it dissolves readily in nitric, slowly in hydrochloric acid. If air be excluded hydrochloric acid fails to dissolve copper, and the same remark applies to ammonia; but if there be free access of air, ammonia also acts as a slow solvent. Metallic copper in a fine state of division can be fused at a white heat to a bright bluish-green globule, which, on cooling, is covered with black oxide.

§ 165. *Cupric Oxide* ($CuO = 79·5$; specific gravity, 6·5; composition in 100 parts, Cu 79·85, O 20·15) is a brownish-black powder, which remains in the absence of reducing gases unaltered at a red heat. It is nearly insoluble in water, but soluble in ClH, NO_3H, &c.; it is hygroscopic, and, as every one who has made a combustion knows, is readily reduced by ignition with charcoal n the presence of reducing gases.

§ 166. *Cupric Sulphide*, $CuS = 95·5$, produced in the wet way, s a brownish powder so insoluble in water that, according to Fresenius, 950,000 parts of water are required to dissolve one part. t is not quite insoluble in ClH, and dissolves readily in nitric acid with separation of sulphur. By ignition in a stream of H_2, it may be converted into the subsulphide of copper. It must always be washed by SH_2 water.

§ 167. *Solubility of Copper in Water and Various Fluids.*—The solubility of copper in water and saline solutions has been very carefully studied by Carnelley.[*] Distilled water exerts some solvent action, the amount varying, as might be expected, according to the time of exposure, the amount of surface exposed, the quantity of water acting upon the copper, &c. It would appear that, under favourable circumstances, 100 cc. of distilled water may dissolve ·3 mgrm. of copper (·2 grain per gallon).

With regard to salts, those of ammonium exert a solvent action on copper, more decided than that of any others known. With the others, however, the nature of the base exerts little influence, the action of the salt depending chiefly on the nature of its acid radical. Thus, beginning with the least affected, the following is the order of dissolving strength :—Nitrates, sulphates, carbonates, and chlorides. It will then at once be evident, that a water contaminated by sewage, and therefore containing plenty of ammonia and chlorides, might exert a very considerable solvent action on copper.

Almost all the oils and fats, as well as syrups, dissolve small quantities of copper, hence its frequent presence in articles of food cooked or prepared in copper vessels. In the very elaborate and careful experiments of Mr. W. Thompson,[†] the only oils which took up no copper, when digested in copper foil, were English neatsfoot oil, tallow oil, one sample of olive oil, palm-nut oil, common tallow oil, and white oil, which was protected from the air by a thick coating of oxidised oil on its surface.

§ 168. *Copper as a Normal Constituent of Animal, Vegetable, and other Matters.*—Copper is very widely distributed throughout the mineral, animal, and vegetable kingdoms. Besides being present in numerous minerals and earths, it is often found in spring and river water, either from the solvent action of the water itself, or from pollution from copper mines or manufactories in which the metal is used.

In the animal kingdom it is nearly always present in the liver and kidneys of domestic animals, as well as in men. Dr. Dupré[‡] found ·035 to ·029 grain (1·8 to 2 mgrms.) in human livers, or about one part in 500,000. Bergeron and L. L. Hote's researches on fourteen bodies, specially examined for copper, fully sub-

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[*] *Journ. Chem. Soc.*, 1876, ii. 4.

[†] Action of Fatty Oils on Metallic Copper, *Chem. News*, xxxiv. 176, 200, 213.

[‡] *Analyst*, No. 13, 1877.

stantiate Dr. Dupré; in twelve, the copper was found in quantities from ·7 to 1·5 mgrm.; in the remaining two the amount of copper was very minute, and was not estimated.[*] Copper is also found normally in the kidneys, and Dupré[†] detected in human kidneys about one in 100,000 parts; it is also found in the gall, and in minute traces in the blood.[‡]

In the kidneys and livers of the ruminants copper may always be found, a sheep's liver containing about one part in 20,000.[§] Church found copper in the feathers of the wings of the turaco; Melopsitt in the feathers of a paraquet (*Melopsittneus undulatus*).[||] If looked for, it is readily discovered in snails, in the crustacea generally, and in the blood of the cephalapoda it is abundant.[¶]

In wheat (and therefore in bread), in barley, mangel-wurzel, swedes (and in both the root and leaf of turnip), as well as in most other vegetables, copper in very minute traces may be detected. Of the different vegetables specified, Dr. Dupré found as a maximum one part of oxide of copper in 240,000 parts of wheat, and as a minimum one part of oxide of copper in 4,375,000 of turnip root.[**]

§ 169. *Copper in Articles of Food and Drink.*—Copper as an impurity, or an adulterant, is found in a great variety of articles of food and drink. It has been discovered in aerated waters, its presence being due to the use of copper cylinders, the lining tin of which had been rendered defective by corrosion.[††]

Accidents may also occur from the use of copper boilers. Mr. W. Thompson found in one case[‡‡] no less than 3·575 grains in a gallon (51 mgrms. per litre) in water drawn from a kitchen boiler.

At Roubaix, in France, sulphide of copper had been deposited on the roof, as a consequence of the use of copper flues; the sulphide was changed into sulphate by the action of the air, and washed by the rain into the water-tanks.[§§]

That preserved vegetables are made of a bright and attractive green colour, by impregnation with copper, from the deliberate use of copper vessels for this purpose, is a fact long known. Green pease especially have been coloured in this way, and a great number of convictions for this offence have lately taken place.

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[*] *Comptes Rendus*, lxxx. 268.

[†] *Op. cit.*

[‡] Hoppe Seyler: "Handbuch der Physiologisch. Analyse," p. 415.

[§] Dupré, *op. cit.*

[||] *Chem. News*, xxviij. 212.

[¶] Hoppe Seyler, *op. cit.*

[**] Dupré, *op. cit.* Sarzeau has found copper in about 200 vegetables.

[††] On the Presence of Lead and Copper in Aerated Waters, by Dr. James Milne. *Chem. News*, xxxi., p. 77.

[‡‡] *Chem. News*, xxxi., No. 801.

[§§] Author's "Dictionary of Hygiène," p. 167.

The following are a few of the more important :—

In one of several similar cases heard at the Marlborough Street Police Court, it was proved by Mr. Piesse, the analyst, that the pound tin contained ·088 of copper, equal to 2½ grains of sulphate of copper.

Dr. Conway Evans, Medical Officer of Health, stated his opinion, that the larger quantity of copper spoken of in a pound of pease, if eaten daily or repeatedly, would be injurious to health, and would produce chronic poisoning; but many persons might eat a quantity of these pease several times without apparently suffering any injurious effects, the period varying in accordance with difference of vigour, age, health, &c. Two or three doses might affect some persons and not others. From 14 to 15 grains of copper were sometimes given as an emetic; and sometimes, in ague or chronic diarrhœa, ⅛ to 3 grains were given as a tonic. It was a well-known medical fact, that in regard to some poisons (such, for instance, as mercury) certain persons were peculiarly susceptible to their influence; and it was possible that these pease containing copper, if swallowed by persons ignorant of their own susceptibilities, might (even in a single dose, or a few doses) lead to injurious consequences. He believed copper to be more fatal, in a smaller dose, than salts of lead. The heightening of the colours of preserves with copper was once a common practice. Cases of poisoning by copper were formerly very common, but copper utensils in cooking having given place to tin and iron saucepans, such cases were of rare occurrence. Pure metallic copper he believed to be harmless, but it was dangerous when in contact with other substances, and when dissolved.

Dr. Guy, F.R.S., said that cases of poisoning by copper had occurred in which the quantity swallowed must have been small. He had studied the question of poisons particularly; the fact of a trace of copper in the human body would not prove its existence in a poisonous form. He had made inquiries for Government into the effects of poisoning in certain trades; palsy followed the poisoning by copper. Two cases had come under his knowledge of poisoning by the green wall-paper in a room; the poisoning in his opinion came from the copper, not the arsenic. Salts of copper he considered more poisonous than lead; the small quantity of copper contained in the pease in question from France might prove injurious, and slowly undermine health. On a nervous person copper was more likely to produce dangerous symptoms than on any one else. With regard to the presence of 3·6 of copper, if taken one-third at a time, it would not affect a healthy person; but if repeated in small doses it would, in his opinion, be ultimately injurious to health. He considered that any article containing the amount of copper stated by Mr. Piesse should not be allowed to be sold for one moment. Sulphate of copper in its virulence ranked fourth in the class of poisons.

Dr. C. Tidy gave similar evidence. If copper, that is, sulphate of copper, were constantly taken to the extent of the amount of copper found in the French pease, it would be injurious to health.

Dr. A. Dupré stated that the quantity found was far beyond the quantity normally present in any vegetable.

Dr. Guy said he considered the sale of an article containing such a quantity of copper as that found in the French pease ought not to be tolerated. Small doses of copper were more dangerous than large ones, as the latter would cause vomiting.

A previous conviction against the defendant for the same offence was proved, but the prosecution stated that they desired publicity, not punishment, and a small fine was inflicted.*

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* *Analyst*, 1877, p. 216.

At the Liverpool Police Court a firm was prosecuted for selling pease containing copper equal to 2½ grains of sulphate to the pound tin. A warranty produced.[*]

A Liverpool grocer was fined 20s. and costs, for selling pease containing copper equal to 2·6 grains of the sulphate to the pound.[†]

At Bradford vendors have been fined for selling coppered pease, the metal equalling 1½ to 2 grains to the pound.[‡]

It will be noticed from the foregoing that—

(1.) The whole question of the injurious action of coppered pease rests entirely upon theory.

(2.) The theory of the poisonous action is based in no single case upon any observed instance of chronic or acute poisoning.

(3.) In no case has the analyst been able to state the form in which the copper exists. Now, Messrs. Paul and Kingzett have shown that when such a soluble compound of sulphate of copper is ingested most of it is excreted by the fæces;[§] and Legrif has found in the intestines of a healthy man from ·036 to 0·40 grm. of copper.[||] Hence, since it is not known in what form the copper in the pease exists, whether as soluble or insoluble, but merely that copper has been added to improve the colour, it is, perhaps, the safest and most just way for the analyst to state simply that so much metallic copper has been separated, and that the substances are, therefore, adulterated; but with regard to injury to health, to offer no opinion. After all, the question of the injury to health produced by copper in pease, is at present by no means settled one way or the other; facts drawn from the known poisonous effects of various salts of copper have but an indirect bearing on the point at issue; and it can only be finally determined by proving in what state of combination the copper exists, and the action of the pease themselves.

Copper may be found in spirits, owing to the use of copper condensers, a remark which applies also to the essential oils, such as *oleum cajuputi menthae*, &c.[¶] In France, it has been added fraudulently to absinthe, to improve its colour.[**] Green sweetmeats, green toys, green papers, have all been found to contain definite compounds of copper to a dangerous extent.

§ 170. *Preparations of Copper used in Medicine and the Arts.*

(1.) *Medicinal Preparations:—*

Sulphate of Copper, *Cupri sulphas*, $CuSO_4 5H_2O$. This well-

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[*] *Sanitary Record*, vj. 335.

[†] *Ibid.*, vj. 351.

[‡] *Ibid.*, vij. 63.

[§] Analyst 1877, p. 98.

[||] Sonnenschein *op. cit.*

[¶] According to Eulenberg ("Gewerbe Hygiène," p. 716), *oleum cajeputi*, *Menth. pip. Melissæ Tanaceti*, &c., are almost always contaminated with copper.

[**] Tardieu: "Etude méd. légale sur l'empoisonnement."

known salt is very soluble in water, reddens litmus, and is slightly efflorescent; its solution responds to all the usual tests for copper and sulphuric acid. A watery solution of the salt to which twice its volume of a solution of chlorine has been added, gives, when treated with ammonia in excess, a clear sapphire-blue solution, leaving nothing undissolved, and thus showing the absence of iron. Besides iron, sulphate of copper has been found to contain zincic sulphate.

Cuprum Aluminatum.—A preparation called cuprum aluminatum (*Pierre divine*) is in use in France and Germany as a medicine. It is composed of 16 parts cupric sulphate, 16 potassic nitrate, 16 alum, and 5 camphor. Regular and irregular medical practitioners, veterinary surgeons, farriers, and grooms, all use sulphate of copper (bluestone) as an application to wounds. Copper as an *internal* remedy, is not in favour either with quacks or vendors of patent medicines. The writer has not yet found any patent pill or liquid containing it.

In veterinary medicine, the sulphate of copper is administered to horses and cattle, and the diniodide is used to some inconsiderable extent.

(2.) *Copper in the Arts.*—Copper is used very extensively in the arts; it enters into the composition of a number of alloys, is one of the chief constituents of the common bronzing powders, is contained in many of the lilac and purple fires of the pyrotechnist, and in a great variety of pigments. The last-mentioned, being of special importance, will be briefly described :—

Pigments :—

*Schweinfurt and Scheele's Green,** are respectively the aceto-arsenite and the arsenite of copper. (See article *Arsenic.*)

Brighton Green is a mixture of impure acetate of copper and chalk.

Brunswick Green, originally a crude chloride of copper, is now generally a mixture of carbonate of copper and chalk or alumina.

Mountain Green, or Mineral Green, is the native green carbonate of copper, either with or without a little orpiment.

Neuwieder Green is either the same as mountain green, or Schweinfurt green mixed with gypsum or sulphate of baryta.

Green Verdites is a mixture of oxide and carbonate of copper with chalk.

Verdigris is an acetate of copper, or a mixture of acetates. Its formula is usually represented as $(C_2H_3O_2),CuO$. It is much used in the arts, and to some extent as an external application

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* The synonyms for Schweinfurt green are extremely numerous. Mitis green, vienna green, imperial green, emerald green, are the principal terms in actual use.

in medicine. Its most frequent impurities or adulterations are chalk and sulphate of copper.

§ 171. *Dose.—Medicinal Dose of Copper*—Since sulphate of copper is practically the only salt administered internally, the dose is generally expressed as so many grains of sulphate. This salt is given in quantities of from ·25 to 2 grains (·167 to ·130 grain) as an astringent or tonic; as an emetic, from 5 to 10 grains (·324 to ·5184 grm.)

The sulphate of copper is given to horses and cattle in such large doses as from 30 up to 120 grains (1·9 to 7·7 grms.); to sheep, from 20 to 40 grains (1·3 to 3·6 grms.); rabbits, 1 to 2 grains (·0648 to ·1296 grm.)

Poisonous Dose.—A dose of 120 grains of sulphate of copper (7·7 grms.) has caused very serious symptoms.* A woman died in seventy-two hours after taking 7 drachms (27 grms.) of sulphate of copper mixed with 3 drachms (11·6 grms.) of sulphide of iron. 2 ounces (62·2 grms.) of the acetate of copper have caused death in three days; half an ounce (15·5 grms.) in sixty hours.†

§ 172. *Detection and Estimation of Copper.*—Copper may occur either in the routine process of precipitating by SH_2, or it may, as is generally the case, be searched for specially. If copper is looked for in a precipitate produced by SH_2, it is taken for granted that the precipitate has first been treated successively by carbonate of ammonia, sulphide of sodium, and hydrochloric acid; in other words, arsenic, antimony, and lead have been removed. The moist precipitate is now treated with warm nitric acid, which dissolves out copper sulphide with separation of sulphur; if there is sufficient copper, the fluid shows a blue colour, which of itself is an indication of copper being present. The further tests are—(1.) Ammonia gives a deeper blue; (2.) ferrocyanide of potash a brown-red colour or precipitate; (3.) a few drops mixed with a solution of tartrate of soda, alkalised with sodic hydrate, and boiled with a crystal or two of grape-sugar, gives quickly a red precipitate of oxide of copper; (4.) a needle or a clean iron wire, or any simple galvanic combination immersed in, or acting on, the liquid, soon becomes coated with the very characteristic reddish metallic film. Various other tests might be mentioned, but the above are ample.

Special Examinations for Copper.

(1.) *In Water and Liquids generally.*—The liquid may be concentrated, and the copper separated by electrolysis. A simple

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* Taylor, *op. cit.*

† Sonnenschein, *op. cit.*

method is to place the liquid in a large platinum dish, and insert a piece of zinc, adding a sufficient quantity of ClH to dissolve the zinc entirely; the copper is found as an adherent film on the inner surface of the dish. It is neater, however, and more accurate, to connect the platinum dish with the negative plate of a battery, suspending in the liquid the positive electrode. The modifications of this method are numerous; some chemists use (especially for small quantities of copper) two small platinum electrodes, either of foil or of wire, and on obtaining the film, weigh the electrode, then dissolve the copper off by nitric acid, and reweigh. Such solid substances as pease are conveniently mashed up into a paste with water and ClH; an aliquot part is carefully weighed and put in a platinum dish, connected, as before described, with a battery; at the end of from twelve to twenty-four hours all the copper is deposited, and the dish with its film dried and weighed. The weight of the clean dish, minus the coppered dish, of course equals the copper. Fat and oils are best thoroughly washed with hot acid water, which will, if properly performed, extract all the copper. By the use of separating funnels and wet filters, the fat or oil can be separated from the watery liquid.

A test has been recently proposed, which is certainly the most delicate known, $\frac{1}{100}$ of a mgrm. in solution being recognised with facility. A zinc platinum couple is made with two wires; on leaving this in an acid liquid containing a mere trace of copper, after several hours the platinum will be found discoloured. If the discoloration is from copper, on exposing the wire to hydrobromic acid fumes (easily produced from the action of potassic bromide and sulphuric acid) and bromine, the wire will become of a violet colour. This colour is easily recognised by rubbing the wire on a piece of porcelain.[*]

(2.) *Animal Matters*, such as liver, brain, spinal cord, &c., are best entirely burnt to an ash, and the copper looked for in the latter.[†] The same remark applies to bread and substances consisting almost entirely of starchy matters. Any injurious quantity of copper can, however, be extracted with nitric acid and water; and although this method of extraction is not quite so accurate, it is quicker.

§ 173. *Volumetric Processes for the Estimation of Copper.*—A number of volumetric processes have been devised for the esti-

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[*] *Chem. News*, Nov. 30, 1877.

[†] In exhumation of long buried bodies, it may be necessary to know the composition of the soil. Sonnenschein mentions a skull, now in the museum at Madrid, which was dug out of an old Roman mine, and is quite green from copper compounds.—Sonnenschein's "Handbuch," p. 83.

mation of copper, but for the purposes of this work it is unnecessary to detail them. When copper is in too small a quantity to be weighed, it may then be estimated by a colorimetric process.

One of the best of these is based upon the brown colour which ferrocyanide of potash produces in very dilute solutions of copper. A standard copper solution is obtained by dissolving ·393 grm. in a litre of water, each cc. then contains 0·1 mgrm. Cu; a solution of ferrocyanide of potash in water, strength 4 per cent. It is also convenient to have a solution of nitrate of ammonia, which is found to render the reaction much more delicate.

The further details of the process are conducted precisely on the same principles as the well-known colorimetric method of estimating ammonia by Nessler's solution.

III.—BISMUTH.

§ 174. *Bismuth,* Bi = 210; specific gravity, 9·799; fusing point, 264°C. (507·2°F.) Bismuth, as obtained in the course of analysis, is either a black metallic powder, or a bead extremely brittle, and of a reddish-white colour. The compounds which it will be necessary to notice briefly will be the teroxide and the tersulphide.

§ 175. *The Teroxide of Bismuth* ($Bi_2O_3 = 468$; specific gravity, 8·211; Bi 89·655 per cent., O 10·345 per cent.), as prepared by igniting the carbonate or nitrate, is a pale lemon-coloured powder, which can be fused without loss of weight, but is reduced in charcoal, or in a stream of carbon dioxide, to the metallic state. It is also reduced by fusion with cyanide of potassium, or by ignition with chloride of ammonium.

§ 176. *The Sulphide of Bismuth* ($Bi_2S_3 = 5·16$; Bi 81·25 per cent., S 18·75 per cent.), occurs in the course of analysis as a brownish-black or quite black precipitate, insoluble in water, dilute acids, alkalies, alkaline sulphides, sulphate of soda, and cyanide of potassium, but dissolving in moderately concentrated nitric acid, with separation of sulphur. It continually increases in weight when dried in the ordinary way, and is completely reduced when fused with cyanide of potash.

§ 177. *Preparations of Bismuth used in Medicine and the Arts.*

(1.) *Pharmaceutical Preparations:—*

Bismuthi Subnitras (Subnitrate of Bismuth, $BiNO_4H_2O$). A heavy white powder insoluble in water, and responding to the usual tests for bismuth and nitric acid. The percentage of bismuth in this preparation often varies within somewhat wide limits, for there are at least two nitrates in commerce, the one containing 79·4 per cent of bismuth oxide, the other 76·48 per cent.

The principal impurities to be looked for are—ammonia,* carbonate of lead, arsenic, chlorine, and sodium salts. The first is easily detected by distilling with potash, and estimating the NH_3 by titration, or, if in small amount, by colorimetric methods; carbonate of lead, by effervescence with nitric and precipitation by sulphuric acids; arsenic, by Davy's test (see p. 383); chlorine, by nitrate of silver; and sodium salts, by boiling the bismuth with water, filtering, evaporating down to dryness, and examining the residue.

Tellurium has recently been suspected in preparations of bismuth; the evidence on the point, however, is not of an analytical character, but is based upon the observation that some persons after taking certain bismuth preparations, have suffered from fœtid breath.† Sir J. Simpson records a case in which a divinity student inadvertently swallowed a dose of tellurium, which was followed by the evolution of such a persistent odour, that for the remainder of the session the patient had to sit apart from his fellow-students.

Bismuth Lozenges, *Trochisci Bismuth*, are composed of subnitrate of bismuth, carbonate of magnesia, precipitated carbonate of lime, sugar, and gum, mixed with rose water. Each lozenge should contain 2 grains (·13 grm.) of nitrate of bismuth.

Solution of Citrate of Bismuth and Ammonia, *Liquor bismuthi et Ammoniæ citratis*, a colourless, neutral, or slightly alkaline fluid; specific gravity, 1·122; responding to the tests for bismuth and ammonia.

The probable impurities are the same as those in the subnitrate, and lead should specially be searched for, because so frequently contained in citric acid.

Carbonate of Bismuth, *Bismuthi carbonas*, $2(Bi_2CO_3)H_2O$, a fine white powder, answering to the tests for bismuth and carbonic anhydride, and likely to contain the same impurities as the subnitrate. It ought to give 89·1 per cent. of bismuth oxide.

The Valerianate of Bismuth, *Bismuthum valerianicum*, a white powder, smelling strongly of valerianic acid: if dissolved in nitric or hydrochloric acids, with separation of the valerianic acid, 100

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[*] Ammonia is, perhaps, formed in the preparation of bismuth as follows:—$2Bi_2 + 15NO_3H = 3NO_34Bi + 6OH_2 + NH_3 + N_2O_3$. — W. G. Piper, *Pharm. Journ.*, April 21, 77.

[†] *Pharm. Journ.* [3.], No. 287, Dict. 21, 76.

parts must contain 79 of oxide of bismuth. The valerianate of bismuth is in the German, but not in the British pharmacopeia.

(2.) *Bismuth in the Arts**.—The principal use of bismuth is in alloys and solders. The chromate is employed in calico-printing, and the subnitrate as a paint, under the name of pearl-white.

The salts of bismuth also occur in washes for the hair, and pearl-white is used as a cosmetic, but only to a small extent.

§ 178. *Medicinal Doses of Bismuth.*—The subnitrate and carbonate are prescribed in doses from 1 to 20 grains (·0648 to 1·286 grm.); the valerianate, from 2 to 10 grains (·1280 to ·640 grm.); and the solution, from ½ drachm to 1½ drachm (1·7 cc. to 5·2 cc.)

Poisonous Doses of Bismuth.—Pure metallic bismuth is not known to possess any poisonous action.† Two drachms of the subnitrate have caused the death of a man in nine days,‡ and other cases of poisoning by larger doses are on record. The evidence, however, as to the smallest dose of bismuth required to produce symptoms of poisoning is not very satisfactory, for in the cases recorded the salt may have been contaminated with arsenic.

§ 179. *Extraction and Detection of Bismuth in Animal Matters.*—Bismuth appears to be excreted principally by the bowels as sulphide of bismuth; but it has also been detected in the urine, spleen, and liver; and Lubinsky has found it in the saliva and in the epithelium of the mouth of persons taking one of its preparations. Without denying the possibility of its existing in a soluble state in the saliva, its presence in the mouth may, under such circumstances, be ascribed to the lodgment of particles of subnitrate or subcarbonate of bismuth in the interstices of the teeth, &c. It will then be evident, that if a person is supposed to have been poisoned by a large dose of bismuth, and the analyst fails to find it in the stomach, the contents of the bowels should be next examined.

The extraction of bismuth must be undertaken by nitric acid, and boiling for at least two hours may be necessary to dissolve it out from the tissues. Such organs as liver and spleen are boiled in a finely divided state with a litre of dilute nitric acid (strength, 5 per cent.), for the time mentioned, filtered, and the filtrate evaporated to dryness; the remainder is then carbonised

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* According to Mr. Field (*Chem. News*, vol. 36, 261), bismuth is contained in all copper coinage—from the Bactrian coins (161 B.C.) to our own; generally, in all cupreous ores except the carbonates; and in nearly all specimens of commercial copper.

† Valenciennes, A., *Beiträge zur Metallurgie des Bismuths; Ann. de Chim. Phys.*, 1874, I., p. 397; Wagner's *Jahresbericht*, 1874, s. 202.

‡ Taylor, "Prin. Med. Juris.," i. 321.

by strong nitric acid; and, finally, the charcoal is boiled wit equal parts of nitric acid and water, and the whole evaporate to dryness. By this method every trace of bismuth is extracted The dry residue may now be brought into solution, and teste for bismuth. The best solvent for the nitrate of bismuth i dilute nitric acid 50 per cent.; the dry residue is therefore dis solved in 100 or 200 cc. of the acid, and fractional parts take for examination :—

(1.) The solution, poured into a large volume of warm distille water, gives a crystalline precipitate of subnitrate of bismuth The only metal giving a similar reaction is antimony, and thi is excluded by the method employed.

(2.) The filtered fluid gives on addition of sodic chloride precipitate of oxychloride. This, again, is distinguished fro oxychloride of antimony by its insolubility in tartaric acid.

(3.) Any bismuth precipitate, mixed with soda or charcoal gives a brittle bead of bismuth; the coal is coated whilst war a dark orange-yellow, on cooling citron-yellow.

(4). The bead may be identified by powdering it, placing i in a short subliming tube, and passing over it dry chlorine. Th powder first turns black, then melts to an amber-yellow fluid and finally, in prolonged heating, sublimes as terchloride o bismuth.

(5.) A very delicate test proposed by Abel and Field, in 1862, specially for the detection of bismuth in copper (but by n means confined to mineral analysis), utilises the fact, that i iodide of lead be precipitated from a fluid containing the leas trace of bismuth, instead of the yellow iodide the scales assume dark orange to a crimson tint. A solution of nitrate of lead is use to the nitric acid solution; ammonia and carbonate of ammoni added; the precipitate washed, and dissolved in acetic acid; and finally, excess of iodide of potassium added. It is said that thu so small a quantity as ·00025 grm. may be detected in coppe with the greatest ease, the iodide of lead becoming dark orange ·001 grain imparts a reddish-brown tinge, and ·01 grain a crimso

(6.) Van Kobell's test, as modified by Hutchings,† and pro posed more especially for the detection of bismuth in minerals is capable of being applied to any solid compound suspected o containing the metal :—A mixture of precipitated and purifie cuprous iodide, with an equal volume of flowers of sulphur, i prepared, and 2 parts of this mixture are made into a paste wit 1 part of the substance, and heated on a slip of charcoal on a aluminium support by the blowpipe flame. If bismuth b

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* *Journ. Chem. Soc.*, 1862, xiv. 290; *Chem. News*, xxxvi. 261.

† *Chem. News*, xxxvi. 249.

present, the red bismuth iodide will sublime, and on clean aluminium is easily distinguishable.

There are many other tests, but the above are more than sufficient.

§ 180. *Estimation of Bismuth.*—The estimation of bismuth, when in any quantity easily weighed, is, perhaps, best accomplished by fusing the sulphide, oxide, or other compound of bismuth, in a porcelain crucible with cyanide of potash; the bismuth is reduced to the metallic state, the cyanide can be dissolved out, and the metallic powder washed (first with water, lastly with spirit), dried, and weighed.

Mr. Pattison Muir has shown* that bismuth may be separated from iron, aluminium, chromium, and manganese, by adding ammonia to the acid solutions of these metals.

This observation admits of many applications, and may be usefully taken advantage of in the separation of bismuth from the nitric acid solution of such animal matters as liver, &c. The acid liquid is partially neutralised by ammonia, and on diluting with warm water containing a little sodium or ammonium chloride, the whole of the bismuth is precipitated as oxychloride, which may be collected, and fused with cyanide of potash, as above.

If the bismuth precipitate is in small quantity, or if a number of estimations of bismuth are to be made, it is most convenient to use a volumetric process. In the case first mentioned, the oxychloride could be dissolved in nitric acid, sodium acetate added in excess, and sufficient acetic acid to dissolve any precipitate which has been produced, and then titrated by the following method, which we also owe to Mr. Pattison Muir :—

Estimation of Bismuth by Potassium Dichromate.†—A solution of recrystallised potassium dichromate (strength, 1 per cent.) is prepared. A known weight of pure bismuthous oxide, Bi_2O_3, is dissolved in excess of nitric acid, and a solution of sodium acetate added to this liquid until a copious white precipitate is thrown down; acetic acid is then added in quantity sufficient to dissolve the precipitate completely, and to insure that when the liquid is made up with water to a fixed volume no precipitate shall be formed. A certain volume of this liquid is withdrawn by means of a pipette, placed in a beaker, and heated to boiling; the potassium dichromate is then gradually run in from a burette, the liquid being boiled between each addition of the solution, until a drop of the supernatant liquid gives a faint reddish-brown coloration when spotted with silver nitrate on a white slab.

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* Pattison Muir on Certain Bismuth Compounds. *Journ. Chem. Soc.*, , 1876.

† *Ibid.*, i. 659.

Another very generally applicable volumetric method fo bismuth has been proposed by Mr. Muir.* This depends on th fact (observed by Sonchay and Leussen†), that normal bismut oxalate splits up on boiling into a basic oxalate of the compos tion $Bi_2O_32C_2O_3 + OH_2$, but slightly soluble in nitric acid. Th process is performed by precipitating the bismuth by excess oxalic acid, dissolving the precipitate (first purified from fre oxalic acid) in dilute hydrochloric acid, and lastly, titratin by permanganate. The absence of free hydrochloric acid befor precipitating must be insured.

IV.—SILVER.

§ 181. *Silver* = 108; specific gravity, 10·5; fusing poin 1023°C. (1873°F.) Silver, as separated in analysis, is either very white, glittering, metallic bead, or a dull grey powder. does not lose weight on ignition, and is soluble in dilute nitr acid.

§ 182. *Chloride of Silver*, $AgCl = 143·5$; specific gravity, 5·55 Ag 75·27 per cent., Cl 24·73 per cent., is a dense, white, curd precipitate, when produced in the wet way. It is very insolub in water, dilute nitric acid, and dilute sulphuric acid; in man warm solutions (especially aqueous solutions of the chlorid generally), the alkaline and alkaline-earthy nitrates, and tartar acid solutions, the silver is dissolved to an appreciable exten but deposited again on diluting and cooling. The complet solvents of chloride of silver are—ammonia, cyanide of potassiun and hyposulphite of soda. Chloride of silver cannot be fused a high heat without some slight loss by volatilisation; on coal i the O.F., it fuses very easily to a globule. It can with soda reduced to metal, and can also readily be reduced by ignition i a current of hydrogen, carbonic oxide, or carburetted hydroge gas.

§ 183. *Sulphide of Silver*, $Ag_2S = 248$; specific gravity, 7· Ag 87·1 per cent., S 12·9 per cent., when prepared in the we way, is a black precipitate, insoluble in water, dilute acids, an alkaline sulphides. If ignited in hydrogen it may be reduce to the metallic state; it is soluble in nitric acid, with separa tion of sulphur.

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* *Journ. Chem. Soc.*, 1877.

† *Ann. Chem. Pharm.*, cv. 245.

§ 184. *Preparations of Silver used in Medicine and the Arts.*

(1.) *Medicinal Preparations*:—

Nitrate of Silver, $AgNO_3$; Ag 63·51 per cent., N_2O_5 36·49 per cent. This salt is either sold crystallised in colourless rhombic prisms, or in the form of small white pencils or sticks. It gives the reaction for silver and nitric acid, and stains the skin black. 100 parts dissolved in distilled water should give, with hydrochloric acid, a precipitate which, when washed and dried, weighs 83·4 parts. The silver is, however, far more quickly estimated by the blowpipe, than in the wet way. 1 grm. fused in a cavity on charcoal should give a little globule of metallic silver, weighing about ·6351 grm. The chief adulterations of this substance are copper, lead, and nitrate of potash. If all the silver is precipitated by hydrochloric acid, carefully filtered off, and the filtrate evaporated to dryness, any residue will denote adulteration or impurity.

Argenti Oxidum, Oxide of Silver, $Ag_2O = 116$; Ag 93·19 per cent. A dark olive-brown powder, soluble in ammonia and nitric acid. By ignition it readily yields metallic silver. The P.B. directs that 29 grains of the oxide should yield 27 of metallic silver.

Nitrate of Silver and Potash, Argentum nitricum cum kali nitrico ($AgNO_3 + KNO_3$). This preparation is contained in the German, Austrian, and Norwegian pharmacopeias. It is directed that 100 parts of the German and Austrian preparation should, on analysis, yield not less than 27 parts of chloride of silver (20·3 Ag), and the Norwegian less than 42·058 parts of chloride of silver (31·64 Ag); the first being prepared in the proportion of 1 of silver nitrate to 2 of potassic nitrate, whilst in the Norwegian equal parts are used.

(2.) *Silver in the Arts.*—The uses of the metal in coinage, rticles for domestic purposes, for ornament, &c., are too well nown to require enumeration. The only forms in which silver s likely to give rise to accident are the salts used in medicine, hotography, in the dyeing of hair, and in the manufacture of arking inks.

Hair-dyes.—About one-half of the hair-dyes in use are made ith nitrate of silver. The following are only a few of the ecipes:—

Aqua Orientalis.—Grain silver 2 drachms, nitric acid 1 oz., steel lings 4 drachms, distilled water 1½ oz.; the whole finally made up o 3½ fluid oz., and filtered.

Argentan Tincture.—Nitrate of silver 1 drachm, rose water 1 uid oz., sufficient nitrate of copper to impart a greenish tint.

Eau d'Afrique.—Two solutions—one of nitrate of silver, the oth of potash, containing ammonium sulphide.

The photographer uses various salts of silver, the chief of whic are—the nitrate, iodide, bromide, cyanide, and chloride of silve

Marking Inks.—Some of the more important recipes for marl ing ink are as follows :—

Nitrate of silver 1·0 part, hot distilled water 3·6 parts, muc lage, previously rubbed with sap-green, 1·0 part. With this sold a "pounce," or preparation consisting of a coloured solutio of sodic carbonate. Another preparation is very similar, bu with the addition of ammonia and some colouring matter, suc as indigo, syrup of buckthorn, or sap-green. A third is ma with tartaric acid and nitrate of silver, dissolved in ammon solution and coloured.

Redwood's consists of equal parts of nitrate of silver and potass bitartrate, dissolved in ammonia, with the addition of archil gre and sugar ; according to the formula, 100 parts should equal 16 of silver nitrate.

Soubeiran's Ink is composed of cupric nitrate 3, argentic nitra 8, sodic carbonate 4, and the whole made up to 100 parts, in sol tion of ammonia. In one of Mr. Reade's inks, besides silver, a ammoniacal solution of a salt of gold is used.

Medicinal Dose of Silver Compounds.—The nitrate and the oxi of silver are given in doses from ¼ grain to 2 grains [·0162 ·1296 grm.] Anything like 3 or 4 grains [·1944 to ·2592 grm would be considered a large, if not a dangerous dose ; but nothi definite is known as to what would be a *poisonous* dose.

§ 185. *Detection and Estimation of Silver.*—The examination the solid salts of silver usually met with (viz., the nitrate, bromid iodide, cyanide, and chloride) is most speedy by the dry meth on charcoal ; in this way in less than 120 seconds any practic chemist could identify each compound. The nitrate, bromid iodide, and cyanide, all, if ignited on charcoal, yield buttons metallic silver—deflagration, bromine vapours, iodine vapour and cyanogen vapours, being the respective phenomena observe Chloride of silver fuses to a pearl-grey, brown, or black globu on charcoal, according to its purity ; but is only in the R. gradually reduced to metal. With soda, or fused in hydrog or coal gas, the reduction is rapid enough.

Nitrate of Silver in solution might be identified by a very lar number of tests, since it forms so many insoluble salts. I practice one is, however, satisfied with three tests—viz., (1.) curdy precipitate of chloride, on the addition of hydrochlor acid or alkaline chlorides, soluble only in ammonia, cyanide potash, or hyposulphite of soda ; (2.) a yellow precipitate, bu little soluble in ammonia, on the addition of iodide of potash; and, (3.) a blood-red precipitate on the addition of chromate of potash.

The separation of silver from the contents of the stomach is best ensured by treating it with cyanide of potash; for unless a very large quantity of silver nitrate has been taken, it is tolerably certain that the whole of it has passed into chloride, and will, therefore, not be attacked easily by acids. The contents of the stomach, then, or the tissues themselves, are placed in a flask and warmed for some time with cyanide of potash, first, if necessary, adding ammonia. The fluid is separated from the solid matters by subsidence (for an alkaline fluid of this kind will scarcely filter), and then decomposed by hydrochloric acid in excess. The flask containing this fluid is put on one side in a warm place, and the clear fluid decanted from the insoluble chloride. The latter is now collected on a filter, well washed with hot water, and then dried and reduced on charcoal; or it may be put in a little porcelain crucible with a rod of zinc and a few drops of hydrochloric acid. The silver is soon deposited, and must be washed with water, then with sulphuric acid. By the aid of a wash-bottle the particles of silver are now collected on a small filter, again washed, and on the moist mass a crystal of nitrate of potash and a little carbonate of soda laid. The whole is then dried, and all the filter cut away, save the small portion ontaining the silver. This small portion is now heated on charoal until a little button of pure silver is obtained, which may irst be weighed, then dissolved in nitric acid, and tested by the nethods detailed.

In a similar way, hair suspected of being dyed with silver an be treated with chlorine gas, and the chloride dissolved in otassic cyanide.

Spots on linen, and, generally, very small quantities of silver nay be detected by a simple galvanic process:—the substance is reated with solution of cyanide of potash, and submitted to a veak galvanic current, using for the negative plate a slip of opper; for the positive, platinum; the silver is deposited on the ormer.

V.—MERCURY.

§ 186. *Mercury*, Hg = 200; specific gravity, 13·596; boiling oint, 350°C. (662°F.) This well-known and familiar fluid metal vaporates and sublimes to a minute extent at all temperatures bove 5°C. When precipitated or deposited in a finely-divided state, the metal can only be united into a single globule, if it i fairly pure; very slight fatty impurities especially will preven the union. It is insoluble in hydrochloric acid, soluble to slight extent in dilute cold sulphuric acid, and completely solubl in concentrated sulphuric and in nitric acid. It combines directl with chlorine, bromine, and iodine, which (in presence of fre alkali) readily dissolve it. It is unalterable at 100°C., and whe exposed to a high temperature sublimes unchanged.

Mercurous Chloride (*Calomel*, HgCl = 23·5; specific gravity 7·178; subliming temperature, 111·6°C.; Hg 84·94 per cent., (15·06 per cent.), when prepared in the wet way is a heavy whit powder, absolutely insoluble in cold, but decomposed by boilin water. It may be converted into the mercuric chloride b chlorine water and aqua regia. Chloride of ammonium, pota sium, and sodium, all decompose calomel into metallic mercur and mercuric chloride. It is easily reduced to metal in a tu with soda potash, or burnt magnesia.

§ 187. *Sulphide of Mercury* (Hg_2S; Hg 86·21 per cent., 13·79 per cent.) is a black powder, dissolving in nitro-muriat acid, but very insoluble in water or other acids. It is also insolub in alkaline sulphides, with the exception of sulphide of potassiu

§ 188. *Medicinal Preparations of Mercury.*

Mercury in the liquid state has been occasionally administere in constipation; its internal use is now obsolete, or ought to b Gmelin has found samples adulterated with metallic bismut a substance which only slightly diminishes the fluidity of me cury; this adulteration may be detected by shaking the mercu in air, and thus oxidising the bismuth. Mercury may al contain various mechanical impurities, which are detected b squeezing the metal through chamois leather. Tin and zinc ma be dissolved out by hydrochloric acid, and all fixed impuriti (such as lead and bismuth) are at once discovered on sublimin the metal.

Mercury and Chalk, *Hydrargyrum cum creta.*—Mercury, 33· per cent.; chalk, 66·67.

Blue Pill, *Pilula hydrargyri.*—Mercury in a finely divided stat mixed with confection of roses and liquorice root; the mercu should be in the proportion of 33·33 per cent.

Mercury Plaster, *Emplastrum hydrargyri*, made with mercur olive oil, sulphur, and lead plaster; it should contain Hg 33 p cent.; sulphur, 18 per cent.

Ammoniac and Mercury Plaster, *Emplastrum ammoniaci cu hydrargyro.*—Gum, ammonia, mercury, olive oil, and sulphu it should contain 19·8 per cent. of Hg, and ·1 per cent. of sulphur.

Mercurial Ointment, Unguentum hydrargyri.—Mercury mixed with lead and suet, all three in equal weights; therefore it should contain 33·3 per cent. of mercury.

Compound Mercury Ointment, Unguentum hydrargyri compositum.—Made with ointment of mercury, yellow wax, olive oil, and camphor; it should contain 14·3 per cent. Hg, and 11·11 per cent. of camphor.

Liniment of Mercury, Linimentum hydrargyri, is made of mercurial ointment, solution of ammonia, and liniment of camphor; it may contain about 10 per cent. of mercury.

Mercurial Suppositories, Suppositoria hydrargyri, composed of ointment of mercury, benzoated lard, white wax, and oil of theobroma. It should contain about 11·11 per cent. of Hg, and each suppository should weigh 15 grains.

Acetate of Mercury, Mercurous acetate, is not contained in the B.P., but is officinal on the Continent. It is a salt occurring in white micaceous scales, soluble in 133 parts of cold water, giving the reaction of acetic acid and mercury, and very readily decomposed.

Mercuric Ethyl Chloride, Hydrargyrum æthylo-chloratum, is used as a medicine on the Continent. It occurs in white, glittering, crystalline scales, which take on pressure a metallic appearance, and possess a peculiar ethereal odour; it is but little soluble in water and ether, with difficulty in cold alcohol, but copiously soluble on boiling, and depositing crystals on cooling. It sublimes about 40°C. without residue; on quick heating it burns with a weak flame, developing a vapour of metallic taste and unpleasant odour. It gives no precipitate with silver nitrate, nor with albumen.

Corrosive Sublimate, Mercuric chloride, $HgCl_2 = 271$; Hg 73·8 per cent., Cl 26·1 per cent. In commerce this salt occurs in transparent, heavy, colourless masses, which have a crystalline fracture; if placed in the subliming cell described at p. 284, it sublimes at about 82·2°C. (180°F.), and melts at higher temperatures. The sublimate is generally in groups of plates drawn to a point at both ends, in crystalline needles, or in octahedra with a rectangular base. It dissolves in 16 parts of cold water and about 3 of boiling, and is very soluble in solutions of the alkaline chlorides; it dissolves also in ether, and can be, to a great extent, withdrawn from aqueous solutions by this agent. Alcohol dissolves nearly one-third its weight of the salt, and its own weight when boiling. It combines with albumen; gives when in solution a precipitate of mercuric oxide, when tested with solution of potash; a white precipitate with ammonia; a scarlet with iodide of potash, and a black precipitate of finely divided mercury with protochloride of tin. If a crystal (when placed in the subliming cell) gives a crystalline sublimate at about the temperature mentioned, and this sublimate becomes of a red colour when treated with a droplet of iodide of potash, it can be no other substance than corrosive sublimate.

Solution of Perchloride of Mercury, Liquor hydrargyri perchloridi, is simply 10 grains of perchloride of mercury and chloride of ammonium in a pint of water; 100 cc. therefore should contain ·114 grm. corrosive sublimate.

Yellow Mercurial Lotion, Lotio hydrargyri flava.—Perchloride of mercury 18 grains, mixed with 1 ounce of solution of lime.

*Calomel,** *Hydrargyri subchloridum.* — The properties of calomel have been already described. It sometimes contains as an impurity corrosive sublimate, which may be dissolved out by ether. Carbonate of lead, sulphate and carbonate of baryta, gum, and starch, are the usual adulterants mentioned. If on the application of heat calomel entirely sublimes, it must be free from the substances mentioned.

Black Mercurial Lotion, Lotio hydrargyri nigra.—Calomel 30 grains, mixed with 10 fluid ounces of lime-water.

Compound Pill of Subchloride of Mercury.—Calomel and sulphurated antimony, each 1 ounce, guiac resin 2 ounces, castor-oil 1 fluid ounce. 1 grain (·0648 grm.) of calomel, and the same quantity of antimony sulphide, are contained in every 5 grains (·324 grm.) of the pill mass—*i.e.*, calomel 20 per cent.

Ointment of Subchloride of Mercury, Unguentum hydrargyri subchloridi.—Calomel mixed with lead; strength about 14·2 per cent.

White Precipitate, Hydrargyrum ammoniatum, NH_2HgCl.—A white, heavy powder, subliming by heat without residue, and insoluble in water, alcohol, and ether. With soda, it yields a metallic sublimate. When boiled with potash, ammonia is evolved, the yellow oxide of mercury formed, and chloride of potash passes into solution. It should contain 79·5 per cent. of mercury.

The fusible white precipitate of the pharmacopeia of the Netherlands does not appear to be of constant composition, varying between 69·4 to 65·6 per cent. of mercury. † It melts on heating, and leaves as a residue chloride of sodium.

Commercial white precipitate is frequently adulterated; Barnes has found carbonates of lead and lime, the latter to the extent of

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* It would appear that in America a cosmetic is in use, consisting of calomel mixed into a paste with water. *Vide* "A Dangerous Cosmetic," by C. H. Piesse. *Analyst* [25], 1878, p. 241.

† Hirsch, "Die Prüfung der Artzneimittel."

nearly 2 per cent.[*] Calomel, according to Nickles,[†] has been substituted for white precipitate, but this was several years ago. The methods for detection are obvious.

Ointment of Ammoniated Mercury, Unguentum hydrargyri ammoniati.—62 grains of the substance mixed with an ounce of simple ointment.

Red Iodide of Mercury, Hydrargyrum iodidum rubrum, HgI_2.—A crystalline powder of a scarlet colour, becoming yellow on gentle heating. It is very insoluble in water, one part requiring from 6000 to 7000 parts; soluble in 130 parts of cold, 150 of hot alcohol; and dissolving freely in ether, or in aqueous solution of iodide of potassium.

Ointment of Red Iodide of Mercury, Unguentum hydrargyri iodidi rubri.—16 grains of the substance mixed with an ounce of simple ointment.

Green Iodide of Mercury, Hydrargyri iodidum viride, HgI.—A dingy, greenish-yellow powder, darkening on exposure to light, and easily decomposed into the red iodide.

Red Oxide of Mercury, Hydrargyri oxidum rubrum, $HgO = 216$; Hg 92·12 per cent.; specific gravity, 11 to 11·3, small, red, shining, crystalline scales, very insoluble in water, requiring about 20,000 parts; entirely soluble in hydrochloric acid. By a heat below redness it may be volatilised, and at the same time decomposed into mercury and oxygen. Its principal impurity is nitric acid, readily detected by the usual tests, or by heating in a test-tube, when, if nitric acid is present, orange vapours will be evolved. Fixed red powders (such as brick-dust and minium) are detected by being left as a residue, after the application of heat sufficient to volatilise the mercury.

Sulphate of Mercury, a white crystalline powder decomposed by water into the very insoluble basic salt of mercury known as *Turbith mineral*, $HgSO_42HgO$.

Turbith, or Turpeth, Mineral, is contained in the French pharmacopeia, $HgSO_42HgO$; Hg 82·4 per cent.; specific gravity 8·319. It requires for solution 2000 parts of cold, and 600 of boiling water; but dissolves with tolerable ease in hydrochloric acid.

The Sulphide of Mercury, known in commerce under the name of *Ethiops mineral*, is officinal in France, the Netherlands, and Germany. Its properties have been already described. The German and Dutch pharmacopeias require in it 50, the French only 33⅓ per cent. of metallic mercury.

Hahneman's Soluble Mercury, Hydrargyrum solubile Hahnemanni, is officinal in the Dutch pharmacopeia. As found in commerce

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[*] *Proceed. Brit. Pharm. Conf.*, 1867, p. 10.

[†] *Journ. Pharm. et Chim.*, 1e série, 1858, viij. p.,399.

it contains metallic mercury, nitric acid, and ammonia. Th mercury should be in the proportion of 86·33 per cent., th ammonia 2·44 per cent.

Crystallised Nitrate of Mercury, Hydrargyrum nitricum oxidu latum, is officinal in the pharmacopeias of Germany, Switzerland and France. The salt is in white crystals, giving the reaction of nitric acid and mercury, decomposed by the addition of water but fully soluble in water, if first moistened with nitric acid The formula of the neutral salt is $2HgO, N_2O_52H_2O$, whic requires 69·4 per cent. of mercury.

An *Ointment of Nitrate of Mercury, Unguentum hydrargyr nitratis,* is contained in the B.P.; it is made with 4 parts o mercury, nitric acid 12, lard 15, olive oil 32.

A *Chloride of Mercury and Quinine* exists in commerce, pre pared by mixing one part of corrosive sublimate in solutio with three parts of quinine chloride, evaporating, and crystal lising.

Cyanide of Mercury, HgCy, is contained in the French phar macopeia. It occurs in small colourless prismatic crystals, easil soluble in water. If to the solution chloride of tin be added, black precipitate of reduced metallic and stannous oxide i thrown down, and the odour of prussic acid is developed.

Mercuric Sulphide, Sulphide of Mercury, Cinnabar, Vermilion, i officinal in Germany, the Netherlands, and France; $HgS = 232$ specific gravity, solid, 8·2; Hg 86·21 per cent., O 13·79 per cent For medicinal purposes it is made artificially. It is a beautifu red powder, insoluble in all alkaline and all acid liquids, wit the exception of aqua regia. The solution gives the reaction of sulphuric acid and mercury. On heating, it must burn awa entirely without residue; adulterations or impurities are— minium, lead, copper, and other metals. The detection o minium is conveniently executed in the dry way. Pure cinna bar, when heated in a matrass, gives a black sublimate, whic becomes red on friction. If minium is present, sulphide of lea remains as a residue, and may be recognised on coal; the sam remark applies to sulphide of antimony. If it be desired to tak the percentage of mercury in cinnabar, equal parts of oxalat and cyanide of potassium should be well mixed with the cinnabar, and heated in the bent tube described at p. 447; by this means the whole of the metallic mercury is readily obtained.*

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* Dr. Sutro has published a case (quoted by Taylor), in which the vapour o vermilion, applied externally, produced poisonous symptoms; yet, accordin to Polak, the Persians inhale it medicinally, smoking it with tobacco, catechu, mucilage, &c., the only bad effect being an occasional stomatitis.— Eulenberg: "Gewerbe Hygiène," p. 741.

Acid Solution of Nitrate of Mercury, Liquor hydrargyri nitratis acidus, a colourless, strongly acid liquid, giving the reactions for nitric acid and mercury; specific gravity, 2·246.

§ 189. *The more Common Patent and Quack Medicines containing Mercury.*

Mordant's Norton's Drops.—This patent medicine is a mixture of the tincture of gentian and ginger, holding in solution a little bichloride of mercury, and coloured with cochineal.

Solomon's Anti-impetigines is a solution of bichloride of mercury, flavoured and coloured.

Poor Man's Friend.—An ointment of nitrate of mercury.

Brown's Lozenges.—Each lozenge contains ½ grain of calomel, and 3½ grains of resinous extract of jalap; the rest is white sugar and tragacanth.

Ching's Worm Lozenges.—Each lozenge contains 1 grain of calomel; the rest white sugar and tragacanth, with saffron as a colouring matter.

Storey's Worm Cakes.—Each cake 2 grains of calomel, 2 grains of cinnabar, 6 grains of jalap, 5 grains of ginger, and the remainder sugar and water.

Wright's Pearl Ointment is said to be made up of 8 ounces of white precipitate rubbed to a cream in 1 pint of Goulard's extract, and to the mixture is added 7 pounds of white wax and 10 pounds of olive oil.

Keyser's Pills.—The receipt for these pills is—red oxide of mercury 1½ ounce, distilled vinegar (dilute acetic acid) 1 pint; dissolve, add to the resulting solution manna 2 lbs., and triturate for a long time before the fire, until a proper consistence is attained; lastly, divide the mass into pills of 1½ grain each.

Mitchell's Pills.—Each pill contains aloes ·8 grain, rhubarb 1·6 grain, calomel ·16 grain, tartar emetic ·05.

Many *Antibilious Pills* will be found to contain calomel, a few mercury in a finely divided state.

§ 190. *Mercury in Veterinary Medicine.*—Farmers and farriers use the ointment (*blue ointment*) to a dangerous extent, as a dressing for the fly, and wholesale poisoning of sheep has been in several instances the consequence.* Ethiops mineral and Turpeth mineral are given to dogs when affected by the distemper, worms, or the mange. Mercury, however, is not very frequently given to cattle by veterinary surgeons, ruminants generally appearing rather susceptible to its poisonous effects;

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* Taylor's "Medical Jurisprudence," i., p. 279.

but to horses it is given in large doses, especially in farcy and glanders.

Dose.—Horses.—Cinnabar ½ ounce (14·174 grms.), calomel ½ ounce (14·174 grms.) or more, corrosive sublimate 2 to 6 grains (·1296 to ·3888 grm.), and as much as 20 grains (1·296 grm.) have been given in farcy.

Cattle.—Mercury with chalk 1 to 3 drachms (3·888 to 11·64 grms.), calomel 1 to 2 drachms (3·888 to 7·7776 grms.); in worms 10 to 20 grains (·648 to 1·286 grm.); as an alterative, Ethiops mineral 2 to 4 drachms (7·777 to 15·552 grms.)

Dogs.—Ethiops or Turpeth mineral 2 to 20 grains (·1296 to 1·296 grm.), according to the size.

Fowls.—Mercury and chalk are given in fractions of a grain.

Hogs are also treated with mercury and chalk; the dose usually given does not exceed 5 grains (·32 grm.)

It may be remarked that many of the doses quoted appear very large; the writer cannot but consider that 20 grains of corrosive sublimate administered to a horse would be more likely to kill the animal than to cure the disease.

§ 191. *Mercury in the Arts.*—The use of mercury in the arts is so extensive, that any one in analytical practice is almost certain occasionally to meet with cases of accidental poisoning, either from the vapour * or some of its combinations.

Quicksilver is used in the extraction of gold, the silvering of mirrors, the construction of barometers, and various scientific instruments and appliances; also for the preservation of insects, and occasionally for their destruction.† An alloy with zinc and cadmium is employed by dentists for stopping teeth; but there is no evidence that it has been at all injurious, the mercury, probably, being in too powerful a state of combination to be attacked by the fluids in the mouth.‡ Cinnabar has also been employed to give a red colour to confections, and it may be found in tapers, cigarette papers, and other coloured articles. The nitrate of mercury in solution finds application in the colouring of horn, in the etching of metals, in the colouring of the finer sorts of wool, and in the hat manufacture.

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* A singular case is cited by Tardieu ("Etude méd.-légale sur l'empoisonnement"), in which a man, supposing he had some minerals containing gold, attempted the extraction by amalgamation with mercury. He used a portable furnace (for the purpose of volatilising the mercury) in a small room, and his wife, who assisted him, suffered from a very well-marked stomatitis and mercurial eruption.

† Forty-three persons were salivated from fumigating rooms with mercury for the purpose of destroying bugs (Sonnenschein's "Handbuch," p. 96).

‡ More danger is to be apprehended from the vulcanised rubber for artificial teeth; and, according to Dr. Taylor, accidents have occurred from the use of such supports or plates.

The sulphocyanide of mercury gives, when burnt, a most abundant ash, a fact utilised in the toy known as Pharaoh's serpent; the products of combustion are mercurial vapours and sulphurous anhydride. That the substance itself is poisonous is evident from the following experiment* :—·5 grm. was given to a pigeon without immediate result; but ten hours afterwards it was indisposed, and refused its food, and in forty hours it died without convulsions.

§ 192. *Dangerous and Fatal Doses of Mercury.*—Corrosive sublimate has been fatal in a dose so small as 3 grains (18 centigrammes); white precipitate has caused dangerous symptoms in doses of from 30 to 40 grains; the cyanide of mercury has killed a person in a dose of 10 grains (*Christison*); and Turpeth mineral has proved fatal in doses of 40 grains.

Other preparations of mercury have also been fatal, but a doubt has existed as to the precise quantity. Sometimes, also, there is probably a chemical change in the substance, so that it is impossible to state the fatal dose. For example, it is well known that calomel, under the influence of alkaline chlorides, can be converted into the bichloride—a fact which probably explains the extensive corrosive lesions that have been found after death from large doses of calomel.

§ 193. *Injury to Vegetation by Mercury*, &c.—The fumes of mercury are extremely injurious to vegetation. Priestley and Boussingault have shown that plants under a glass shade, in which some mercury is exposed in a saucer, first exhibit black spots on the leaves, ultimately the latter blacken entirely, and the plants die. Water in the neighbourhood of works and manufactures in which mercury is used or prepared in any way, may become contaminated, and both fish and cattle have in this way been poisoned.

§ 194. *Elimination of Mercury.*—The question of the channels by which mercury is eliminated is of the first importance. It would appear certain that it can exist in the body for some time in an inactive state, and then, from some change, be carried into the circulation and show its effects.† Voit considers that mercury combines with the albuminous bodies, separating upon their oxidation, and then becoming free and active.‡

However this may be, it is tolerably clear that in the administration of mercury, most of it is excreted by the bowels, and,

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* Eulenberg: "Gewerbe Hygiène," p. 742.

† Tuson gave a mare—first, 4 grains, and afterwards 5 grains of corrosive sublimate twice a day; at the end of fourteen days, in a pint of urine no mercury was detected, but at the end of three weeks it was found.

‡ Voit, "Physiol. Chem." Augsburg, 1857.

therefore that the analyst (in any recent case) should be sent the whole length of the intestinal canal, or its contents, as well as the ordinary organs.

From the body of a hound that, in the course of thirty-one days, took 2·789 grms. of calomel (2·368 Hg) in eighty-seven doses, about 94 per cent. of the substance was recovered on analysis.

	Mercurous Sulphide.
In the fæces,	2·1175
" urine,	0·0550
" brain, heart, lungs, spleen, pancreas, kidneys, scrotum, and penis,	0·0090
" liver,	0·0140
" muscles,	0·0114
	2·2069

This equals 1·9 of metallic mercury.* Thus, of the whole 2·2 grms. of mercuric sulphide separated, over 95 per cent. was obtained from the fæces.

This case is of considerable interest, for there are recorded in toxicological treatises a few cases of undoubted mercurial poisoning in which no poison had been detected, although there was ample evidence that it had been administered by the mouth In such cases it is probable that the whole length of the intestinal canal had not been examined, and the analysis failed from this cause. When (as not unfrequently happens) the mercurial poison has entered by the skin, it is evident that the most likely localities are the urine, the liver, and the kidneys.†

In a case related by Vidal,‡ the *Liquor Bellostii* (or solution of mercuric nitrate) was ordered by mistake instead of a liniment. Although externally applied, it caused salivation, profuse diarrhœa, and death in nine days. The whole of the intestinal track was found inflamed with extravasations, and mercury detected in the liver.

In any case of external application, if death ensues directly from the poison, evidence of its presence will probably be found but too much stress must not be laid upon the detection o

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* Riederer, in Buchner's *Neues Repert. f. Pharm.* Bd. x. vij.

† Very recently a woman died from the effects of a corrosive sublimate lotion applied by a quack to a wound in her leg. The writer found no poison in the stomach, but separated a milligramme of metallic mercury from the liver; the urine and intestines were not sent.

‡ *Gaz. de hôpital*, Juillet, 1864.

mercury, for, as Dr. Taylor says, "Nothing is more common than to discover traces of mercury in the stomach, bowels, liver, kidneys, or other organs of a dead body."*

§ 195. *Tests for Mercury.*—Mercury, in combination and in the solid form, is most readily detected by mixing the substance intimately with dry anhydrous sodic carbonate, transferring the mixture to a glass tube, sealed at one end, and applying heat. If mercury be present, a ring of minute globules condenses in the cool part of the tube. If the quantity of mercury is likely to be very minute, it is best to modify the process by using a subliming cell (p. 284), and thus obtain the sublimate on a circle of thin glass in a convenient form for microscopical examination. If there is any doubt whether the globules are those of mercury or not, this may be resolved by putting a fragment of iodine on the lower disc of the subliming cell, and then completing it by the disc which contains the sublimate (of course, the supposed mercurial surface must be undermost); on placing the cell in a warm, light place, after a time the scarlet iodide is formed and the identification is complete. Similarly, a glass tube containing an ill-defined metallic ring of mercury can be sealed or corked up with a crystal of iodine, and after a few hours the yellow iodide, changing to scarlet, will become apparent. There are few (if any) tests of greater delicacy than this.

Mercury in solution can be withdrawn by acidulating the liquid, and then inserting either simply a piece of gold foil, gold wire, or bright copper foil; or else by a galvanic arrangement, such as iron wire wound round a gold coin or gold foil, attached to a rod of zinc; or, lastly, by the aid of gold or copper electrodes in connection with a battery. By any of these methods, mercury is obtained in the metallic state, and the metal with its film can be placed in a subliming cell, and globules deposited and identified, as before described.

The *Precipitating Reagents* for mercury are numerous: a solution of stannous chloride, heated with a solution of mercury, or any combination, whether soluble or insoluble, reduces it to the metallic state.

Mercurous Salts in solution yield with potash, soda, or lime, a black precipitate of mercurous oxide. *Mercuric Salts,* a bright yellow precipitate of mercuric oxide.

Mercurous Salts yield black precipitates, with sulphides of ammonium and hydrogen. *Mercuric Salts* give a similar reaction, but with sulphuretted hydrogen first a whitish precipitate, passing slowly through red to black.

Mercurous Salts and solutions of the chlorides give a white

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* Taylor: "Medical Jurisprudence," I., p. 288.

precipitate of calomel; the *Mercuric Salts* yield no precipitate under similar circumstances. *Mercurous Salts* treated with iodide of potash give a green mercurous iodide; *Mercuric*, a scarlet.

§ 196. *The Detection of Mercury in Organic Substances and Fluids.*—The galvanic process, previously described, is found in practice the best. Fluids, such as urine, must be evaporated to dryness, and then treated with hydrochloric acid. Such organs as the liver are cut up and dissolved in hydrochloric acid (1 : 4), and the strained fluid tested by electrolysis. Dr. Taylor relates* how by this process distinct evidence of mercury in the liver was obtained on a piece of copper gauze, in a case where a child had been given two grains of calomel before death. "Four ounces of the liver were treated with hydrochloric acid and water, and a small piece of pure copper placed in the acid liquid while warm, and kept there for about forty-eight hours. It acquired a slight silvery lustre, and globules of mercury were obtained from it by sublimation."

In those cases where no special search is made for mercury, but an acid (hydrochloric) solution is treated with sulphuretted hydrogen, mercury is indicated by the presence of a black precipitate, which does not dissolve in warm nitric acid.

The further treatment of the black sulphide may be undertaken in two ways:—

(1.) It is collected on a porcelain dish, with the addition of a little nitric acid, and evaporated to dryness in order to destroy organic matter. Hydrochloric and a few drops of nitric acid are next added; the action is aided by a gentle heat, the solution finally evaporated to dryness on the water-bath, and the residue taken up by warm distilled water. The solution is that of a persalt of mercury, and the mercury can be separated by electrolysis, or indicated by the tests already detailed.

(2.) The other method, and the most satisfactory, is to mix the sulphide while moist with dry carbonate of soda, make it into a pellet which will easily enter a reduction or subliming tube, dry it carefully, and obtain a sublimate of metallic mercury.

Estimation of Mercury.—All pharmaceutical substances containing mercury, as well as the sulphide prepared in the wet way, and minerals, are best dealt with by obtaining and weighing the metal in the solid state. The assay is very simple and easy when carried out on the method that was first, perhaps, proposed by Domeyko. A glass tube (which should not be too thin), closed at one end, is bent, as shown in Fig. 18; the diameter

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* *Op. cit.*, p. 289.

should be about three lines, the length from seven to eight inches, the shorter arm not exceeding two inches. The powdered substance is mixed with two or three times its weight of litharge, and introduced into the tube at *a*. The portion of the tube containing the mercury is at first heated gently, but finally brought to a temperature sufficient to fuse the substance and soften the glass. The mercury collects in an annular film at *b* in the cooler limb, and may now, with a little management of the lamp, be concentrated in a well defined ring; the portion of the tube containing this ring is cut off, weighed, then cleansed from mercury, and reweighed. Many of the pharmaceutical preparations do not require litharge, which is specially adapted for ores, and heating with sodic carbonate (in great excess) will suffice. Mercury mixed with organic matter must be first separated as described, by copper or gold, the silvered foil rolled up, dried, introduced into the bent tube, and simply heated without admixture with any substance; the weight may be obtained either by weighing the foil before and after the operation, or as above.

Fig. 18.

§ 197. *Volumetric Processes for the Estimation of Mercury.*— When a great number of mercurial preparations are to be examined, a volumetric process is extremely convenient. There are several of these processes, some adapted more particularly for mercuric, and others for mercurous compounds. For mercuric, the method of Personne* is the best. The conversion of the various forms of mercury into corrosive sublimate may be effected by evaporation with aqua regia, care being taken that the bath shall not be at a boiling temperature, or there will be a slight loss.

Personne prefers to heat with caustic soda or potash, and then pass chlorine gas into the mixture; the excess of chlorine is expelled by boiling, mercuric chloride in presence of an alkaline chloride not being volatilised at 100°C. The standard solutions required for this process are—

(1.) 33·2 grms. of potassic iodide in 1 litre of water, 1 cc. = 0·01 grm. Hg, or 0·01355 grm. $HgCl_2$.

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* *Comptes Rendus*, lvi. 68; Sutton's "Vol. Anal.," 177.

(2.) A solution of mercuric chloride containing 13·55 grms. to the litre, 1 cc. = 0·1 grm. Hg.

The process is founded on the fact that if a solution of mercuric chloride be added to one of potassic iodide, in the proportion of one of the former to four of the latter, mercuric iodide is formed, and immediately dissolved, until the balance is overstepped, when the red colour is developed; the final reaction is very sharp, and with solutions properly made is very accurate. The mercuric solution must always be added to the alkaline iodide; a reversal of the process does not answer. It therefore follows that the solution to be tested must be made up to a definite bulk, and added to a known quantity of the iodide of potash solution, until the red colour appears.

Mercurous Salts may be titrated with great accuracy by a decinormal solution of sodic chloride. This is added to the cold solution in very slight excess, the calomel filtered off, the filtrate neutralised by pure carbonate of soda, and the amount of chloride of soda still unused found by titration with nitrate of silver, the end reaction being indicated by chromate of potash. Several other volumetric processes are fully described in works treating upon this branch of analysis.

(III.) NO PRECIPITATE BY HYDRIC SULPHIDE IN A SOLUTION STRONGLY ACIDIFIED BY THE MINERAL ACIDS; BUT A WHITE PRECIPITATE IN NEUTRAL, ALKALINE, OR ACETIC ACID SOLUTIONS.

ZINC.

§ 198. *Zinc* = 65·0; specific gravity, 6·8 to 7·1; fusing point, 412°C. (773°F.), is a hard, bluish-white, brittle metal, with a crystalline fracture. Between 100° and 150°C. it becomes ductile, and may be easily wrought; but at a little higher temperature it again becomes brittle, and at a bright red heat it fuses, and then volatilises, the fumes taking fire when exposed to the air. In analysis zinc occurs either as a metallic deposit on a platinum foil or dish, or as a brittle bead, obtained by reducing a zinc compound with soda on charcoal.

The salts of zinc to be briefly described here are the carbonate, the oxide, and the sulphide—all of which are likely to occur in the separation and estimation of zinc, and the sulphate and chloride—salts more especially found in commerce, and causing accidents from time to time.

§ 199. *Carbonate of Zinc*, in the native form of calamine, contains, as is well known, 64·8 per cent. of oxide of zinc; but the carbonate obtained in the course of an analysis by precipitating the neutral hot solution of a soluble salt of zinc by carbonate of potash or soda, is carbonate of zinc *plus* a variable quantity of hydrated oxide of zinc. Unless the precipitation takes place at a boiling temperature, the carbonic anhydride retains a portion of the oxide of zinc in solution. By ignition of the carbonate, oxide of zinc results.

§ 200. *Oxide of Zinc* ($ZnO = 81$; specific gravity, 5·612; Zu 80·24, O 19·76) is a white powder when cool, yellow when hot. If mixed with sufficient powdered sulphur, and ignited in a stream of hydrogen, the sulphide is produced; if ignited in the pure state in a rapid stream of hydrogen gas, metallic zinc is obtained; but if it is only a feeble current, the oxide of zinc becomes crystalline, a portion only being reduced.

§ 201. *Sulphide of Zinc* ($ZnS = 97$; specific gravity, 4·1; Zu 67·01, S 32·99).—The sulphide obtained by treating a neutral solution of a soluble salt of zinc by hydric sulphide, is hydrated sulphide, insoluble in water, caustic alkalies, and alkaline sulphides, but dissolving completely in nitric or in hydrochloric acid. When dry, it is a white powder, and if ignited contains some oxide of zinc. The anhydrous sulphide is produced by mixing the precipitated sulphide with sulphur, and igniting in a crucible in a stream of hydrogen gas.

Sulphate of Zinc ($ZnSO_4 7H_2O$ 101 + 126; specific gravity, crystals, 1·931). This salt is officinal in all the pharmacopeias, is used in calico-printing, and is commonly known as *white vitriol.* By varying the temperature at which the crystals are allowed to be formed, it may be obtained with 6, 5, 2, or 1, atoms of water. The commercial sulphate is in crystals exactly similar to those of Epsom salts; it is slightly efflorescent, and gives the reactions of zinc and sulphuric acid.

§ 202. *Chloride of Zinc* is obtained by dissolving zinc in hydro-hloric acid, or by direct union of zinc and chloride. Chloride f zinc is the only constituent in the well-known "Burnett's isinfectant fluid." A solution of chloride of zinc may be heated ntil it becomes water-free; when this takes place it still remains uid, and makes a convenient bath, for warmth may be applied to it above 370°C. without its emitting fumes to inconvenience;

at a red heat it distils. A concentrated solution of zinco ammonic chloride ($2H_4NClZnCl_2$) is used for the purpose o removing the film of oxide from various metals preparatory t soldering.

§ 203. *Zinc in the Arts.*—The use of zinc as a metal in sheeting cisterns, articles for domestic use, alloys, &c., is well known. Sulphide of zinc has lately been employed as a substitute fo white lead, and may possibly supersede it. Zinc white is furthe employed as a pigment, and mixed with albumen is an agent in calico-printing; it is also used in the decoloration of glass, in the polishing of optical glasses, and in the manufacture of artificial meerschaum pipes.*

Chromate of Zinc ($ZnCrO_4$) is used in calico-printing, and there is also in commerce a basic chromate known as *zinc-yellow.* Zinc Green, or Rinman's Green, is a beautiful innocuous colour, formed by igniting a mixture of dry zincic and cobaltous carbonates.

The use of zinc vessels in the preparation of foods may occasionally bring the metal under the notice of the analyst. When exposed to a moist atmosphere, zinc becomes covered with a thin film of oxide, perfectly insoluble in ordinary water but if the water should be charged with common salt, a considerable quantity may be dissolved. It may generally be laid down as a rule that the solvent power of water on zinc has a direct relation to the chlorides present, whilst carbonate of lime greatly diminishes this solubility.†

Milk may become contaminated by zinc; for it is a matte of common knowledge, that milk contained in zinc vessels does not readily turn sour. This may be explained by the zinc oxid combining with the lactic acid, and forming the sparingly solubl lactate of zinc $(C_3H_5O_3)Zn + 3H_2O$, thus withdrawing the lacti acid as fast as it is formed, preventing the coagulation of th caseine. With regard to this important practical subject, MM Payen and Chevallier made several experiments on the actio of brandy, wine, vinegar, olive oil, soup, milk, &c., and prove that zinc is acted on by all these, and especially by the alcoholic acetic, and saline liquids. M. Schemfele has repeated these experi ments, and determined the amount of zinc dissolved in fiftee days by different liquids from a galvanised iron as well as zinc vessel.

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* Artificial meerschaum pipes are composed of zinc white, magnesia usta and caseine ammonium.

† Ziurek, indeed, found in a litre of water contained in a zinc cistern n less than 1·0104 grm. of zinc (10·7 grains to the gallon), and the same wate showed only 0·074 grm. of common salt to the litre (5·18 grains to the gallon) *Vierteljahrsschr. für Gericht. Medicin,* 1867, Bd. 6, p. 356.

The amount found was as follows :—

	The liquid from the zinc vessel, grms. per litre.	The liquid from the galvanised iron vessel, grms. per litre.
Brandy,	0·95	0·70
Wine,	3·95	4·10
Orange-flower water,	0·50	0·75
Vinegar,	31·75	60·75
Fatty soup,	0·46	1·00
Weak soup,	0·86	1·76
Milk,	5·13	7·00
Salt water,	1·75	0·40
Seltzer water,	0·35	0·30
Distilled water,	traces.	traces.
Ordinary water,	traces.	traces.
Olive oil,	none.	none.

§ 204. *Zinc as a Poison.*[*]—Only the sulphate and the chloride of zinc are likely to act as poisons. Large quantities of the oxide can be taken without a fatal result; for Busse saved a boy who had taken 3246 grains as a remedy for epilepsy.[†]

The workmen also in zinc manufactories cover themselves with oxide of zinc from head to foot without any very apparent injury; but that this dust is not in all instances innocuous, is certain—*e.g.*,[‡] a pharmacy student filled a laboratory with oxide of zinc vapour, and suffered from well-marked and even serious poisonous symptoms, consisting of pain in the head, vomiting, salivation, and a short fever.[§]

Sulphate of zinc is strongly emetic, and acts as a pure irritant; the fatal dose may be considered as about an ounce, although recovery has taken place from that quantity.

Chloride of Zinc is a powerfully corrosive and irritant poison, which may kill by its primary or its secondary effects; the latter

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[*] Plants grow and thrive on earth holding zinc compounds, and absorb a small quantity of zinc oxide without injury; the greatest portion being found in the leaves and stems, the smallest in the seeds. Solutions of salts of zinc, however, act injuriously on plant life; a solution of zinc sulphate, even in the strength of 1:50, soon influencing the growth of plants; but if the salt be filtered through earth, the result is decomposition, and the zinc is combined in a form insoluble in water. In the neighbourhood of zinc manufactories it is not uncommon for vegetation to be injured by sulphate of zinc, and fowls, &c., may be poisoned by feeding on ground thus contaminated.

Caspar's *Wochenschr.*, 1837, No. 19.

[†] Dr. Marcet states that one of his patients took 1 lb. [453·6 grms.] in a month for epilepsy without apparent injury.—Taylor's "Jurisprudence," i. 317.

[‡] Rust's *Magazin*, xxi., Bd. S., 563.

[§] The so-called zinc fever has only been noticed in the founding of brass; t is always preceded by well-marked shivering, the other symptoms being imilar to those described.

are generally marked by nervous symptoms. Very serious illness has followed the ingestion of Burnett's fluid in quantity equal to 12 grains of the chloride. Death has taken place from about 100 grains of the chloride, and recovery after 200 grains. A few years ago, a quack applied a solution of chloride of zinc to the cancerous breast of a woman in Barnstaple; death followed with symptoms of poisoning, and zinc was found in the liver and other organs. This instance proves that the external application of the chloride may induce zinc poisoning. In cases of external absorption, the muscles and bones would appear to be the best tissues to examine chemically; for Matzkewitsch investigated very carefully a dog poisoned by 100 parts of zinc, subcutaneously injected in the form of acetate, and found it distributed over the several organs of the body in the following ratios:—Muscles 60·5, bones 35·49, stomach and intestines 4·63, skin 3·70, place of injection 2·19, liver 1·75, lungs and heart 1·68, kidneys, bladder, and urine 1·14.

§ 205. *Detection of Zinc in Organic Liquids or Solids.*—The only certain method of detection is to produce the sulphide of zinc, best effected by saturating a neutral or feebly acid liquid with hydric sulphide. If an organic liquid which can be easily filtered, is operated upon, it may be strongly acidulated with acetic acid, and at once treated with hydric sulphide. If, however, zinc is sought for as a part of a systematic examination (as will most likely be the case), the substance will have been treated with hydrochloric acid, and already tested for arsenic, antimony, lead, &c., and filtered from any precipitate. In such a case the hydrochloric acid must first be replaced by acetic, which is effected by adding a slight excess of sodic acetate; the right quantity of the latter is easily known, if the hydrochloric acid originally added was carefully measured, and its specific gravity ascertained; 3·72 o crystallised sodic acetate saturating one of HCl($NaC_2H_3O_23H_2O$ + $HCl = NaCl + HC_2H_3O_2 + 3H_2O$). Lastly, should the distillation process given at p. 399 have been adopted, the contents of the retort will only require to be treated with water, filtered, and saturated with sulphurated hydrogen. In any of the above cases should a white, dirty-white, or lightish-coloured precipitate (which is not sulphur) be thrown down, zinc may be suspected; it will however, be absolutely necessary to identify the sulphide, for there are many sources of error. The most satisfactory of all identifications is the production of Rinman's green. The supposed sulphide is dissolved off the filter with hot nitric acid, a drop or more (according to the quantity of the original precipitate) o solution of cobalt nitrate added, the solution precipitated with carbonate of soda and boiled, to expel all carbonic anhydride; the precipitate is then collected on a filter, washed, dried, and ignited in a platinum dish. If zinc be present in so small a proportion as 1 : 100,000 parts, the mass will be permanently green.

Other methods of procedure are as follows :—

The supposed zinc sulphide (after being well washed) is collected in a porcelain dish, and dissolved in a few drops of sulphuric acid, filtered, nitric acid added, evaporated to dryness, and heated to destroy all organic matter. When cool, the mass is treated with water acidulated by sulphuric acid, and again filtered. The solution may contain iron as well as zinc; and if the former (on testing a drop with ferrocyanide of potash) appears in any quantity, it must be separated by the addition of ammonia in excess. To the ammoniacal filtrate carbonate of soda is added in excess, the liquid well boiled, and the precipitate collected on a filter and washed. The carbonate of zinc thus obtained is converted into the oxide by ignition, and weighed. If oxide of zinc, it will be yellow when hot, white when cold; it will dissolve in acetic acid, and give a white precipitate with sulphuretted hydrogen; and finally, if heated on charcoal in the oxidising flame, and moistened with cobalt nitrate solution, a green colour will result.

Zinc may also be separated from liquids by electrolysis; the simplest way is to place the fluid under examination in a platinum dish of sufficient size, acidify, and insert a piece of magnesium tape—the metallic film so obtained may be dissolved in hydrochloric acid, and the usual tests applied.

(IV). ALKALINE EARTHS.

BARIUM.

§ 206. The soluble salts of barium are undoubtedly poisonous, and are of frequent occurrence in the arts. The chloride of barium is used in the staining of wool; the nitrate and the chlorate, in the green fires of the pyrotechnist; the oxide and the carbonate in the manufacture of glass; the chromate of baryta is used by artists under the name of "yellow ultramarine;" while the sulphate (technically known as "permanent white") is, on account of its weight and cheapness, occasionally used as an adulterant of white powders and other substances.*

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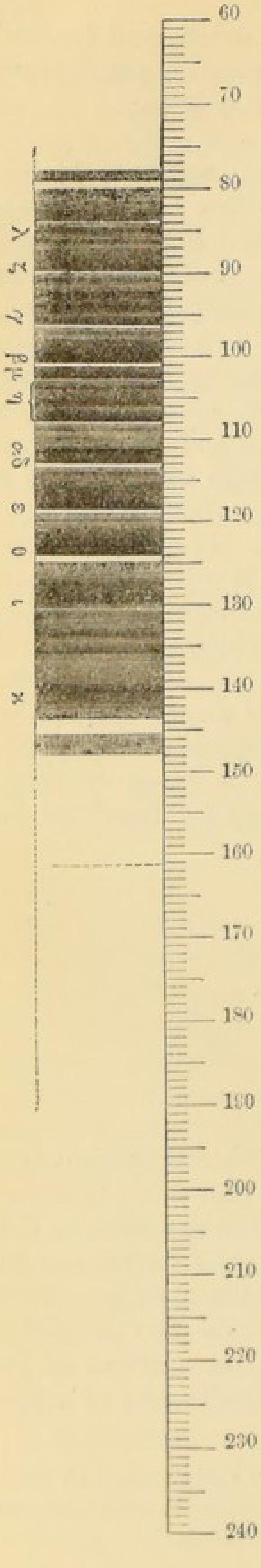
* The carbonate and sulphate of baryta are usually enumerated as occasional adulterants of bread. There is, however, no modern authentic instance of this; and the occurrence is doubtful, though not impossible.



§ 207. *Chloride of Barium*, $BaCl_2H_2O$ 208 + 36; anhydrous, Ba 65·86 per cent., Cl 34·14; specific gravity, 3·75—is in commerce in the form of white, four-sided, tabular crystals; water dissolves about half its weight at ordinary temperatures, three-fourths at 100°C. Its solution gives a white precipitate with sulphuric acid, quite insoluble in water and nitric acid.

The salt imparts a green hue to an otherwise colourless flame; viewed by the spectroscope, green bands will be visible. We may note that chloride of barium gives two different spectra, the one at the moment of the introduction of the salt, the other when the substance has been exposed for some time to a high temperature. This is caused by a rapid loss of chlorine, so that the first spectrum is due to $BaCl_2$, with a variable mixture of BaCl, the second to BaCl alone. The accompanying diagram represents the phenomenon most usually seen, viz., the flame after exposure for some seconds.*

§ 208. *Baric Carbonate*, $BaCO_3 = 197$; specific gravity, 4·3; BaO 77·69 per cent., CO_2 22·31—in its native form termed *Witherite*, is a dense heavy powder, insoluble in pure water, but dissolving in acetic, nitric, and hydrochloric acids, the solution giving the reactions of barium.

A rat-poison may be met with composed of baric carbonate, sugar, and oatmeal, flavoured with a little oil of aniseed and caraway.

§ 209. *Sulphate of Barium*, $BaSO_4$; specific gravity, 4·59; BaO 65·66 per cent., SO_3 34·34 per cent., is a pure white powder when recently precipitated, absolutely insoluble in water, and practically insoluble in cold dilute acids. It is quite unalterable in the air at a red heat; on ignition with charcoal it may be converted almost entirely into sulphide of barium; and by ignition with $CaCl_2$ into chloride.

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* From *Spectres Lumineux*, Lecoq de Boisbaudran. Paris, 1874.

§ 210. *Dose, &c.*—Chloride of barium is occasionally prescribed in doses not exceeding 2 grains (·1296 grm.); to horses as much as 60 grains have been given; and a case is on record of a person having been killed by 100 grains. The carbonate of baryta has poisoned a person who took only 60 grains (3·888 grms.), and about 12 grains (·7776 grm.) are sufficient to kill a dog. Hence it may be inferred, that from 6 to 7 grains (·386 to ·4536 grm.) of either the carbonate or the chloride would probably produce poisonous, although not necessarily fatal, symptoms.

§ 211. *The Separation of Barium Salts from Organic Solids or Fluids, and their Identification.*—In the usual course of examination of an unknown substance, the matter will already have been extracted by hydrochloric acid, and the solution successively treated with hydric and ammonic sulphides. The filtrate from any precipitate, after being boiled, would in such a case give a precipitate if treated with sulphuric acid, should a salt of barium be present.

If there, however, should be *special* grounds to search for baryta in particular, it is best to extract the substances with pure boiling water, to concentrate the solution, and then add sulphuric acid, collecting any precipitate which may form. If the latter is found to be sulphate of baryta, it must be derived from some soluble salt, such as the nitrate or the chloride. The substances which have been exhausted with water are now treated with hydrochloric acid, and to the acid filtrate sulphuric acid is added. If sulphate of baryta is thrown down, the baryta present must have been a salt insoluble in water, soluble in acids—probably the carbonate. Lastly, the organic substances may be burnt to an ash, the ash fused with carbonate of soda, the mass, when cool, dissolved in HCl, and the solution precipitated with sulphuric acid. Any baryta now obtained was present, probably, in the form of sulphate; nevertheless, if obtained from the tissues, it would prove that a soluble salt had been administered, for (so far as is known) sulphate of barium is not taken up by the animal fluids, and is innocuous.

The sulphate of barium is identified as follows:—

(1.) A part of the well-washed precipitate is boiled with distilled water, filtered, and to the filtrate a solution of chloride of barium added. If there is no precipitate, the sulphate can be none other than baric sulphate, for all the rest, without exception, are soluble enough to give a slight cloud with baric chloride.

(2.) The sulphate may be changed into sulphide by ignition on charcoal, the sulphide treated with HCl, the solution evaporated to dryness, and the resulting chloride examined spectroscopically. Or, the sulphate may be mixed with chloride of calcium, taken up on a loop of platinum wire, heated strongly in the flame of a Bunsen burner, and the flame examined by the spectroscope.

(3.) A solution of the chloride of barium obtained from (2) gives a yellow precipitate with neutral chromate of potash, insoluble in water, but soluble in nitric acid.

ADDENDUM TO ARTICLE "MILK" (p. 37).

It is stated in the chapter on Milk (p. 38), that, according to some of the Continental chemists, the albumen in milk varies from 3·14 to 3·43 per cent.; but it would appear that this estimate is much too high, for several analyses of genuine milk made in the writer's laboratory, whilst these sheets were going through the press, give the percentage from ·07 to ·7 per cent., and that of urea from ·001 to ·002 per cent. It may, however, be conceded that the albumen at the commencement of lactation may much exceed the above values.

Special researches have also been made by the writer lately, as to whether nitrates or nitrites are to be found in milk, but none have been discovered. The separation of nitrates, then, from any milk may occasionally be a valuable confirmatory evidence of adulteration, showing that not only has water been added, but a water, probably, of considerable impurity.

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A

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