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WATER ANALYSIS.

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WATER ANALYSIS

FOR

SANITARY PURPOSES,

WITH HINTS

FOR THE INTERPRETATION OF RESULTS.

BY

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WATER ANALYSIS.

INTRODUCTION.

PURE water, strictly so called, is not to be found in nature. Whether rain be received directly from the clouds, or obtained indirectly after it has washed the surface of the earth and has formed streams, or has percolated deep into the ground and issued forth again from springs—in every case the water contains substances which, from a chemical point of view, are impurities.

It rests with the analyst now-a-days to determine, what formerly the consumer had to discover for himself by long and perhaps hazardous experience, whether the impurities found in water are of such a nature as to render it unsuitable for the particular purpose for which it is intended to be used.

The *exhaustive* chemical examination of a sample of water is one of the most tedious and troublesome operations known to chemists. It requires weeks, sometimes even months, for its completion. This arises partly from the great multiplicity of separate substances which may be present in the water, both in solution and in suspension, partly from the very minute proportion in which these substances sometimes exist, and partly on account of the difficulties attending their exact determination when they are diffused through vast volumes of water. Such an exhaustive examination includes:—

1. The extraction and separate volumetric measurement of the dissolved gases.

2. The separate determination of the weight of each constituent of the saline matters in solution.

3. The determination of the two chief elements of the organic matters in solution.

4. The separation of the suspended matters, if any, and the determination of their total weight when dry.

5. The separation and determination of each mineral constituent of the suspended matters.

6. The separation and determination, as far as possible, of each organic constituent of the suspended matters.

Fortunately, many of the more tedious and laborious of these operations may be omitted, if the object of the analysis be only to ascertain the suitability or otherwise of the water for domestic or manufacturing purposes. Thus, the extraction and volumetric measurement of the gases may be safely dispensed with; since, in the present state of our knowledge, the gaseous constituents of water throw but little light upon its character. The existence of dissolved atmospheric gases in water doubtless adds to its palatability: recently boiled water, for instance, is notoriously flat and vapid. The solution of these gases by water, however, is exceedingly rapid, and no lack of aëration is likely to occur in natural waters. This is seen from the following comparison of the proportional volumes of atmospheric gases expelled on boiling 100 cubic inches of rain water, Cumberland upper surface water, Loch Katrine water as delivered in Glasgow, Thames water as delivered in London, and water drawn from deep wells in the chalk, respectively:—

Volume and Composition of the Gases dissolved in 100 *Cubic Inches of Various Waters.*

—	Rain Water.	Cumberland Mountain Water.	Loch Katrine Water.	Thames Water.	Deep Chalk Well Water.
	cubic inches.	cubic inches.	cubic inches.	cubic inches.	cubic inches.
Nitrogen.............	1·308	1·424	1·731	1·325	1·944
Oxygen..............	·637	·726	·704	·588	·028
Carbonic acid.........	·128	·281	·113	4·021	5·520
	2·073	2·431	2·548	5·934	7·492

A comparison of the numbers in the foregoing table shows that the total volume of dissolved atmospheric gases differs but little, even in waters from the most widely different sources. It was at one time supposed that the proportion of oxygen in these gases was an important item in the history of the water, and it was believed to indicate, if small, the presence of putrescent organic matters; but the subsequent discovery that deep well waters (in which putrescent organic matter is certainly not present) contained but little or no dissolved oxygen deprived this analytical fact of much of its importance. The large proportion of carbonic acid which is present in Thames water and in deep chalk well water scarcely adds to the effective aëration of these waters, because nearly the whole of this carbonic acid is in chemical combination with lime, and not in the condition of dissolved gas.

The separate determination of the weight of each constituent of the saline matters in solution is also rarely required. These constituents have, with very few exceptions, no appreciable influence upon the wholesomeness of the water; hence, in the great majority of cases, it is not necessary to determine the weight of each. Certain of them, however, are very useful in tracing the previous history of the water, and their separate determination must, therefore, on no account be omitted. These are ammonia, nitrates, nitrites, and chlorides. Moreover, if the presence of lead, copper, arsenic, or barium be suspected, these metals must be carefully sought for and (if found in more than mere traces) their respective quantities determined. The degree of hardness ought also to be ascertained in all cases.

The separation and determination of each mineral constituent of the suspended matters may be dispensed with, unless poisonous substances occur amongst them.

The separate determination of each organic constituent of the suspended matters is of comparatively little use in the present state of our knowledge, because it is impossible to distinguish, amongst the suspended matters in water, those which are injurious from those which are harmless. The really injurious organic suspended matters are not merely organic but organised, *e.g.*, entozoic ova or zymotic germs capable of reproduction in the human body with the simultaneous development of disease. Investigations of this class belong rather to microscopical than to chemical analysis; but even microscopical research is scarcely yet competent to reveal any facts of direct importance in connection with such organised suspended matters. The microscope has rarely found, even in the most polluted drinking water, any germ or organism which is known to be deleterious to human health: but, by showing the presence of living organisms in water, it proves either that the water has not been so efficiently filtered as to remove these organisms, or that it has subsequently become polluted by them, and thus it is indirectly demonstrated that the water has not been treated, preserved, or stored under such conditions as would preclude the access of deleterious germs or organisms. A microscopic examination of the suspended matters in potable waters thus becomes indirectly of considerable importance.

The object of this book is not to describe the *exhaustive* analysis of water, but to point out the means whereby the chemist may obtain trustworthy data from which to judge of the merits of a water for drinking or other purposes.

Some of these data can only be obtained by delicate and somewhat elaborate processes involving a knowledge of gas analysis. The quality of drinking water has, however, frequently to be investigated by persons who are either not instructed in the analysis of gases, or are not possessed of the apparatus necessary for performing the operations; and for their convenience I have, accordingly, divided this work into two parts, the first being wholly devoted to processes which may be carried out without the aid of eudiometric apparatus, while the second treats exclusively of the processes in which such apparatus is essential. Thus, at the beginning will be found such information as will enable an experimenter to determine the quantities of the inorganic indicators of pollution, *e.g.*, solid matter, ammonia, chlorine, and hardening ingredients, and also to ascertain whether poisonous metals are present. In short, here are given in detail various processes which ought always to be put into operation in water analysis, whether combustion of the organic matter be resorted to or not, and these are supplemented by particulars which will enable the analyst, without resorting to gas apparatus, to determine the amount of nitrates, and likewise to estimate *approximately* the proportion of the organic elements present in a sample of water.

I have italicised the word "*approximately*," because long experience has convinced me that there is no process, except the actual combustion of the organic matter present in water, which affords thoroughly trustworthy evidence of the fitness or otherwise of the sample for dietetic purposes.

The "ignition" and so-called "albuminoid ammonia" processes are not here described, for reasons which will be found in the "Journal of the Chemical Society," Vol. XXI, pp. 79–81; Vol. XXIX, pp. 847–850; and Vol. I for 1879, pp. 61–66 and 94–96.

In the analytical examination of the water supplies (whether actual or contemplated) of towns, and the investigation of well and other waters in connection with the propagation of disease, facility of manipulation is obviously a minor consideration in comparison with accuracy of result. In such cases, I deem it essential to have recourse to the process of analysis described in Part II; for, in order to gain a sound basis for an opinion, not only should the proportional amount of organic elements be determined, but also, as far as possible, the nature of the organic matter, that is to say, whether it is of animal or vegetable origin.

Trustworthy information on these points can only be obtained by observing the proportion of carbon to nitrogen in the organic matter found in the water, and it is chiefly in respect of such details that the more simple methods of estimation fall short of the accuracy which is essential.

Hence, I strongly recommend that recourse should be had to the combustion process of analysis in all cases of real importance.

It must be borne in mind, however, that a correct determination of the various matters contained in a sample of water is not the sole purpose of the investigation, but simply the means to an end. The desire of those who send water for analysis is not to obtain an array of figures, which, however accurate, affords little information to the unskilled public; their chief object is to procure the authoritative opinion which is deducible from the data thus furnished. Therefore, in order to assist the experimenter in drawing inferences from the facts acquired, I have given, in the respective chapters, an explanation of the interpretation to be put upon each determination; and to supplement these details, I have appended at the end of the volume an extended list of representative analyses (Appendices Nos. IV, V, and VI), and a reprint of the general conclusions adopted by the Rivers Pollution Commissioners, as the result of their investigation into the water supply of Great Britain. (Appendices Nos. VII and VIII.)

A careful study of the methods here set forth for the acquisition of facts, and of the principles laid down for the interpretation of such facts when elicited, will, it is hoped, be of practical use both to the chemist and the medical officer of health, who have to advise on the qualities of water; and hence, indirectly, to the public, whose interest in the character of the supply is often of the most vital importance.

THE COLLECTION OF SAMPLES.

When water is sent to be analysed, it is obviously of the greatest importance that the sample should fairly represent the supply which is to be submitted to the judgment of the chemist. With the view of ensuring the necessary care in this respect, it has been my custom to furnish the senders of samples with a printed copy of directions, containing a list of precautions to be observed. Of these directions I here give a copy, not only to show how a fair sample of the water is to be obtained, but also what information, relative to its source, ought in every case to be communicated to the analyst.

The quantities enumerated in these directions are such as will suffice for determining the quality of a water for dietetic and general domestic purposes. When, however, the suitability of the supply for brewing, dyeing, or other technical uses is the object of investigation, and a complete analysis of the inorganic constituents has consequently to be executed, the quantity forwarded must be at least doubled.

Directions for the Collection of Samples of Drinking Water for Analysis.

I. Stoppered glass bottles of the kind technically known as "Winchester Quarts," and procurable from any druggist, should be used for this purpose. These bottles hold about two imperial quarts, and must be perfectly clean; it is desirable that they should not have been previously used for any other purpose.

Waters for analysis must not be put into stoneware jars Corks should also be avoided if possible, but if used they ought to be quite new and well washed with the water before insertion into the bottle.

II. Before collecting the sample, rinse the bottle well three times with the water, filling it each time about one-third full. Then fill it within half an inch of the stopper, tie the stopper tightly down with a piece of calico over it, and seal the string.

If the sample be taken from a well with a pump fixed in it, pump about four gallons of water before filling the bottle; then pump the water directly from the spout of the pump into the bottle.

If the sample be taken from a tap, let a couple of gallons flow before filling the bottle; then allow the water to flow directly into the bottle from the tap.

If the sample be intended to represent the water supply of a town, it ought to be taken from a pipe in direct communication with the street main, and not from a cistern or from any pipe supplied from a cistern.

In taking a sample of water from a tank, well (in which a pump is not fixed), or stream, plunge the neck of the bottle completely below the surface when practicable, and if a can or dipper be used, let it, and the fine steel wire used in drawing it up, be scrupulously clean, and avoid, as much as possible, collecting the water from the surface. On the other hand, be careful not to disturb any mud or sediment at the bottom of the water.

III. The following are the quantities of water necessary for such analyses as are required for sanitary purposes.

Sewage. Polluted Rivers and Streams. Shallow Well Waters.	One Winchester Quart.

Deep Wells. Ordinary Unpolluted Rivers, Streams, and Springs.	Two Winchester Quarts.
Lakes and Tarns. Mountain Springs and Streams.	Three Winchester Quarts.

At the time the samples are forwarded for analysis, give the following particulars:—

(*a.*) From what source the samples are collected,—wells, rivers, or streams.

If from wells,—

(*b.*) Describe the soil and subsoil, also the water-bearing stratum into which the well is sunk.

(*c.*) The diameter and depth of well.

(*d.*) The distance of the well from either cesspools or drains.

If from rivers or streams,—

(*e.*) State the distance from the source to the point at which the sample was collected.

(*f.*) State whether sewage or other animal polluting matter is known to gain access to the river or stream above the point at which the sample is collected.

If from springs,—

(*g.*) Describe the stratum from which the spring issues.

(*h.*) State whether the sample is taken direct from the spring or otherwise.

The analysis of every sample of water involves considerable time and labour; it is therefore important that the above instructions should be strictly attended to, in order that the result may not be rendered worthless. For the same reason, it is desirable that the samples should not be unnecessarily multiplied.

IV. All bottles should be distinctly labelled.

PART I.

WATER ANALYSIS WITHOUT GAS APPARATUS.

Preliminary Examination.

ON the receipt of a sample of water, if the analysis cannot be proceeded with at once, it is advisable to place the bottle in a cool dark cellar, so as to moderate any tendency to change. Exposure to sunlight should especially be avoided.

As the substances most liable to alteration are the organic elements and ammonia, the analyst should endeavour to commence their determination as early as possible after the receipt of the water. He should, at the same time, subject the sample to a preliminary examination for the purpose of recording its general appearance and properties, and of eliciting information for which quantitative results are not required.

In submitting the samples to the various operations enumerated below, he should make it a rule to secure uniformity by well shaking the bottle previously to pouring out the water.

The first things to be noted are the taste and odour. These are most marked when the water is made lukewarm.

In observing the colour, a white surface should be viewed through a stratum of sufficient thickness, say, about two feet. Such a stratum may be secured, either by pouring the water into a tall glass cylinder standing on white porcelain, and then looking downward through the liquid; or by using a tube fitted with glass ends, and placed horizontally in a frame, a white card being inclined at the end opposite to the eye, so as to reflect light through the layer of water. The tube is filled by means of a small stoppered hole in one of the ends.

As colour is very often a matter of comparison, it is advisable to compare the sample under examination with a standard sample of known quality (colourless, if possible), placed in a similar tube.

Turbidity is ascertained by holding a flask of water (say, of a litre or quart size) between the eye and a source of light, having at the same time some dark object, such as a window bar, in the field of vision. It will depend on the purpose of an analysis whether the solid matter causing the turbidity is to be filtered off before the commencement of the analysis, or is to be shaken up and treated as part of the water.

In waters turbid from exceptional causes, and rendered so by rust, chalk, or other innocuous mineral matter which would naturally settle down, or be separated if a filter were used, the suspended matter may be filtered off and disregarded. In the case of sewage, liquid refuse from factories, or polluted water containing solid organic particles, the liquid should be passed through a tared filter of double Swedish paper, and the residue (dried at 100° C.) weighed. The increase in weight gives "the total suspended matter;" and the weight of residue, after ignition, treatment with solution of ammonic carbonate, and drying at 150° C. (less weight of filter ash), gives the "mineral suspended matter." The "organic suspended matter" is represented by the difference of the two weights.

If a sample of water intended for dietetic purposes be turbid, a tall cylinder may be filled with it and allowed to rest, and after the supernatant liquid has been removed by a syphon, the residue may be examined microscopically for low forms of animal or vegetable life, and for evidence of organic pollution from town sewage or manufactories, such as cotton, linen, or woollen fibres, muscular tissue, &c.

No analysis of a potable water can be considered satisfactory without a search for poisonous metals; and, as the method of testing for them is very simple, it is always advisable to apply it to all waters whose character is unknown.

The poisonous metals most likely to be found in water are lead and copper; and the presence or absence of these metals and of iron may be ascertained by adding a drop of colourless sulphide of ammonium to a portion of the water contained in a small cylinder standing on a white surface. If these metals are absent, the liquid will remain unaffected; but it will darken if they are present. Should a solution of coloured sulphide of ammonium be used, it will be safer, if the water appears darker after the addition of the test, to compare the tint with a cylinder of pure water, to which a drop of the sulphide has also been added. When the presence of the above-mentioned metals is indicated by this test, it should be confirmed and their amount estimated by the methods described in the chapter on "poisonous metals," page 42.

To prove whether the water is likely to have any action on lead, two strips of that metal, one tarnished and the other brightly polished, should be placed in beakers of the water, and left for twenty-four hours, when they may be removed, and the liquid in the respective beakers tested with sulphuretted hydrogen.

The object of using a tarnished and a polished slip of lead is to find out whether the water will attack old as well as new pipes. Many soft waters which attack the latter have no action on pipes protected by a tarnished surface. It is generally found that, after a time, a coating of peaty and other matters forms even on bright or new pipes, and stops further mischief.

Some waters, on the other hand, attack both bright and tarnished lead, and that continuously. This is most frequently the case among badly polluted shallow well waters.

There are other waters (Loch Katrine, for example) which act continuously on lead pipes filled at intervals, and yet have no action when the pipes are kept full of water, on the constant system of supply.

Water polluted by refuse from manufactures should be tested with litmus, and its acid or alkaline reaction noted.

The inferences to be drawn from the result of the foregoing experiments are in most cases self-evident; nevertheless, a few remarks may not be altogether out of place.

Water is not liked for potable purposes unless it is clear and colourless; and inasmuch as pure water answers this description, and colour and turbidity must be due to impurities, it is seldom advisable to recommend, for drinking purposes, waters that are markedly coloured or turbid.

It is true that some waters (peaty lake waters, for example) are dark in tint, from the presence of matter which is purely vegetable; but even these are apt to cause diarrhœa if the peaty matter is sufficient to render the water decidedly brown in tint. Moreover, they impart to it an unpleasantly bitter taste.

On the other hand, it by no means follows that clear and colourless waters are necessarily good. Looking, for example, at the order of merit of the different sources as regards colour (viz., springs, wells, streams, rivers, lakes, drainage and surface water from peaty districts), it will be seen that well waters come very high up in the list; and yet among shallow well waters will be found many which, though excellent in appearance, and even in flavour, are nevertheless akin to sewage as regards the abominations they contain in solution.

Very often such waters have percolated through ground that is honeycombed with cesspools, and the depth of soil they have passed through has been so small that it has only served, like some of the so-called filters, to separate from the liquid the solids in suspension without having oxidised the filth that was dissolved.

Total Solid Matter in Solution.

The total solid matter in solution is determined by evaporating a known volume of water, filtered if necessary, to dryness, and taking the weight of the residue.

About half a litre is a convenient quantity, and it must be evaporated in a clean platinum capsule which has been recently heated to redness and carefully weighed after cooling. The capsule is heated over a steam- or water-bath until all the water is evaporated, and it is then placed in an oven at 100° C. for about three hours. At the end of that time it is taken out and placed under a desiccator to cool, then weighed as rapidly as possible and returned to the oven. It is reweighed at intervals of an hour, until the variations between two successive weighings do not exceed a milligram.

The weight of the dish, subtracted from the final weight, gives the amount of solid residue in the quantity operated on, and this, when calculated to the litre, must be multiplied by 100 to give parts per 100,000, or by 70 to give grains per gallon.

It is important to have a suitable support for the platinum dish during the evaporation. Any metal except platinum is inadmissible. Circular holes cut in discs of glass are apt to abrade the platinum, but short glass cylinders answer the purpose well. They should be about half an inch deep, and of a diameter a little less than the platinum dish, and spread out into a flange at one end like the top of a beaker. These fit into the metal rings of the water-bath and keep the dishes clean. Instead of these, however, a suitable sized beaker may be used as a water-bath.

If the residue, after being weighed, is not intended for any other purpose, it may be used as a qualitative test for organic matter by heating it gently over a Bunsen lamp. If there is very little organic contamination, the residue will remain white, or nearly so; with more, it will turn brown; and with highly polluted waters the residue turns almost black.

Peaty matter gives a darker coloured residue than the animal matters of sewage; but by practice it can be distinguished from them. The odour of peat when burning is also very different from that of sewage matter.

Leaving out of consideration the quality of the ingredients contained in potable waters, the proportion of solid residue left on evaporation affords an approximate, though somewhat rough, indication of the comparative purity of water. On the one hand, it may be safely concluded that waters leaving very large residues on evaporation are unfit for domestic use, whilst on the other, those containing very small residues are, on this account alone, well adapted for such purposes, and but very rarely contain, amongst their constituents, any which are seriously objectionable. Not only do waters leaving small residues on evaporation generally possess a superiority for domestic purposes, but they are also more valuable than less pure water for a large number of manufacturing purposes. Thus, in feeding steam-boilers, their use precludes the formation of incrustations, which not only seriously interfere with the transmission of heat from the fuel to the water, but are probably a frequent cause of disastrous explosions.

The solid matters left on evaporating a sample of water may be regarded as impurities, for they are quite useless, and act injuriously in several of the processes to which water is applied. It is true that some persons prefer waters which leave large solid residues, because the saline constituents, with which such waters abound, impart a piquant flavour; but this preference cannot be accepted as a trustworthy guide, because those who are influenced by it will often resort to shallow wells, fed by sewers and cesspools. It is also worthy of note, that a very large proportion of the potable water supplied to towns is employed for washing and for manufacturing purposes; and here the presence of a large amount of solid matter, giving hardness to the water, is undoubtedly injurious.

Ammonia.

As the amount of ammonia in water is very liable to diminish, it is desirable to proceed with its determination without delay. In judging of the quantity of water to be taken for the estimation, the operator must be guided by the supposed quality, and by the bulk of the sample at his disposal. Half a litre will, as a rule, be found a suitable quantity, but it is preferable to take a litre of deep well or river water, whilst a quarter of a litre, or even less, of shallow well water, or of water likely to be of bad quality, is generally sufficient.

The distillation of the ammonia is carried on in a capacious retort connected with a Liebig's condenser, and the distillate is collected in colourless glass cylinders of 50 c.c. capacity.

The apparatus must be proved to be free from ammonia before starting the operation, by distilling 100 c.c. of common water with sodic carbonate till the distillate is free from ammonia. The residue left in the retort may then be removed by syphon without disconnecting the apparatus; or if a small quantity of water only is to be tested, this residue may be left, in order to keep the volume up to half a litre.

A measured quantity of water is now introduced into the retort along with a gram of freshly ignited sodic carbonate, and the volume made up, if necessary, to half a litre or a litre with water free from ammonia.

The water is heated by the direct application of a Bunsen rose burner to the retort, care being taken that the flame does not play above the level of the liquid. When three cylinders have been filled by the distillate, the lamp may be removed.

The estimation of the ammonia depends on the fact that an alkaline solution of mercuric iodide (Nessler's solution, see Appendix I, A) betrays the presence of a very minute trace of ammonia (1 part in 100,000,000) by the production of a brown compound. A minute quantity of this compound colours the liquid very faint brown, and the colour increases with the amount of ammonia, through various shades of red brown until a precipitate is produced. The amount of ammonia in each cylinder is estimated by comparison with the colours produced by the test in other cylinders containing equal volumes of pure water to which known quantities of ammonic chloride have been added. The solution of ammonia must never be so concentrated as to produce a precipitate, otherwise the estimation is vitiated and must be commenced *de novo* with a more dilute solution.

The operation is conducted as follows:—A cylinder containing 50 c.c. of distillate is placed on a white tile, and 1 c.c. of Nessler solution is added. The contents of the cylinder are stirred up, and the liquid is allowed to stand five minutes.

To imitate the tint then produced a clean cylinder is taken, and into it is measured, from a suitable burette, as much of the standard solution of dilute ammonic chloride as experience would suggest.

The cylinder is then filled up to the 50 c.c. mark with water free from ammonia, and 1 c.c. of Nessler solution added as before, and the trial cylinder placed on the white tile beside the one to be tested. The tints are best observed by placing the cylinders in a good light and looking down on the *surfaces* of the liquids at an angle of about 60 degrees. If the colours are the same in each cylinder, the amount of standard solution used indicates the amount of ammonia contained in the cylinder tested. If the colours are unequal, a second trial is carried out with more or less, as the case may require, of the standard solution of ammonia.

The colour produced by more than 2 c.c. of the standard solution of ammonic chloride (see Appendix I, A, 2) is too intense for accurate comparison. It is therefore often advisable to leave the first cylinder of distillate (containing the greater part of the ammonia) until the second has been tested. If, then, the ammonia contained in the second amounts to 0·5 and upwards, the first will contain too much ammonia for accurate estimation. It must therefore be measured, and an aliquot part taken and diluted to 50 c.c. with pure water.

The various amounts of ammonia in the distillates must be added together, and the total calculated into parts per 100,000 of the water taken.

When the evolution of ammonia is long continued, it is owing to the decomposition of urea. In such cases collect the distillate in smaller quantities and Nesslerise only that which is rapidly evolved. The lingering ammonia, which comes off after this, is due to the decomposing urea, and may be neglected.

The estimation of ammonia is undertaken chiefly because this compound is often derived from animal matters just beginning to decompose, and its presence therefore gives an indication of the recent, and probable present, existence of animal pollution. Unpolluted waters seldom contain much ammonia, the greatest amount being found in rain water, which, when collected in towns, sometimes contains as much as ·210 part in 100,000 parts of water. Rain water collected in the country, however, contains on an average only ·030 part per 100,000. This quantity, which is solely derived from the air, is soon absorbed by vegetation; hence upland surface waters show but ·002 on the average, or ·008 as the maximum. In river water the proportion rarely exceeds ·01, and in good well water it is usually still less; whilst in spring water it is either absent altogether or present in very minute proportions.

On the other hand, sewage always contains a large quantity of ammonia (about 5 parts per 100,000 on the average, but varying from 2 parts to 10), and so in general do waters to which sewage gains access. The proportion of ammonia, however, in water polluted by sewage, varies between very wide limits. In shallow wells, for instance, it varies from 0 to as much as 2·75. Ammonia in the presence of oxygen and animal matters is rapidly converted, during the filtration of water through porous earth, into nitrates and nitrites; and its presence, therefore, in considerable quantities in shallow well waters indicates their very recent contamination with animal matters. This rule does not, however, apply to deep well waters, for these, though of undoubted purity, sometimes contain a considerable quantity of ammonia derived from the reduction of nitrates. A large proportion of ammonia is, for instance, almost invariably found in the excellent water obtained from the Lower Tertiaries beneath the London Clay. The ammonia which occurs under such circumstances is obviously still more remote from the animal matter whence it originated than the nitrates from which it was immediately derived, and which were themselves generated by the oxidation of animal matter. It is therefore necessary to take the source of the water into account before deciding on the inferences to be drawn from this estimation.

Chlorine.

Chlorine is present in water chiefly as a constituent of common salt. The determination of this constituent of so wholesome a compound is therefore obviously not undertaken in order to obtain therefrom direct evidence of the quality of the water. Indirectly, however, a knowledge of the proportion of chlorine is often of considerable service, as will be seen from the following considerations.

Sewage, the polluting agent most to be dreaded in water, contains a large proportion of chlorine in the form of common salt derived chiefly from the liquid excrements of animals. The analyses of 58 samples of sewage from midden and water-closet towns gave an average of 11 parts of chlorine per 100,000; on the other hand, the amount of chlorine found in unpolluted water is usually small. The Rivers Pollution Commissioners give, as averages deduced from nearly 600 analyses, 0·22 part per 100,000 for rain water, 1·13 for upland surface water, 5·11 for deep well water, and 2·49 for spring water. These are the quantities naturally washed out of the air and soil by rain. If now we find a sample of water which should be expected to contain, naturally, only 1 part of chlorine per 100,000, showing say 8 parts, we may usually infer that this excess is derived from that very frequent source of danger, sewage.

Human urine contains about 500 parts of chlorine or 824 parts of sodic chloride in 100,000 parts, whilst the solid excrements of animals contain a comparatively minute proportion. Hence the determination of chlorine in polluted water often affords trustworthy evidence as to whether the pollution arose from the liquid as distinguished from the solid excrements of animals, that is to say, whether the polluting matter was sewage or agricultural manure.

Nevertheless, the presence of sewage in water cannot be inferred with confidence, unless the chlorine is found in proportions very considerably in excess of the normal, on account of the variation occurring in natural samples; whilst in the case of waters from places near the sea, or from salt-bearing strata, the estimation becomes valueless. On the one hand, however, the condemnation of water because it contains more than 5 parts of chlorine per 100,000 is really unmerited; whilst, on the other, a water containing less than 1 part of chlorine per 100,000 may, with great probability, be declared free from sewage contamination.

For the determination of chlorine, 50 c.c. of the water are measured out into a small flask standing on a white surface, and a drop or two of a solution of yellow potassic chromate is added. A standard solution of argentic nitrate (*see* Appendix I, D) is then run in drop by drop from a small burette until the liquid turns a faint red. This estimation depends on the facts that chromate of silver has a deep orange-red colour, and that whilst both chromate and chloride of silver are insoluble in water, no red chromate will be permanently formed until the last trace of chlorine has been precipitated by the silver. The number of cubic centimetres of silver solution used will indicate, without further calculation, the amount of chlorine in 100,000 parts of the water.

Towards the close of the operation, the yellow liquid is rendered so opalescent by the precipitated argentic chloride, that it is somewhat difficult to detect exactly the completion of the reaction. In cases requiring great accuracy, therefore, it is advisable, after the amount of chlorides has been roughly determined in one flask, to pour into it a little of the water or of a solution of any chloride, so as to destroy the red tint, and to permit the flask to remain beside the one in which a second volume of 50 c.c. of the water is being tested.

By comparing the tint of the liquid in the second flask with that in the first (known to be underdone), the first tinge of red is easily distinguished.

Before throwing away the contents of the second flask, the experimenter may make sure that the reaction was really finished by adding another drop of the silver solution, when a much more marked red tint will be produced if all the chlorine has already been precipitated.

Hardness.

The method of procedure for this estimation is simple, and there will be no difficulty in obtaining concordant and accurate results if the following directions are adhered to; but uniformity of working is essential.

Take a bottle of say 8 ounces capacity, with an accurately fitting stopper, pour in 50 c.c. of the water, agitate thoroughly, and then suck out the air from the bottle through a glass tube, so that any carbonic anhydride given off by the water may be thereby removed. Next add 1 c.c. of a standard solution of soap (instructions for making this are given in Appendix I, E), shake the bottle vigorously, and repeat the process after each addition, decreasing the quantity of soap test added from time to time until, as the reaction is approaching completion, the soap solution must be added drop by drop. When a good froth has been obtained by shaking, the bottle is laid down on its side; and, if the lather remains permanent for the space of five minutes, the operation is finished, and the quantity of soap solution used must be accurately noted. If, however, the lather breaks up before the expiration of the five minutes, more of the soap solution must be added until the lather acquires the requisite stability.

As the experimenter gains experience, he will be able to tell, by the ear even quicker than by the eye, how the test is progressing; for by listening to the concussion of the water against the bottle when shaking, and noting how it moderates and mellows down, the approaching completion can be readily recognised. An overdone water scarcely sounds at all.

The number of cubic centimetres of soap solution required to produce a lather being known, the degree of hardness can be ascertained from Table No. 1 or 2 in Appendix II.

Even when the hardness of the water is approximately known, the amount of soap solution required should never be added in bulk; for the result will not be so exact as if the addition is made gradually, as before described. And in like manner, when titrating the soap solution with the water of standard hardness, it is not advisable to run in large quantities at once.

If it is found that the quantity of soap solution required to produce a permanent lather exceeds 16 volumes of the solution to 50 of the water, a fresh experiment must be commenced with a smaller quantity of the sample of water (say 25 or even 10 c.c. if the water appears to be very hard), to which sufficient recently boiled distilled water has been added to raise the bulk to the required 50 c.c. The process is then gone through as before described, but the number expressive of hardness will now have to be multiplied by 2 or some other figure according to the degree of dilution of the sample. When the excessive hardness is caused by the presence of magnesic salts, indicated by a characteristic lightness of the curd, the water should be diluted with distilled water until less than 7 c.c. of soap are required for 50 c.c. of the diluted water. And it should be allowed to stand for at least half-an-hour after a lather has been obtained. If it will no longer lather at the end of this time more soap solution must be added, and this process repeated until a permanent lather is obtained.

The soap-destroying measure thus obtained is called the "total hardness"; but many waters become softer on boiling. The decrease produced by boiling is called "temporary hardness," whilst the remaining hardness is termed "permanent." The permanent hardness is ascertained by first boiling some of the water gently, allowing the steam to escape freely, and then, after it has cooled and the loss by evaporation has been made up with recently boiled distilled water, applying to it the soap test as before.

On no account must the steam from the flask be condensed and allowed to flow back into the boiling liquid, because the condensed water dissolves the escaping carbonic anhydride, which is thus continually returned to the contents of the flask in sufficient quantity to prevent the complete precipitation of carbonate of lime. Many serious errors have arisen from the neglect of this precaution.

The making up to the original volume, as mentioned above, is often accomplished by adding distilled water until the mixture reaches a mark on the glass indicative of the previous level of the liquid; but it is more convenient to take flasks of about the same weight, and make them all up to the same weight with water (say 200 grms.) before starting, and then to fill them up with the necessary weight of distilled water at the close of the boiling.

The alleged effect of soft and hard waters upon the public health has been carefully investigated; but the evidence hitherto produced, when thoroughly sifted, has only gone to show that no material difference in the death-rate of towns can be attributed to either kind of water. This subject is treated of fully in the Sixth Report of the Rivers Pollution Commissioners, pp. 184 to 201. The Commissioners, who contrasted the death-rates of towns which were as nearly as may be on an equality with regard to their sanitary arrangements, arrived at the following conclusion:—

"In an aggregate population of 242,149 living in five towns and districts and drinking soft water, the annual rate of mortality averaged 18·5 per 1,000, and amongst an aggregate population of 100,439 living in three towns and districts and consuming moderately hard water, the annual death-rate was 19·2 per 1,000; whilst in an aggregate population of 638,038 living in twelve towns and districts supplied with hard water, the average mortality was at the rate of 20·4 per 1,000 per annum. Thus, where the chief sanitary conditions prevail with tolerable uniformity, the rate of mortality is practically uninfluenced by the softness or hardness of the water supplied to the different towns, and the average rate of mortality in the different water divisions varies far less than the actual mortality of the different towns of the same division. We are therefore of opinion that, whilst waters of excessive hardness may be productive of calculous and perhaps other diseases, soft and hard waters, if equally free from deleterious organic substances, are equally wholesome."

It is probable that moderately hard water is most suitable for growing children, and very soft water for persons beyond middle age.

On economic grounds, however, the estimation of the hardness of water is a matter of great importance, both to the householder and to the manufacturer, for when soap comes in contact with waters containing salts of lime and magnesia, the soluble alkaline oleates, stearates, and palmitates composing the soap are decomposed, with the formation of insoluble calcium and magnesium salts of the fatty acids. These precipitated salts produce the turbid appearances seen when soap has been used with hard water, and they continue to form so long as any lime or magnesia is present in solution. Hence no soap is available for detergent purposes until the water has been thus softened at the expense of the soap.

If the hands be washed in water before this artificial softening is complete, the insoluble lime soap will be precipitated on the skin, producing a harsh, unpleasant sensation; and if linen be washed in such water, the insoluble soap precipitate is deposited within and between the fibres of the fabric.

Soft water, moreover, is a better solvent, and therefore more useful in many cooking and manufacturing operations.

The hardness called "temporary" is caused by the presence of carbonates of lime and magnesia held in solution by an excess of carbonic acid. When the water is boiled, carbonic anhydride escapes, and the insoluble carbonates are precipitated, leaving the water so much softer, but causing a deposit or fur on the sides of the vessel. This fur is always inconvenient, often productive of great loss of heat, and is sometimes the cause of disastrous boiler explosions, owing to the superheating of the iron plates beneath the crust.

It is manifest that, if these lime and magnesia salts could be removed before the soap is added, or the fur deposited before the water is put into the boiler, much inconvenience and expense would be avoided.

This can be done, as far as the salts causing temporary hardness are concerned, by means of a process invented by the late Dr. Clark, of Aberdeen, which depends on the fact that when lime comes in contact with carbonate of lime and magnesia held in solution by excess of carbonic acid, the lime unites with the excess of carbonic acid, forming carbonate of lime, and the insoluble carbonate thus formed, together with the carbonates of lime and magnesia which are thrown out of solution by the abstraction of their solvent, is deposited.

As this operation is attended with but little trouble or expense, and not only improves the value of a water economically, but often increases and never diminishes its value for dietetic purposes, it is desirable to supplement the report on waters suitable for treatment by this process by a memorandum to the following effect, filled in according to the results of analysis:—

Clark's Process for Softening Hard Water.

The method of softening consists in adding lime to the hard water. It is only applicable to water which owes its hardness entirely or chiefly to the carbonates of lime and magnesia held in solution by carbonic acid (*temporary hardness*). Water which owes its hardness to sulphate of lime or sulphate of magnesia (*permanent hardness*) cannot be thus softened; but almost any water which softens on boiling for half an hour will be softened to an equal extent by Clark's process. The hard water derived from chalk, limestone, or oolite districts is generally well adapted for this operation.

To soften 700 gallons of water, 1 oz. of quicklime is required for each part of temporary hardness in 100,000 parts of water (*see* Analytical Table). Thus, to soften 700 gallons of   oz. of quicklime would be required. Slake this thoroughly in a pailful of water. Stir up the milk of lime thus obtained, and pour it immediately into the cistern containing at least 50 gallons of the water to be softened, taking care to leave in the pail any heavy sediment that may have settled to the bottom in the few seconds that intervened between the stirring and pouring. Fill the pail again with water, and stir and pour as before. The remainder of the 700 gallons of water must then be added, or allowed to run into the cistern from the supply pipe. If the rush of the water thus added does not thoroughly mix the contents of the cistern, this must be accomplished by stirring with a suitable wooden or iron paddle. The water will now appear very milky, owing to the precipitation of the chalk which it previously contained in solution, together with an equal quantity of chalk, which is formed from the quicklime added.

After standing for three hours, the water will be sufficiently clear to use for washing, but to render it clear enough for drinking at least twelve hours' settlement is required.

The water of   will, by being submitted to this process, have its hardness reduced from parts to parts in 100,000.

By following these directions, a fairly good result will be obtained; but, by the use of a very simple chemical test, the proportion of lime may be much more accurately adjusted. A solution of nitrate of silver strikes a yellow or brownish-yellow colour when it is added to water containing even a very minute trace of uncombined lime. During the final running of the water into the cistern, as above described, a dessert spoonful of the milky water should be, from time to time, taken from the cistern and put into a white teacup containing a couple of drops of the nitrate of silver solution; if a brownish coloration be produced the slaked lime is still in great excess, and more hard water must be admitted; if the tint produced be a very faint yellow, only just visible, the proper proportion of lime to hard water has been attained, and the inflow of the latter must be stopped; but if the milky liquid continue white after its admixture with the nitrate of silver, more milk of lime must be added to the water.

Nitrogen as Nitrates and Nitrites.

By decomposition in water containing dissolved oxygen, nitrogenous organic matter of animal origin yields nitrous and nitric acids, which by union with bases form nitrates and nitrites. Nitric acid is also formed by electric discharges in the atmosphere, and thus becomes a constituent of rain water. As, however, the amount of nitrates in rain is small, large quantities convict water of previous pollution by organic matters of animal origin. They tell only of the contamination which is past; but, by inference, they also declare the probable nature of the organic matter now present.

The occurrence of nitrates indicates that the water is undergoing, or has undergone, a process of natural purification; and the quantity found frequently shows the proportion of nitrogenous organic matter destroyed.

Whether or no the analyst should form an unfavourable opinion of the water from the amount of nitrates, must depend upon the proportion of organic matter actually present, and on his confidence in the efficiency and uniform action of the purifying process.

On this account a proportion of nitrates may pass unchallenged in deep well water, which would relegate that of a shallow well to the category of suspicious or even dangerous waters.

Very little organic matter survives the exhaustive process of intermittent filtration which water suffers on its way to deep wells and springs. In shallow wells, on the other hand, while much organic matter in the water may be oxidised, living spores and germs capable of propagating disease may survive: the purifying effect of filtration into such wells is therefore not to be depended upon, as it may cease altogether if overtaxed.

Nitrates are formed very slowly in rivers and streams, animal organic matter being oxidised much more slowly in running than in percolating water. They are not formed in waters deficient in dissolved oxygen; and are, if already present, reduced by the addition of more organic matter. Thus they are not usually found in sewage.

Nitrates are absorbed by vegetation, and may therefore be partially or completely removed when the water containing them flows over growing plants.

The amount of nitrates in rain varies with the locality, being greatest near towns. Seventy samples from Rothamsted (25 miles from any large town) showed nitrogen as nitrates from *nil* to ·04 approximately, with an average of ·007 in 100,000 parts of water. Upland surface waters are commonly free from nitrates and nitrites, or contain but a mere trace. In them the range of nitrogen in this form is from *nil* to about ·05, with an average of about ·009 part. Surface waters from cultivated districts show an average of ·25 part, ranging from *nil* (which occurs but seldom) to 1 part.

Shallow wells, as a class, contain the greatest proportion of these compounds. The range, however, is so considerable, that an average is useless: 2 to 5 parts is a common quantity. The range in deep wells is from *nil* to 3 parts, and in spring water about the same, with an average of about 0·4 part in 100,000 parts of water in both cases.

There are three distinct modes of estimating nitrogen as nitrates and nitrites in common use among chemists, and each has its own especial advantages and drawbacks.

The nitric and nitrous acids of the salts may (1) be decomposed into nitric oxide, and their amount determined by the quantity of evolved gas; or (2) they may, by the action of nascent hydrogen, be converted into their equivalent of ammonia, and estimated as such; or (3) the nitrates may be estimated volumetrically by the bleaching effect of free nitric acid on indigo.

The first method yields the most accurate results; and, as now carried out, is as simple, and is executed in as short a time, as any process coming under the second or third head. It requires, however, gas apparatus, and is hence treated of in Part II.

The second mode admits of several variations in the means of generating the nascent hydrogen. Of these the "zinc-copper couple" of Gladstone and Tribe, and the aluminium process of Chapman, have been found most convenient in practice.

The Zinc-Copper Method.—The "zinc-copper couple" is an electrical pair formed by the intimate contact of the metals zinc and copper without, however, the production of an alloy. For the mode of preparing the couple see Appendix I, B.

In estimating nitrates by this method, the quantity of water to be tested must be reduced to a small bulk, and be free from ammonia.

Professor Thorpe extracts the residue used in the determination of the total solid matter with about 25 c.c. of distilled water, and then, in order to destroy urea, boils the liquid down to a fourth of its bulk with a fragment of recently ignited lime about the size of a hemp-seed.

This liquid, together with the washings of the dish containing the residue, is then transferred to a small retort or flask, the requisite amount of zinc-copper couple is introduced, and the water distilled off.

An 8-ounce Wurtz's distilling flask, attached to a Liebig's condenser of small bore, answers very well for the distillation, a stoppered funnel passing through the cork in the neck of the flask. The distillation is carried on till almost all the water has passed over; hot distilled water is then run into the flask at intervals, and the distillation continued till about two cylinders of 50 c.c. each have been filled.

For the estimation, 5 c.c. (or such a quantity as admits of accurate observation by colorimetry) is put into a cylinder and made up to 50 c.c., and the amount of ammonia is then estimated by Nessler's solution in the usual way. The second cylinder may be tested without dilution, as nearly all the ammonia will usually be found in the first. This method is both expeditious and accurate. If used again immediately, the same quantity of zinc-copper couple will serve for a second sample of water.

The Aluminium Method.—According to this method, the nascent hydrogen is liberated by the action of strong solution of soda or potash on aluminium foil. 100 c.c. of the water should be introduced into a distilling flask, along with 10 c.c. of a solution of sodic hydrate, free from nitrates (Appendix I, B), and boiled briskly until reduced to about one-fourth. It is then made up to its original bulk with water free from ammonia, and when quite cold a piece of aluminium foil about 2 inches square is dropped in.

The aluminium foil is prevented from floating by rolling it round a piece of clean glass rod. The hydrogen, as it is given off, escapes by the distilling tube; and to prevent loss of ammonia, the opening is guarded by a small tube filled with pumice moistened with ammonia-free hydrochloric acid. A second tube may be attached to the last, to prevent the access of atmospheric ammonia.

About six hours afterwards the pumice and washings of the first tube are added to the liquid in the flask, a small and freshly washed Liebig's condenser is attached, and the ammonia distilled off and estimated as just described.

It is as well to test the apparatus and chemicals by blank experiment, to ascertain if any correction is required.

The Indigo Method.—This method has found favour on account of its simplicity and the short time required to perform the estimation. It is, however, liable to give very fallacious results, unless certain precautions are strictly adhered to. The process is entirely an empirical one. Pure indigotin is dissolved in water by the aid of Nordhausen oil of vitriol. The value of the solution is determined by observing the number of cubic centimetres bleached by a given amount of a standard solution of nitre. The indigo solution is tried on the water for examination under the same conditions.

This process has been greatly improved of late by R. Warrington, F.R.S., who has used it very extensively, and pointed out the precautions necessary to success. I am indebted to him for the following description of the operations which, after long experience, he has adopted.

Four grams of sublimed indigotin are digested for some hours with five times their weight of Nordhausen oil of vitriol, the liquid is then diluted with water, filtered, and brought to the volume of two litres. The strength of the indigo is next ascertained with a normal solution of nitre, by the method presently to be described. The indigo solution, which will be found too strong, is finally diluted, so that 10 c.c. correspond with the same volume of the normal nitre solution. There is no object in bringing the indigo absolutely to the normal strength; a near approximation will suffice. To preserve the indigo solution, Sutton recommends that 4 per cent. by volume of pure oil of vitriol should be added to it; indigo so fortified undergoes no change when kept in the dark.

The normal indigo solution is diluted, as required, to four times its volume, for the purpose of water analysis, oil of vitriol being added in such quantities as to maintain the proportion of 4 per cent. The indigo solution is to be used in a burette graduated to lengths of a cubic centimetre. As the solution is too dark to be seen through, the height of the liquid may be read from its upper surface, or an Erdmann's float may be employed. The solution being slightly viscid, the burette should not be read till the level of the liquid becomes constant.

A series of standard solutions of pure nitre will be required to determine the value of the indigo in nitric acid, as this is not uniform throughout the scale. A normal solution of nitre is first prepared by dissolving 1·011 grm. of pure nitre (gently fused over a spirit lamp before weighing) in one litre of water. From this normal solution, other solutions of $\frac{1}{4}$, $\frac{1}{8}$, $\frac{1}{16}$, $\frac{1}{32}$, and $\frac{1}{64}$ the normal strength are prepared, and preserved for use.

In water analysis, it is most convenient to work with 20 c.c. of the water; when this is done, it is necessary to standardise the indigo with 20 c.c. of the $\frac{1}{8}$, $\frac{1}{16}$, $\frac{1}{32}$, and $\frac{1}{64}$ nitre solutions. If 10 c.c. of water are to be employed, the indigo must be also standardised with 10 c.c. of the $\frac{1}{4}$ and $\frac{1}{8}$ nitre solutions. It is most useful to standardise both for 10 c.c. and 20 c.c. of water, as waters of a greater range of strength can then be analysed without dilution. It is unnecessary to standardise with 10 c.c. of the weaker nitre solutions; if the amount of nitrate in a water is not greater than that in   nitre solution, 20 c.c. of the water may be at once taken for the estimation.

A large supply of pure distilled oil of vitriol will be required for extensive water analysis. It should be colourless, quite free from nitrous compounds, and contain as little as possible of sulphurous acid, and must be of nearly full gravity. As any variation in the acid affects the determination, it is best to mix the contents of all the bottles purchased before proceeding to standardise the indigo. The oil of vitriol is measured for use in a tolerably wide burette, provided with a glass stopcock.

A further requisite is a chloride of calcium bath, provided with a thermometer; the bath is conveniently made in a porcelain basin. The temperature to be maintained is 140°, and as the temperature keeps rising from the evaporation of the solution, it is necessary to bring it down to the required point by the addition of a little water or chloride of calcium solution immediately before each experiment. The chloride of calcium bath is not required when strong solutions of nitrate are analysed by a normal solution of indigo, the reaction in such cases being almost immediate. With weak solutions of indigo and nitrate, the reaction may take some time, in extreme cases as much as five minutes, and it becomes essential for accuracy that the temperature should be maintained throughout at the normal point.

The standardising of the indigo solution is performed as follows:—

In a wide-mouth flask of about 150 c.c. capacity, are placed 10 c.c. or 20 c.c. of the standard nitre solution; as much indigo solution is measured in as is judged sufficient, and the whole mixed. Oil of vitriol is next run from the burette into a test-tube, in quantity exactly equal to the united volumes of the nitre and indigo solutions. The contents of the test-tube are then poured as suddenly as possible into the solution in the flask, the whole rapidly mixed, and the flask at once transferred to the chloride of calcium bath. It is essential for concordant results that the oil of vitriol should be uniformly mixed with the solution as quickly as possible. This is especially necessary in the case of strong solutions of nitrate, in which the action begins immediately after the addition of the sulphuric acid; with such solutions, it is more difficult to get duplicate experiments to agree than with weaker solutions, when the action does not begin at once, and in which, therefore, time is afforded for mixing. The operator should not attempt to drain the test-tube; the oil of vitriol adhering to the tube is a fairly constant quantity, and after the first experiment the tube will deliver the quantity measured into it.

It is well to have the flask covered by a watch glass while holding it in the chloride of calcium bath. The progress of the reaction should be watched, and as soon as the greater part of the indigo has been oxidised, the contents of the flask should be gently rotated for a moment. With very weak solutions of pure nitre, no change is observable for some time, and it may be necessary, in some cases to keep the flask in the chloride of calcium bath for five minutes. If the colour of the indigo is suddenly discharged, it is a sign that the nitric acid is in considerable excess, and that a much larger amount of indigo must be taken for the next experiment. If some of the indigo remains unoxidised, a little experience will enable the operator to judge its probable amount, and so decide on the quantity of indigo suitable for the next experiment.

The amount of indigo which corresponds to the solution of nitrate is found by a series of approximating experiments made as just described with varying quantities of indigo, the oil of vitriol used being always equal in volume to the united volumes of the nitrate solution and indigo. The determination is finished when a quantity of indigo is left unoxidised, not exceeding 0·1 c.c. of the indigo solution used; this amount can be readily estimated by the eye. It is well, until considerable experience has been gained, to check the result by making a further experiment with 0·1 c.c. less indigo, when the colour should be entirely discharged. The tint produced by a small excess of indigo is best seen by filling up the flask with water. The estimated excess of indigo is, of course, deducted from the reading of the burette.

To reduce the number of experiments required to obtain the result, it is well to proceed with some boldness, and ascertain as soon as possible what are the limits between which the quantity of indigo must fall. Seven experiments will be a maximum rarely exceeded, and four about the average required, where the character of the waters is already known.

The direction has been given to employ oil of vitriol equal in volume to the united nitrate and indigo solutions. It is most important that the same proportion of oil of vitriol should be used in every experiment, as the quantity of indigo oxidised is much affected by the proportion of acid present, being considerably greater when the acid equals the volume of the other solutions than when the acid is used in larger proportion.

When the indigo solution has been standardised with the series of nitre solutions already mentioned, it will be found that the quantity of indigo consumed is not strictly in proportion to the nitric acid present, but diminishes as the nitrate solution becomes more dilute. In round numbers, a diminution of the amount of nitre present to $\frac{1}{8}$ is accompanied by diminution of the indigo oxidised to $\frac{1}{10}$; or, in other words, if 20 c.c. of the $\frac{1}{8}$ normal solution of nitre require 10 c.c. of indigo, 20 c.c. of the $\frac{1}{64}$ nitre solution will require only 1 c.c. of indigo. This is a very important fact, and necessitates the standardising of the indigo with solutions of graduated strength, so that the value of the indigo may be known for all parts of its scale.

Experience has shown that, with a $\frac{1}{2}$ normal solution of indigo, 10 c.c. of a $\frac{1}{4}$ normal solution of nitre will oxidise distinctly less than half the indigo required by 10 c.c. of a $\frac{1}{2}$ normal nitre solution, and with the $\frac{1}{4}$ normal solution of indigo employed in water analysis the differences produced by dilution are still more considerable.

It becomes necessary then to form a table of the value in nitrogen corresponding to each part of the indigo scale, and by the help of this table every analysis subsequently made is calculated. Below is given an ideal table of this description. It is assumed, which is very near the truth, that a diminution to one-eighth in the strength of the nitrate solution is accompanied by a diminution to one-tenth in the indigo consumed. It is further assumed, which is also near the truth, that the alteration in the relation of the indigo to the nitrate proceeds at a uniform rate between the limits actually determined. The following will be the results arrived at when using 20 c.c. of the nitrate solution for each experiment.

Value of Indigo, in Nitrogen, for different strengths of Nitre Solutions.

Strength of nitre solution used.	Indigo required.	Difference between amounts of indigo.	Nitrogen corresponding to 1 c.c. of indigo.	Difference between the nitrogen values.	Difference in the nitrogen values for a difference of 1 c.c. in the amount of indigo.
	c.c.	c.c.	gram.	gram.	gram.
$\frac{8}{64}$ normal..	10·00	..	·000035000		
$\frac{7}{64}$,,	8·71	1·29	·0 0035161	·000000161	·000000125
$\frac{6}{64}$,,	7·43	1·28	·000035330	·000000169	·000000132
$\frac{5}{64}$,,	6·14	1·29	·000035627	·000000298	·000000231
$\frac{4}{64}$,,	4·86	1·28	·000036008	·000000381	·000000298
$\frac{3}{64}$,,	3·57	1·29	·000036764	·000000756	·000000586
$\frac{2}{64}$,,	2·29	1 28	·000038209	·000001445	·000001129
$\frac{1}{6}$,,	1·00	1·29	·000043750	·000005541	·000004295

The mode of using this table is very simple. Supposing that 20 c.c. of a water have required 5·36 c.c. of indigo, this amount is seen to be 0·5 c.c. above the nearest point (4·86 c.c.) given in the table. We learn from the right-hand column that ·000000149 must consequently be subtracted from the unit value in nitrogen (·000036008 gram) belonging to 4·86 c.c. of indigo. We thus find that the 5·36 c.c. of indigo should be reckoned at ·000035859 gram of nitrogen per cubic centimetre: the water, therefore, contains 0·96 part of nitrogen as nitric acid per 100,000. If 20 c.c. of the water have required less than 1 c.c. of indigo, the unit value corresponding to 1 c.c. of indigo is employed for calculating the amount; this will give an accurate result if the oil of vitriol used be quite pure.

It is not necessary in practice to form so complete a table as that now given; it will suffice to determine the indigo with nitre solutions of $\frac{1}{8}$, $\frac{1}{16}$, $\frac{1}{32}$, and $\frac{1}{64}$ normal strength: if another solution is used, that of $\frac{3}{64}$ normal strength seems the most important. It may be sufficient, even, in some cases simply to determine the indigo with the $\frac{1}{8}$ and $\frac{1}{64}$ nitre solutions, and to find all the intermediate values by calculation. If 10 c.c. of water are to be employed as well as 20 c.c., separate tables should be formed, giving the value of the indigo in each case.

There is one important advantage that follows from the troublesome necessity of standardising the indigo with various nitrate solutions; it tends to remove the errors due to impurities in the oil of vitriol. As the volume of the oil of vitriol used depends far more on the volume of water taken than on the quantity of nitric acid it contains, all errors due to oxidising or reducing matter contained in the oil of vitriol fall far more heavily on determinations of small quantities of nitric acid than on determinations of larger quantities. Unless, therefore, the oil of vitriol used was absolutely pure, it would always be necessary to standardise the indigo as now recommended, even if the relation of indigo to nitric acid were exactly the same in weak and strong solutions. By standardising as now described, the errors due to the sulphuric acid affect the figures of the table, but not the result of the analysis. Such standardising has also the effect, as far as it goes, of calibrating the burette, any inequalities of capacity falling on the table, and not on the analyses calculated from it.

In standardising the indigo solution, and in the subsequent experiments with it, some regard must be paid to the initial temperature of the solutions. A rise in the initial temperature will be attended by a diminution in the quantity of indigo oxidised; this is most perceptible in the case of the stronger solutions of nitrate. The following table shows the results obtained by standardising the same indigo solution at two temperatures, representing nearly the extreme limits at which the solution would be used in practice. The temperature of the room during the experiment was 10°. For the trials at the higher temperature, the flask containing the indigo and nitrate, and the test-tube containing the oil of vitriol, were placed for some time in a water-bath at 22—23° previously to being mixed.

Indigo Solution Standardised with 10 *c.c. of Nitre Solution.*

Strength of nitre solution.	At 10° C.		At 22° C.	
	Indigo required (actual).	Indigo calculated from two extremes.	Indigo required (actual).	Indigo calculated from two extremes.
	c.c.	c.c.	c.c.	c.c.
$\frac{1}{4}$ normal	10·28	10·28	9·76	9·76
$\frac{1}{8}$ "	4·97	4·97	4·78	4·73
$\frac{1}{16}$ "	2·30	2·32	2·18	2·22
$\frac{1}{32}$ "	0·99*	0·99	0·96	0·96
Standardised with 20 *c.c. of Nitre Solution.*				
$\frac{1}{8}$ "	10·26	10·26	9·74	9·74
$\frac{1}{16}$ "	4·84	4·96	4·65	4·74
$\frac{1}{32}$ "	2·21	2·31	2·21	2·24
$\frac{1}{64}$ "	0·99	0·99	0·99	0·99

It is seen that a rise of 12° in temperature diminishes the indigo consumed by about 5 per cent. in the case of the stronger solutions of nitrate; it is evident, therefore, that

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* It must not be supposed that it was possible to work to $\frac{1}{100}$th of a cubic centimetre; in all the figures given the errors shown by calibrating the measuring vessels employed have been taken account of and minute fractions thus introduced.

the indigo solution should be standardised at nearly the same temperature at which it is to be used.

In the table, the quantity of indigo corresponding to the intermediate strengths of nitre solution has been calculated from the determinations made with the two extreme strengths to show the amount of accuracy to be attained by this plan. The agreement of calculation with the results actually obtained is sometimes very close, but in others the difference is somewhat greater than the errors of experiment.

If the indigo solution has been standardised with 20 c.c. of the nitre solutions recommended, the operator will be able to analyse waters containing nitric acid up to 1·75 part of nitrogen per 100,000. If the indigo has also been standardised with 10 c.c. of the $\frac{1}{4}$ and $\frac{1}{8}$ nitre solutions, the operator can, by employing 10 c.c. of the water, extend the range of his analysis to waters containing 3·4 parts of nitrogen per 100,000. Waters stronger than this should be diluted for analysis. The natural error of the determination, shown by the performance of duplicate experiments, will not exceed 1 per cent. of the nitric acid present in the case of waters containing 1·7 of nitrogen per 100,000, but may amount to 5 per cent. with waters containing as little as 0·2 of nitrogen per 100,000.

Chlorides are of course generally present in waters containing nitrates; they are not altogether without effect on the determination with indigo, but the error thus introduced is not sufficient to be of importance.

The general conclusion respecting the indigo method for determining nitric acid will be that it is excellently adapted by its simplicity, rapidity, and delicacy for general use in water analysis; but that accuracy can be secured only by working under the same conditions which obtained when the indigo solution was standardised. In the presence of organic matter, the indications obtained with indigo must be accepted as probably below the truth.

The mercury method, described at page 86, may be used with advantage, even where gas analysis apparatus is not available, by graduating and calibrating the tube in which the operation is performed, and reading off in the tube itself the volume of nitric oxide produced. In this way the determination is much more rapid and, unless the proportion of nitrates is very small, quite as accurate as when made by any of the processes just described.

Nitrites.

It is very rarely necessary to distinguish between nitrites and nitrates in water. If, however, the "Oxygen or Forchammer" process, presently to be described, is employed to estimate the organic pollution, it is desirable to have a delicate means of testing for and estimating traces of nitrites. One part of sodic nitrite deoxidises some twenty times as much potassic permanganate as an equal quantity of urea, creatin, or starch. The practice, suggested by Tidy, of considering the permanganate reduced by a sample of water within three minutes to be due to nitrites, is not satisfactory; for a sample of sewage free from nitrites reduced in that time as much permanganate as Thames water did in three hours.

As nitrites, when present in water, are soon oxidised to nitrates, it is important to begin their detection or estimation as soon as possible after the collection of the samples.

Griess's process, as elaborated by Messrs. Preusse and Tiemann ("Deut. Chem. Ges. Ber.," XI, 624, 637), is the only trustworthy one for estimating nitrites. It is easy of execution and of excessive delicacy, being capable of detecting one part of nitrous acid in thirty million parts of water. The method consists in the observation of the depth of colour developed in 100 c.c. of the water under examination on the addition of 1 c.c. of a solution of meta-phenylenediamine and one of dilute sulphuric acid; a comparative observation being made on a standard solution of sodic nitrite, as in the estimation of ammonia by the Nessler test.

The solutions required are (1) meta-phenylenediamine,—5 grams of the base, in a litre of water, decolorised if necessary by animal charcoal, and made acid with sulphuric acid; (2) dilute sulphuric acid, one part to two of distilled water; and (3) a solution of pure potassic nitrite, prepared from silver nitrite and potassic chloride,—strength ·01 milligram N_2O_3 per cubic centimetre. To prepare this last solution, dissolve 0·406 gram of pure and dry silver nitrite in hot water, and decompose it with a slight excess of potassic chloride. After cooling, make up the solution to one litre, allow the chloride of silver to settle, dilute each 100 c.c. of the clear supernatant liquid again to one litre.

The following apparatus is required:—

1. Four narrow cylinders of colourless glass, in which 100 c.c. of water should rise to a height of 16 to 18 c., and which must be marked with a diamond at this point.

2. A graduated burette or pipette for the dilute sulphuric acid, and another for the solution of meta-phenylenediamine.

The operation is performed as follows:—100 c.c. of the water to be tested is poured into one of the before-mentioned glass cylinders, and 1 c.c. each of the dilute sulphuric acid and solution of meta-phenylenediamine consecutively added. If a red colour is immediately developed on stirring the contents of the cylinder with a glass rod, the experiment must be repeated with 50, 20, or 10 c.c. of the water previously made up to 100 c.c. with distilled water free from nitrous acid. The dilution is sufficient when colour is just perceptible at the end of one or two minutes. Of course the amount of nitrous acid thus found must be multiplied by the coefficient of dilution.

As nearly as possible cotemporaneously with the above experiment, there must be put into three other cylinders 0·3 to 2·5 c.c. of the standard solution of potassic nitrite, filling up each cylinder to 100 c.c. with pure distilled water, and adding to each, consecutively, 1 c.c. of dilute sulphuric acid and 1 c.c. of the solution of meta-phenylenediamine. The colour developed in these cylinders is then to be compared with that given by the sample of water similarly treated.

By repeating these experiments with such different proportions of the standard solution of potassic nitrite as will be suggested by the first series, there is eventually obtained a diluted solution of the nitrite of known strength which exhibits exactly the same tint as the sample of water. Since, however, the intensity of tint in all the solutions gradually increases for a considerable length of time, it is necessary to make a final pair of experiments, starting them simultaneously. The observation of the shade of colour may be conveniently extended to twenty or twenty-five minutes.

For the success of this estimation it is necessary that the water should be colourless. Tinted waters can generally be decolorised by adding to them a few drops of solutions of caustic soda and carbonate of soda, the colouring matter being precipitated along with the carbonates of the alkaline earths. If the water does not contain a sufficient amount of earthy salts, a little alum may be added to it either before or after the addition of the alkaline solutions, care being of course taken that the water remains alkaline. The precipitate must be filtered off before the water is used.

The inference to be drawn from the presence of nitrites depends upon the source of the water. The presence of these salts in spring and deep well waters is absolutely without significance; for, although they are in these cases generated by the deoxidation of nitrates, this deoxidation is brought about either by the action of reducing mineral substances, such as ferrous oxide, or by that of organic matter which has either been embedded for ages in the water-bearing stratum, or, if dissolved in the water, has been subjected to exhaustive filtration. In such waters the presence of nitrites has no more bearing upon their wholesomeness than the absence of dissolved oxygen, which is characteristic of the most excellent waters from deep sources.

When, however, nitrites occur in shallow well or river waters, it is highly probable that these waters have been very recently contaminated with sewage, for it seems that in the ordinary oxidation of sewage by percolation through porous earth, its nitrogen is at once oxidised to the maximum—nitrites being absent from the effluent water of intermittent sewage filters for instance. But when fresh sewage is added to water already containing nitrates, the latter are generally reduced to nitrites. It is much to be desired that the origin of nitrites in these classes of waters should be more thoroughly investigated.

Poisonous Metals.

A method of general application was described in the chapter on Preliminary Examination (page 12) by which the presence or absence of poisonous metals, such as *lead* and *copper*, might be ascertained.

If the presence of *lead* be indicated, it should be confirmed and the amount of metal estimated by the late W. A. Miller's method. One hundred cubic centimetres of the water is acidulated with a drop or two of acetic acid, and about 5 c.c. of a saturated solution of sulphuretted hydrogen is then added. The tint thus produced is imitated with an artificial sample made by adding a known quantity of a standard solution of a lead salt to 100 c.c. of distilled water.

As each cubic centimetre of lead solution contains 0·0001 gram of metallic lead (made by dissolving 0·1831 gram of crystallised normal lead acetate in a litre of distilled water), the amount of lead in 100,0000 parts of the water under analysis is found by dividing, by ten, the number of cubic centimetres needed to produce the same tint in the sample of distilled water used for comparison.

Copper is estimated in a similar manner, using for comparison a solution containing in each cubic centimetre 0·0001 gram of metallic copper (made by dissolving ·3929 gram of crystallised sulphate of copper in a litre of distilled water).

If both lead and copper be present, a large quantity of the water must be evaporated, and the metals separately determined by the usual processes.

Arsenic is sometimes found in waters polluted by mining and manufacturing operations, and is best detected and estimated by Marsh's test.

Half a litre of the water is rendered slightly alkaline by sodic or potassic hydrate free from arsenic, and evaporated to dryness. The residue is extracted with strong hydrochloric acid, and the liquid poured down the funnel tube of a small apparatus which has been generating pure hydrogen for some minutes. The escaping gas, which should be generated slowly, is first made to pass through a small U-tube filled with pumice moistened with plumbic acetate and through a piece of drawn-out combustion tube (about six inches long, and one-eighth of an inch in diameter) heated to redness in the middle by a small lamp. Any arseniuretted hydrogen present will deposit its arsenic as a brown metallic ring on the cooler part of the tube.

The quantity is estimated by comparing the ring formed with a series of standard rings obtained in a similar way with known quantities of arsenic. It is safer to continue the passage of the gas for an hour, but nearly the whole of the arsenic comes off in the first five or ten minutes.

A blank experiment should, of course, be performed previous to commencing the determination, to ensure that the zinc, acid, and apparatus are free from arsenic.

Barium is best detected by slightly acidulating the concentrated water with hydrochloric acid, filtering if necessary, and then adding a solution of gypsum.

Zinc is generally present as bicarbonate, and gradually forms a film of carbonate on the surface of the water. To identify it, a little of this film must be collected and heated on platinum foil. If after the volatile matter has disappeared a residue remains which is yellow when hot and turns white on cooling, zinc is present. This reaction is extremely delicate.

Suspended Matter.

If a water contains a considerable amount of suspended matter, it is usually advisable to filter it before analysis; but, if the turbidity be due to innocuous mineral matter, the introduction of which is temporary and exceptional, as from careless collection of the sample, the amount of the suspended matter need not be determined. When, however, the matters in suspension are not of this temporary or exceptional character, their amount should be ascertained, and the relative proportions of organic and mineral matter in them determined. For this purpose, a small filter of Swedish paper, the ash of which is a known quantity, is dried at 120—130° C., in a weighing tube, till a constant weight is obtained. A sufficient volume of the water (a quarter of a litre for sewage, half a litre for polluted water, and a litre in other cases), is to be passed through this filter, and the flask rinsed out with distilled water to remove deposited matters, the rinsings being poured on the filter. The filter, with the matter upon it, is dried in its funnel at 100° C., and then transferred to the weighing tube previously used, and dried at 120—130° C., till a constant weight is obtained.

This weight, less that of the tube and filter, represents the total suspended matter. The amount of mineral matter in it is ascertained by incinerating the filter in a platinum crucible, recarbonating alkaline earths if present, and deducting, from the weight of the residue obtained, the known weight of the filter ash.

Estimation of Organic Impurity.

No process is known by which the actual weight of organic matter dissolved in water can be ascertained, but the amounts of carbon and nitrogen contained in that organic matter can be accurately determined, and they furnish a quantitative measure of the extent of the organic contamination.

This information, however, can only be obtained by means of ultimate analysis, *i.e.*, the combustion of the residue left on evaporating the water. No liquid reagent has, so far, proved sufficiently uniform in its action on the complex and varying substances found in water, to yield even comparative quantitative results of a trustworthy character.

The "combustion process" described in Part II contains all requirements on the score of accuracy and delicacy, but it has been objected to on account of the trouble and special skill required to execute the necessary gas analyses. I will, therefore, here describe two other methods, which have been suggested for the determination of organic elements; since, although they appear to me to be more troublesome than the process described in Part II, they will doubtless commend themselves to those chemists who are not in the habit of making gas analyses. For those who are satisfied with a less accurate acquaintance with the organic constituents of potable water, I have added a description of the so-called "oxygen process," which is not only extremely simple and rapid, but is also the only volumetric method deserving of any confidence whatever.

GRAVIMETRIC METHOD OF DITTMAR AND ROBINSON.

Determination of Organic Carbon.—A litre, or other suitable quantity of water, is treated with $\frac{1}{1000}$th of its bulk of a saturated solution of sulphurous acid, boiled down to a small volume in an inclined pear-shaped flask, and finally evaporated to dryness in a glass dish. If, during boiling down, the water deposits any solid matter which cannot be removed from the flask, the operation must be rejected, and a new one performed in a glass dish as described in Part II, page 61.

A combustion tube wide enough to receive a conveniently sized platinum boat is drawn out at one end into a bayonet shape, and charged with (1) a spiral of silver wire gauze to reduce oxides of nitrogen; and (2) a layer of granulated oxide of copper. The posterior end of the tube is reserved for the platinum boat; it is closed by a cork perforated to admit a glass tube connected with a gas-holder filled with air. The air used during the combustion is carefully freed from carbonic acid by passing it through potash solution; and to prevent carburetted hydrogen being absorbed from the india-rubber tubing, as little as possible of this material is used for connections. Before an analysis is commenced, the tube must be proved to be in good order by heating it to redness in a current of air, free from carbonic acid, till the air, as it comes out of the tube, no longer precipitates baryta-water. Then there is attached to the drawn-out end of the tube a little V-shaped tube, charged with a solution of chromic acid in 60 per cent. sulphuric acid, with which is permanently united a short tube filled with granulated calcic chloride. In front of all is a small and light soda-lime tube, with a layer of calcic chloride at the end where the gases escape.

The residue from the glass dish is transferred to the platinum boat, which is then introduced into the combustion tube, and the combustion conducted in a stream of purified air in the usual way. The products of combustion are freed from moisture and sulphurous acid during their transit through the V-tube, and they then enter the soda-lime tube, where the carbonic acid is absorbed.

The amount of organic carbon is calculated from the increase in weight of the soda-lime tube.

When several analyses are being made at the same time, this process is very convenient, for, with two soda-lime tubes, three or even four combustions can be performed in the same tube in a couple of hours.

Determination of Organic Nitrogen.—Half a litre of water is boiled down in a pear-shaped flask connected with a condenser, so as to estimate the ammonia in the same operation. The evaporation is continued as far as it is possible, without overheating any of the dissolved matter. To the residual liquid (say 25—30 c.c.) is added the requisite quantity of sulphurous acid and ferric chloride, to destroy nitrates (see Part II, pp. 60-63), and, if necessary, something to give body to the residue—sulphate of potash for instance. The evaporation is completed on a water-bath of a construction similar to that described in Part II, page 61.

This residue is placed in a large copper or silver boat, moistened with a drop of water, and covered with about 3 grams of a fused mixture of equal weights of pure baryta and soda (or soda alone may be used).

The boat is introduced into a short combustion tube connected, at one end, with an absorption apparatus charged with highly dilute hydrochloric acid, and at the other end with some arrangement for sending a regular current of hydrogen through the apparatus. The tube is gradually heated to redness, and the ammonia given off from the decomposition of the organic matter is estimated by the Nessler test, one-tenth of the solution in the absorption apparatus mixed with 50 c.c. of water being employed for the purpose.

Previous to use the tube must be heated, with the absorption tube attached, till all traces of adventitious ammonia are expelled, and it must then be allowed to cool in a slow stream of hydrogen. Deduction must also be made, when necessary, for any ammonia introduced with the baryta and soda.

In order to test the trustworthiness of this process, the following comparative experiments were made:—

Organic Carbon.

Samples of Water.	Dittmar's Process.	Frankland's Process.
	Part per 100,000.	Part per 100,000.
Chelsea Company	·286	·226
Honiton	·417	·317
New River Company........	·142	·104
Chelsea ,, ...	·248	·256
New River ,, ...	·232	·183
Southwark ,, ...	·259	·329
,, ,, ...	·158	·188
Kent ,, ...	·090	·090
Chelsea ,, ...	·220	·195
Blank	·009	·005

The excess in the first three cases was probably due to too much india-rubber in the connections; the loss in the fourth and sixth to the use of too strong sulphuric acid.

Organic Nitrogen.

Samples of Water.	Dittmar's Process.	Frankland's Process.
	Part per 100,000.	Part per 100,000.
New River Company........	·0346	·040
Southwark ,, ...	·0411	·042
West Middlesex ,, ...	·032	·040
Kent ,, ...	·0165	·018
Southwark ,, ...	·058	·056
New River ,, ...	·045	·034

METHODS OF DUPRÉ AND HAKE.*

Estimation of Organic Carbon.—Two methods are proposed for estimating minute quantities of carbon, such as those dealt with in water analysis:—(1) a gravimetric method applicable to the determination of 1 mgrm. of carbon and upwards, and (2) a "nephelometric" method, available for even considerably smaller quantities. These processes are all that can be desired on the score of exactness, and no expensive special apparatus is needed. At the same time the number of precautions which must be observed render them far from simple, and the absence of means for estimating organic nitrogen also diminishes their value to the water analyst.

The Gravimetric Method.—A convenient quantity of the water to be analysed is acidulated with phosphoric acid† to decompose carbonates, then evaporated to dryness, and the residue transferred without loss to a platinum boat.

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* "Chemical Soc. Jour.," 1879, vol. i, 159.

† Sulphurous acid would be preferable, because phosphoric acid is apt to form a glaze around organic matter, and thus to prevent its complete combustion. If sulphurous acid be used it is necessary to boil the acidulated water for a few seconds, otherwise the whole of the carbonic acid is not expelled.

A combustion tube 2 feet long is previously filled for half its length with granulated cupric oxide, kept in position by plugs of asbestos or platinum foil. It is drawn out and bent downwards at the front end at an angle of 120°, so that it may be conveniently attached to a Pettenkofer's absorption tube, the other end being connected by means of a caoutchouc stopper and glass tube with a reservoir of oxygen. The tube has to be heated to redness in a stream of oxygen free from carbonic acid, till the issuing gas ceases to render baryta water turbid, even after long bubbling. The oxide is allowed to cool, and the Pettenkofer's tube, charged with perfectly bright baryta solution, is attached. The cork at the posterior end of the combustion tube is then momentarily removed to allow the boat containing the water residue to be pushed into the tube. The combustion is then conducted in a stream of oxygen in the usual way.

In about fifteen to twenty minutes the substance will be burnt, and the slow current of oxygen may be quickened for a couple of minutes. The absorption tube is then detached, carefully stoppered, and set aside to be filtered. After cooling five minutes, the combustion tube is ready for a second experiment. The baric carbonate after being collected on a filter and carefully washed, is dissolved in dilute hydrochloric acid (1 in 50), precipitated as sulphate, dried and weighed; the result divided by 19·4 gives the quantity of organic carbon present.

Such is the outline of the process, but to obtain trustworthy results elaborate precautions against the access of adventitious carbonic anhydride are necessary.

The stock solution of baric hydrate (1·5 per cent. strength) is kept in a bottle, the cork of which is traversed by two tubes, one a syphon reaching below the liquid, the other a short tube just passing through the stopper. This latter tube is connected with a tube containing potash, to the free end of which is joined the tubing from a small hand bellows.

Previous to filling, the Pettenkofer's tube must be carefully cleansed and rinsed with distilled water, and then air, which has passed through potash solution, is forced through the tube for about two minutes. It is afterwards connected by flexible tubing with the syphon tube of the stock bottle, and sufficient baryta water is forced over to half fill the tube by working the hand bellows. The flow of baryta is then arrested, and the ends of the absorption tube are immediately stoppered by short pieces of india-rubber tubing closed at the free ends by glass rods to await the proper moment for connecting them with the combustion tube. During the experiment the tube stands in front of the furnace in such a manner that its bulb end is somewhat higher than the end to be connected with the combustion tube.

In order that no carbonic acid may be absorbed during the filtering, the funnel and filter are supported over a beaker containing a layer of caustic potash, and the whole is covered by a bell-jar standing in caustic potash. The mouth of this jar is closed by an india-rubber cap with two openings, one for a potash or soda-lime tube; the other, which is temporarily stoppered, contains a straight glass tube placed immediately over the filter, and capable when not clamped of being freely moved in all directions. When this apparatus has remained sufficiently long for all enclosed carbonic acid to be absorbed, the one end of the Pettenkofer's tube is connected by india-rubber tubing with the straight tube over the funnel, the other stopper is also replaced by a potash tube, and then the contents of the absorption tube are transferred to the filter. The washing of the tube and precipitate is effected by pouring down the absorption tube (not blowing from a wash bottle) boiling distilled water, which has been previously saturated with carbonate of baryta (solubility 1 part in 15,000). When this has been done several times, the washing is completed with a small quantity of pure boiling distilled water, and then the absorption tube is disconnected. By manipulating with the freely moving glass tube the filter receives a final rinsing round, and then the bell-jar is removed. The precipitate may be now washed to the bottom of the filter if necessary. The

Pettenkofer tube receives two rinsings with dilute hydrochloric acid (1 in 50) to dissolve any baric carbonate not washed off, and the liquid is poured into the filter. The filter is washed with distilled water, and if necessary with more dilute acid, till every trace of the carbonate has disappeared. The filtrate, which need not exceed 50 c.c., is collected in a beaker, but is afterwards concentrated to a much smaller bulk by evaporation in a platinum dish on a water-bath. The more concentrated liquor is transferred without loss to a smaller platinum dish (weighing about 5 grams), and evaporated to dryness with a few drops of pure sulphuric acid. The dish and its contents have then to be ignited, the residue moistened with nitric acid, re-dried, and the whole re-ignited and weighed.

The total carbon (*i.e.*, the sulphate of baryta divided by 19·4) is subject to a small correction due to constant error.

Nephelometric Method.—This method differs from that described above in the fact that a two per cent. solution of basic acetate of lead takes the place of the solution of baryta, and that the amount of carbon is estimated from the turbidity* of the solution at the end of the combustion. A slightly modified and enlarged Mills's colorimeter† is used in the estimation, and the turbidity produced by a known and fairly comparable quantity of carbonic acid being taken as the standard, the amount of carbon in the water residue is calculated from the proportionate lengths of the discs from the surface of the liquids.

As an additional refinement in the ultimate analysis of water residues, the authors have used dishes of silver foil. These are ignited before being used, are supported in platinum dishes during the evaporation, and are finally crumpled up and introduced bodily into the combustion tube without being handled in any way.

Drs. Dupré and Hake cite the following experiments as indicative of the delicacy of their processes :—

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* Hence the name "nephelometric," from νεφέλη, a cloud.

† See "Chem. News," vol. xxxv, p. 161.

(*a*) 200, (*b*) 100, (*c*) 50 c.c. of London water were evaporated in the dishes already mentioned, with an excess of phosphoric acid to destroy carbonates. *a* was examined by the gravimetric method, *b* and *c* by the nephelometric method. The results were 0·34, 0·31, and 0·26 part of organic carbon respectively, in 100,000 parts of water.

Oxygen or Forchammer Process.

This process, first suggested by Forchammer, depends upon the estimation of the amount of oxygen which a known volume of the water abstracts from a standard solution of permanganate of potash. With waters of a similar character the oxygen process furnishes a ready and fairly efficient means of comparing their relative organic purity, but it is not trustworthy when waters of heterogeneous origin are submitted to it.

The amount of "oxygen abstracted" can be ascertained with great exactitude and little trouble. It is, however, essential to employ an excess of permanganate, and to allow the action to go on for a considerable time. The amount of permanganate in excess can be accurately determined by the employment of hyposulphite of soda and the iodine and starch reaction, as recommended by Tidy.* Convenient strengths for the different solutions are given in the Appendix, but the potassic permanganate cannot long maintain its full value, and must therefore be re-standardised at short intervals, whilst the sodic hyposulphite loses strength so rapidly, that its value has to be re-determined by a blank experiment for each set of analyses undertaken.

The following is the method of procedure :—Cleanse two flasks first with strong sulphuric acid, and then with water. Place in one 500 septems (or 250 c.c.) of the water to be examined, in the other an equal volume of distilled water. Add to each 20 septems (10 c.c.) of the dilute sulphuric acid and 20 septems (10 c.c.) of the standard solution of per-

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* "Chem. Soc. Journ.," January, 1879.

manganate of potash, and allow the mixture to stand for three hours.

At the end of that time, the amount of undecomposed permanganate of potash remaining in the water must be determined as follows:—

Add to each flask two drops of solution of potassic iodide (See Appendix I, F), when an amount of iodine will be liberated exactly equivalent to the quantity of permanganate still present in the water. Now run in from a burette the solution of hyposulphite of soda until the whole of the free iodine is removed, judging of the exact moment when this is attained by the addition of a drop of clear starch solution towards the end of the operation.

Note the amount of hyposulphite used for (A) blank experiment with pure distilled water, (B) the water under examination.

It is evident that A expresses the amount of permanganate added to the water under examination, B the amount of permanganate in excess of what the organic matter in the water could destroy, and A—B the amount actually consumed after three hours' contact.

If the amount of available oxygen in the quantity of permanganate solution originally added be a, the oxygen consumed by the quantity of water operated on would be

$$\frac{(A—B)a}{A}.$$

That is to say, if 10 c.c. of permanganate solution (equivalent to ·001 grm. of oxygen) were added to a quarter litre of distilled water and of the water under analysis, and 40 c.c. and 15 c.c. of solution of hyposulphite were the respective quantities required for the flasks at the end of three hours, the oxygen consumed would be $\frac{40 - 15 \times {\cdot}001}{40}$ = oxygen per quarter litre, or $\frac{40 - 15 \times {\cdot}4}{40} = {\cdot}250$ part oxygen per 100,000 parts of water.

It is obvious that, if the water contains nitrites, ferrous salts, or sulphuretted hydrogen, the above estimation is valueless, unless these reducing substances are first removed, or afterwards allowed for.

The objections to the Forchammer process are. first, that its indications are only comparative and not absolute; and, secondly, that its comparisons are only true when the organic matter compared is substantially identical in composition.

For many years, indeed, after this process was first introduced, the action of the permanganate of potash was tacitly assumed to extend to the complete oxidation of the organic matter in the water, and therefore the result of the experiment was generally stated as "the amount of oxygen required to oxidise the organic matter;" while some chemists even employed the number so obtained to calculate the actual weight of organic matter in the water on the assumption that equal weights of all kinds of organic matter required the same weight of oxygen for their complete oxidation.

Both these assumptions have been conclusively proved to be entirely fallacious, for it has been experimentally demonstrated by operating upon known quantities of organic substances dissolved in water, that there is no relation either between the absolute or relative weight of different organic matters and the oxygen which such matters abstract from permanganate of potash.

Nevertheless, in the periodical examination of waters *from the same source*, I have noticed a remarkable parallelism between the proportions of organic carbon and of oxygen abstracted from permanganate of potash. Thus, for many years past, I have seen in the monthly examination of the waters of the Thames and Lea supplied to London such a parallelism between the numbers given by Dr. Tidy, expressing "oxygen consumed," and those obtained by myself in the determination of "organic carbon."

This remarkable agreement of the two processes, extending, as it did, to 1,418 out of 1,686 samples, encouraged me to hope that a constant multiplier might be found by which the "oxygen consumed," of the Forchammer process could be translated into the "organic carbon" of the combustion method of analysis. To test the possibility of such a conversion, my pupil, Mr. Woodland Toms, made, at my suggestion, the comparative experiments recorded in the following tables:—

I.—*River Water.*

Source of Sample.	Oxygen consumed.	×	$\frac{C}{O}$	=	Organic carbon by combustion.
Chelsea Company's supply ..	·098	×	2·6	=	·256
West Middlesex Co.'s ,, ..	·116	×	2·5	=	·291
Lambeth Co.'s ,, ..	·119	×	2·43	=	·282
Southwark Co.'s ,, ..	·121	×	2·22	=	·269
New River Co.'s ,, ..	·076	×	2·4	=	·183
Chelsea Co.'s 2nd sample ..	·070	×	2·69	=	·188
Lambeth Co.'s ,, ..	·119	×	1·99	=	·234
New River Co.'s ,, ..	·107	×	2·25	=	·221

As the result of these experiments, the average multiplier is 2·38, and the maximum errors incurred by its use would be − ·021 part of organic carbon in the case of the second sample of the Chelsea Company's water, and + ·049 part in that of the second example of the Lambeth Company's water. These errors would practically have little or no influence upon the analyst's opinion of the quality of the water. It is desirable that this comparison should be extended to the water of other moderately polluted rivers.

II.—*Deep Well Water.*

Source of Sample.	Oxygen consumed.	×	$\frac{C}{O}$	=	Organic carbon by combustion.
Kent Company's supply	·015	×	5·1	=	·077
Colne Valley Co.'s ,, ...	·0135	×	6·9	=	·094
Hodgson's Brewery well	·03	×	5·3	=	·158

The relation between "oxygen consumed" and "organic carbon" in the case of deep well waters is thus very different from that which obtains in the case of river waters, and the average multiplier deduced from the foregoing examples is 5·8, with maximum errors of + ·01 of organic carbon in the case of the Kent Company's water, and − ·015 in that of the Colne Valley water. Such slight errors are quite unimportant.

Similar comparative experiments made with shallow well and upland surface waters showed amongst themselves a wider divergence, but pointed to an average multiplier of 2·28 for shallow well water, approximately the same as that found for moderately polluted river water, and 1·8 for upland surface water.

In the interpretation of the results obtained, either by the Forchammer or combustion processes, the adoption of a scale of organic purity is often useful to the analyst, although a classification according to such a scale may require to be modified by considerations derived from the other analytical data. It is indeed necessary to have a separate and more liberal scale for upland surface water, the organic matter of which is usually of a very innocent nature and derived from sources precluding its infection by zymotic poisons.

Subject to modification by the other analytical data, the following scale of classification has been suggested by Dr. Tidy and myself:—

SECTION I.—Upland Surface Water.

Class I. Water of great organic purity, absorbing from permanganate of potash not more than 0·1 part of oxygen per 100,000 parts of water, or 0·07 grain per gallon.

Class II. Water of medium purity, absorbing from 0·1 to 0·3 part of oxygen per 100,000 parts of water, or 0·07 to 0·21 grain per gallon.

Class III. Water of doubtful purity, absorbing from 0·3 to 0·4 part per 100,000, or 0·21 to 0·28 grain per gallon.

Class IV. Impure water, absorbing more than 0·4 part per 100,000, or 0·28 grain per gallon.

SECTION II.—WATER OTHER THAN UPLAND SURFACE.

Class I. Water of great organic purity, absorbing from permanganate of potash not more than 0·05 part of oxygen per 100,000 parts of water, or 0·035 grain per gallon.

Class II. Water of medium purity, absorbing from 0·05 to 0·15 part of oxygen per 100,000, or 0·035 to 0·1 grain per gallon.

Class III. Water of doubtful purity, absorbing from 0·15 to 0·2 part of oxygen per 100,000, or 0·1 to 0·15 grain per gallon.

Class IV. Impure water, absorbing more than 0·2 part of oxygen per 100,000, to 0·15 grain per gallon.

Whenever it is of great importance to know the amount and nature of the organic contamination of water, reliance ought not to be placed on the Forchammer process, for the action of the permanganate of potash test is not only liable to considerable uncertainty, but it makes no distinction between nitrogenous and non-nitrogenous organic matters, and may even confuse innocent inorganic substances with organic matters of most objectionable origin. In cases of minor importance, however, and when the analyst shrinks from the labour and cost of determining the organic elements by actual combustion, he will be much more likely to rate a water at its proper value by this process than by any other now in use. It must be confessed, however, that prolonged experience with this process has not increased my confidence in its trustworthiness, even for roughly approximate estimations.

PART II.

WATER ANALYSIS REQUIRING THE USE OF GAS APPARATUS.

THERE now remain to be described those processes of water analysis in which the amounts of the final products are determined, not by the balance nor in terms of any standard solution, but by the volume they occupy in the gaseous condition. As inappreciable weights occupy in the state of gas very appreciable volumes, a eudiometric process with an accurate means of measurement possesses manifest advantages over any ordinary gravimetric one, where the minute quantities of some of the substances existing in a water residue are concerned.

When, therefore, in 1866, the author, after careful examination, became convinced of the inefficiency of the processes then in use, he availed himself of eudiometric measurements, in order to render his new method of analysis sufficiently delicate. These measurements are used in the so-cllaed "combustion" method of ascertaining the extent of organic pollution, and in the "mercury" method of determining the amount of nitrogen as nitrates and nitrites in potable and other waters.

THE COMBUSTION PROCESS.

Determination of the Carbon and Nitrogen of the Organic Matter.

The chief features of the eudiometric method of determining organic carbon and nitrogen in water were first made known by the author at the Royal Institution in March, 1867. They may be rendered most easy of comprehension by describing them under four heads:—(1) the evaporation of the water; (2) the preparation for combustion of the residue thus obtained; (3) the combustion; and (4) the actual volumetric measurement.

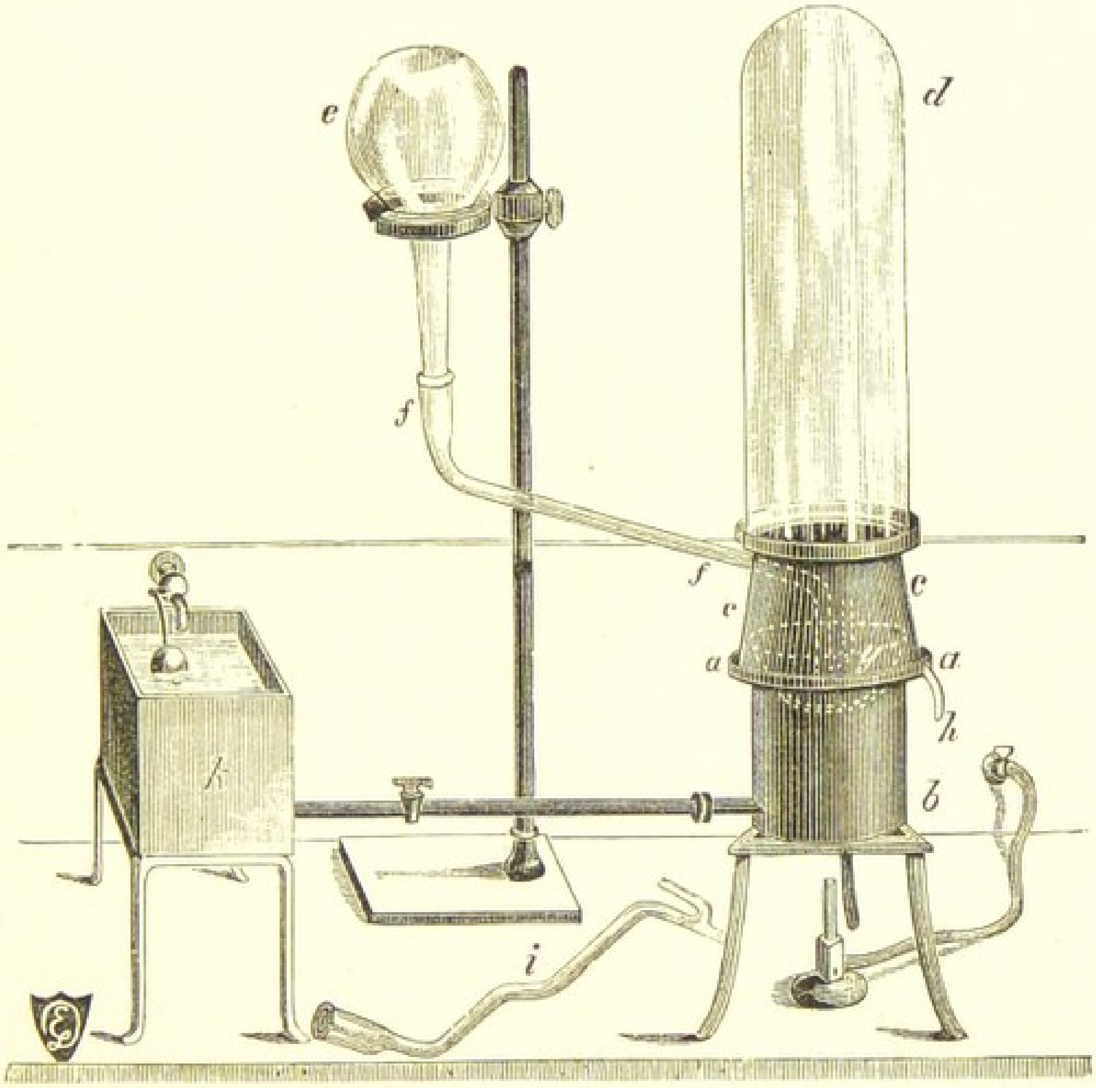
(1) *The Evaporation.*—As soon as possible after the receipt of the water, and directly after the ammonia has been estimated, the evaporation should be commenced. The quantity of the water to be taken must depend upon the quality. When the water is, organically, of high purity, it is necessary to evaporate more than when it contains a considerable proportion of organic elements, the object being to obtain a sufficiency of organic matter for accurate determination. It is an inconvenience rather than an advantage to use a large quantity when the water is much polluted.

One litre is the maximum quantity required; but, as an almost invariable rule, less will suffice if the proportion of ammonia be large. If in 100,000 parts of water the ammonia be more than 0·05 part, half a litre is sufficient; if more than 0·2, a quarter of a litre; and if more than 1·0 part, 100 c.c. will suffice.

The measured quantity of water is transferred to a suitable flask, with 20 c.c. of a saturated solution of sulphurous acid (see Appendix I, G 2), and the mixture boiled briskly for a few seconds. By the sulphurous acid, all the carbon and nitrogen which exist in the water in an inorganic form (the nitrogen as ammonia excepted) are eliminated; the nitrates and nitrites being reduced with the expulsion of their nitrogen, and the carbonates decomposed. The preliminary boiling is required to expel effectually from solution the liberated carbonic acid. Nitrogen as ammonia, on the other hand, is fixed (except a small loss, see Appendix II, Tables 3 and 4) by adding sulphurous acid, and has to be deducted from the gross amount of nitrogen yielded by combustion. The proportion of ammonia in water rapidly diminishes, and hence it is important to start the evaporation within a short time of the estimation of the ammonia.

The acidulated water is next to be evaporated to dryness in a thin glass dish, which should be rather under than over 4 inches in diameter, hemispherical in shape, and without a lip. During the evaporation, operations requiring the use of ammonia should be avoided in the laboratory. The apparatus shown in the annexed figure is devised for conducting the evaporation in a limited volume of air.

FIG. 1.



Upon a self-filling water-bath (*b*) rests a flanged copper capsule (*aa*), the concavity of which is made to fit round the glass dish, but is about an inch less in depth. The water-bath (*b*) has a diameter a trifle greater than the hemispherical part of this copper capsule, and allows the flange of the capsule to project about half an inch all round.

This flange has a rim about one-eighth of an inch high running round it, except where it is turned down to form a lip. A thin glass shade (*d*), such as is used for covering statuettes, fits within this rim, and should be wide enough to prevent it from touching the glass dish. The shade does not, however, ordinarily rest upon the rim of the copper capsule, but upon the corresponding rim of the copper ring (*cc*), which is 3 inches high and somewhat conical, as shown in the figure. The water to be evaporated is placed in the flask (*e*), the neck of which is ground to fit accurately into the self-regulating supply tube (*ff*), whereby the water is only permitted to flow into the dish when the junction (*g*) is above the water level. By bending the supply tube (*ff*), as shown at (*i*) in the figure, the water in the flask and that in the glass dish may be isolated by an entrapped bubble of air, thus preventing convection between the dish and the flask. The flask (*e*) is supported upon the ring of a large filter-stand, out of which a small segment has been cut to allow of the passage of the neck. The supply tube rests in a notch cut in the copper ring (*c*), just deep enough to admit it without touching the glass shade, so as to prevent the water condensing on the inside of the latter from running back into the dish.

During the evaporation the condensed water trickles down the interior of the shade, collects in the copper capsule underneath the glass dish, and is finally conducted away by a piece of tape (*h*) passing over the lip. It is found in practice that the water evaporates beneath the glass shade at about the same rate as in the open air.

The apparatus having been got ready, the acidified water in the boiling flask is transferred when cold to the flask (*e*). The water may be rapidly cooled, if necessary, by inverting a beaker over the neck of the flask and placing the whole under a stream of cold water. The supply pipe (*ff*) is next fitted on, and, by a dexterous movement, the flask is inverted whilst the open end of the supply pipe is held over the glass dish so as to avoid any loss. Care must be taken not to invert this flask while the water is still warm, or the supply pipe may be forced off by the expansion of the inclosed air. The flask is then placed firmly on the filter ring, and the supply tube in the notch, while the end of the tube reaches down to, without actually touching, the centre of the dish. The water will now descend from the flask and nearly fill the dish. The glass shade must then be put on, and the lamp lighted beneath the water-bath.

The evaporation of a litre of water by this process occupies from eighteen to twenty-four hours, so that, if it be commenced in the forenoon, and continued with a constant gas flame and self-supplying water-bath throughout the night, the residue will be left in a condition to burn by the morning of the following day. Before all the water has evaporated the arrangement (*eff*) may be removed and the exit end rinsed with a few cubic centimetres of water free from organic matter (Appendix I, G 1). The ring (*cc*) may also be removed, and the shade (*d*) placed directly on the flange (*aa*). Immediately the residue in the dish appears to be dry it should be removed, mixed with oxide of copper, and transferred to the tube destined for its combustion as described below.

To ensure the destruction of nitrates, one drop of ferrous chloride (Appendix I, G 4) should be added to the first dish full of water.

When the water contains very large quantities of nitrates and nitrites, their reduction and the dissipation of their nitrogen require the use of a larger amount of sulphurous acid than the 20 c.c. previously mentioned. Thus, when the nitrogen as nitrates exceeds 0·5 part in 100,000 parts of water, the glass dish containing the solid residue from one litre of that sample must be filled with organically pure distilled water, to which has been added one-tenth of its volume of a saturated solution of sulphurous acid, and then the evaporation is again carried to dryness.

If the nitrogen as nitrates and nitrites exceed 1 part in 100,000, a quarter of a litre of this 10 per cent. solution should be evaporated on the residue; if 2 parts, half a litre; if 5 parts, a litre. Should the quantity of water evaporated be less than a litre, a proportionate reduction must, of course, be made in the quantity of the sulphurous acid solution used. In the ordinary course of analysis the nitrogen as nitrates and nitrites will have been determined before the evaporation of the water is finished.

The sulphuric acid produced by the oxidation of the sulphurous acid does not remain free if a fair amount of carbonates is contained in the water, but, if little or none is present, a small quantity of a saturated solution of hydric sodic sulphite (1 or 2 c.c.) may be added, in order to supply base for the sulphuric acid to combine with. A knowledge of the source, or of the temporary hardness, of the water will generally suffice to inform the analyst on this point.

When sewage, or other liquid containing much ammonia and no nitrates or nitrites, is to be analysed, it will be found advantageous to substitute 10 c.c. of a solution of metaphosphoric acid (Appendix I, G 9) for the sulphurous acid previously mentioned, as ammonic phosphate loses much less ammonia during evaporation than ammonic sulphite. This reagent, however, cannot be used with ordinary waters, because it does not reduce nitrates. When employed, it is best to add half a gram of calcic phosphate (Appendix I, G 10) to dry the residue, which is otherwise difficult to manipulate, owing to its viscidity. Boiling is not necessary with the metaphosphate, nor is any other reagent requisite. Waters containing very large quantities of ammonia very rarely contain nitrates.

2. *Preparation for the Combustion of the Residue.*—Select some combustion tubing of rather smaller bore than that ordinarily used for organic analysis, and cut it into lengths

of about 18 inches. Carefully wash them out with water and a clean linen rag bound round a stout iron wire; rinse with distilled water, and dry in an oven; then seal up one end of each in the blowpipe flame. If the other end has been broken diagonally instead of transversely, it will be found more convenient for filling.

Preparatory to charging the tube, place the glass dish containing the dry residue upon a sheet of glazed paper, and have at hand bottles of granulated and of powdered "assayed oxide of copper" (Appendix I, G II), also a small and very elastic steel spatula (about 4 inches in length by half an inch in breadth), and a little scoop or shoot formed of a thin piece of metal.

The dry water residue, as it lies in the dish, must be sprinkled with a few grains of fine oxide of copper, then carefully detached from the glass by the aid of the spatula, and mixed with the oxide. There will be no difficulty in scraping a dish clean, if the spatula is sufficiently flexible to adapt itself easily to the shape of the dish.

Before transferring it to the combustion-tube, the detached residue is mixed also with a very little coarse oxide of copper, so as to prevent its lying too compactly when in the tube. In charging the combustion-tube, one inch of coarse oxide of copper is first introduced by scooping with the open end in the supply bottle, and then most of the residue in the glass dish is transferred to the tube in a similar way. That which remains is transferred by the aid of the bent piece of metal, and so also are the two portions of fine oxide of copper subsequently used to rinse out the dish. The residue and rinsings will not occupy more than 2 inches in length of the tube. The tube is filled up with coarse oxide to a distance of 10 inches from the closed end. Above that are placed two cylinders of metallic copper, 1½ inch long, made by wrapping copper gauze round a stout wire. The copper is succeeded by an inch of oxide of copper. (See E, fig. 2, p. 67.)

The oxide must be shaken down, during the process of filling, by tapping the closed end of the tube sharply on a wooden block or bench. The copper rolls, too, should fit the tube and come in direct contact with the oxide in order to prevent the occurrence of empty spaces, which are liable to collapse when the exhausted tube is exposed to a high temperature.

The copper cylinders must be oxidised in air and reduced in hydrogen before being used the first time; but, if put into a stoppered bottle after use, they can be employed several times without repeating the operation. The coarse oxide of copper may also be used many times, if transferred at once from the broken combustion-tube to a stoppered bottle. The oxide in front of the copper is placed there to oxidise any traces of carbonic oxide and hydrogen formed by the reducing action of foreign metals in the copper gauze.

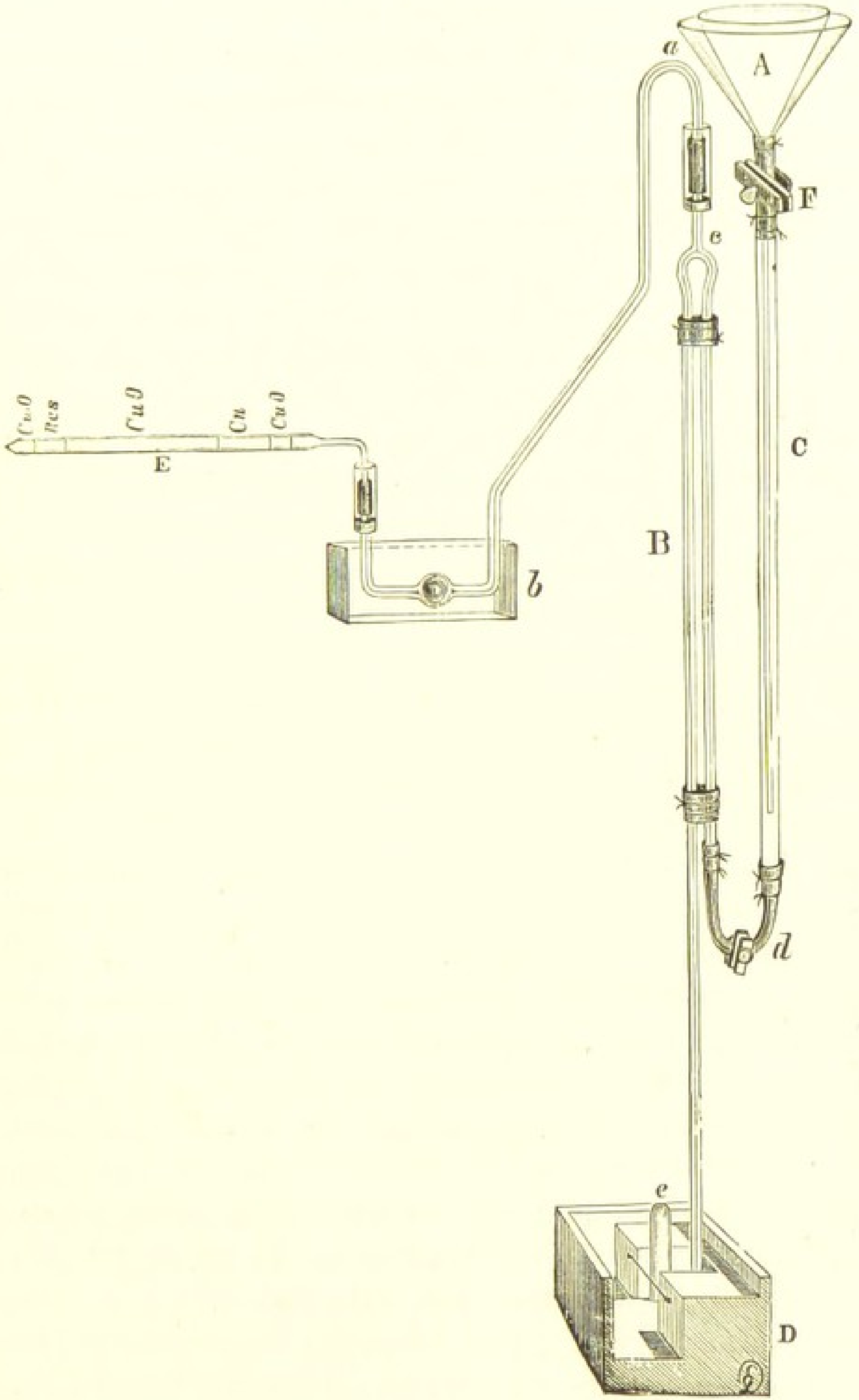
When the combustion-tube is charged, the open end is heated uniformly about an inch above the final layer of oxide of copper, and drawn out to a stout tube about 6 inches long and one-fifth of an inch in diameter. The end of this drawn-out tube is then rounded in the blowpipe flame, and the long neck bent at right angles, after which it is ready to be introduced into the combustion furnace.

3. *The Combustion.*—This is performed in vacuo. The prepared combustion-tube is placed in the usual furnace and attached to a Sprengel pump, as shown in fig. 2, p. 67. The combustion furnace is, by preference, a double one; as much time is saved if two combustions are carried on simultaneously. The combustion-tubes are laid in iron gutters lined with asbestos, to protect them from the direct action of the flame.

The form of Sprengel pump best adapted for this work is shown in fig. 2, page 67. Its construction is not beyond the capabilities of most amateur glass-blowers.

B is the pump proper, with the longer leg re-curved at its lower extremity, for the convenient delivery of gas into the test-tube (*e*). The flow of mercury from the inner funnel (A)

FIG. 2.



may be regulated either by the screw clamp (F) placed on the india-rubber tube connecting A with C, or, better, by the similar clamp upon the flexible tube (*d*). As soon as the pump has been placed in position, its short exhaust-tube (*c*) is attached to the bent tube (*a*) in the following manner:—A small perforated cork is first slipped over the tube (*c*), and then over the cork a piece of glass tube 2 inches long and of suitable bore. A short piece of sound india-rubber tubing serves to connect *a* and *c* together, the glass tubes being inserted so far as to touch each other. This joint is secured by wire. The cork and the piece of wide glass tube are then pushed up over the joint, and the tube filled with glycerin, to prevent the possibility of any leakage of air. The joint which connects the tube (*a*) with the combustion-tube is made in a similar manner, except that, being disconnected after each combustion, water is used instead of glycerin, and the india-rubber need not be wired on to the combustion-tube.

The tube (*a*) is bent twice at right angles, so as to admit of its immersion in a small tin trough (*b*). The submerged portion of it has a bulb blown on it, to collect the water produced during the combustion. The length of the tube (*a*) is governed by the distance between the pump and the furnace.

To start the pump the funnel is filled with mercury, and enough to cover the re-curved end of the delivery tube is poured into the trough (D). Then the screw clip (*d*) is cautiously opened, and the mercury allowed to rise up one limb of B and fall in pellets down the other, each pellet drawing in a small portion of air from *a* in its passage. Whilst the tube is being exhausted, the trough (*b*) is filled with hot water, so as to drive off rapidly any water which may have been left in the bulb from a previous operation. At the same time sufficient burners at the front end of the furnace are lit, to heat to redness the copper roll and about half an inch of oxide. An iron screen is temporarily placed across the combustion-tube, to prevent the further heating of it towards the closed end.

At the expiration of about ten minutes the alternate pistons of mercury and enclosed air in the descending tube of B will have disappeared, and an unbroken column of mercury, of nearly the barometric height, will fill the lower part of the tube, while the fresh pistons of mercury will fall upon this column with an audible click.

To expel the last traces of air, the flow of mercury may be increased for a few seconds, while the hot water in the trough is replaced by cold, and then the pump must be stopped.

The only place where leakage into this apparatus could possibly occur is at the connection between the combustion-tube (E) and the tube (*a*). It is always well, therefore, to watch this water-joint, to see if any liquid is drawn into the interior of the tube. The level in the water-joint will always be lowered somewhat by evaporation, owing to the proximity of the furnace; but it must not be allowed to fall low enough to expose the india-rubber.

The screen may be removed when the exhaustion is complete, and the burners turned on one or two at a time till the whole length of the tube is at a dull red heat.

The operator will know, by the mercury column ceasing to fall, that the combustion is complete; this will usually be the case in about an hour.

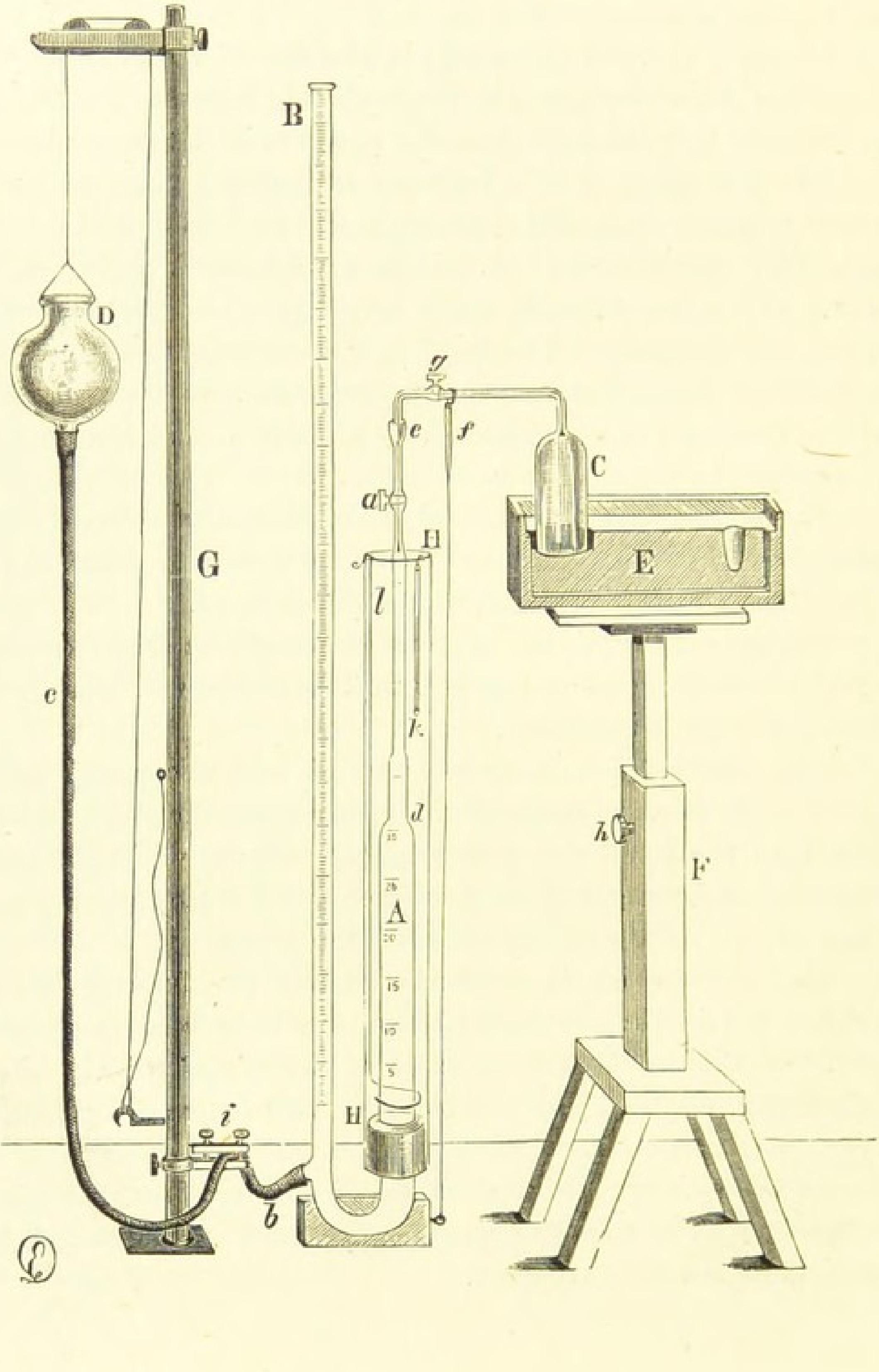
The clamp (*d*) is now unscrewed, and the pump again set to work so as to transfer the gaseous products of combustion into the small dry test-tube (*e*), which, while the combustion has been going on, has been filled with mercury and inverted over the delivery tube of the pump.

The exhaustion is conducted while the furnace is still alight; for if the contents of the tube have been previously properly shaken together, there is little risk of the glass collapsing, whilst, if allowed to cool, the tube would probably crack and admit air.

As soon as the exhaustion is again complete, the small tube (*e*) containing the gaseous products is removed for eudiometrical measurement.

4.—*The Gas-measuring Apparatus.*—The apparatus required for this operation is of very simple construction. It consists of a U-shaped tube with unequal limbs. In the shorter limb

FIG. 3.

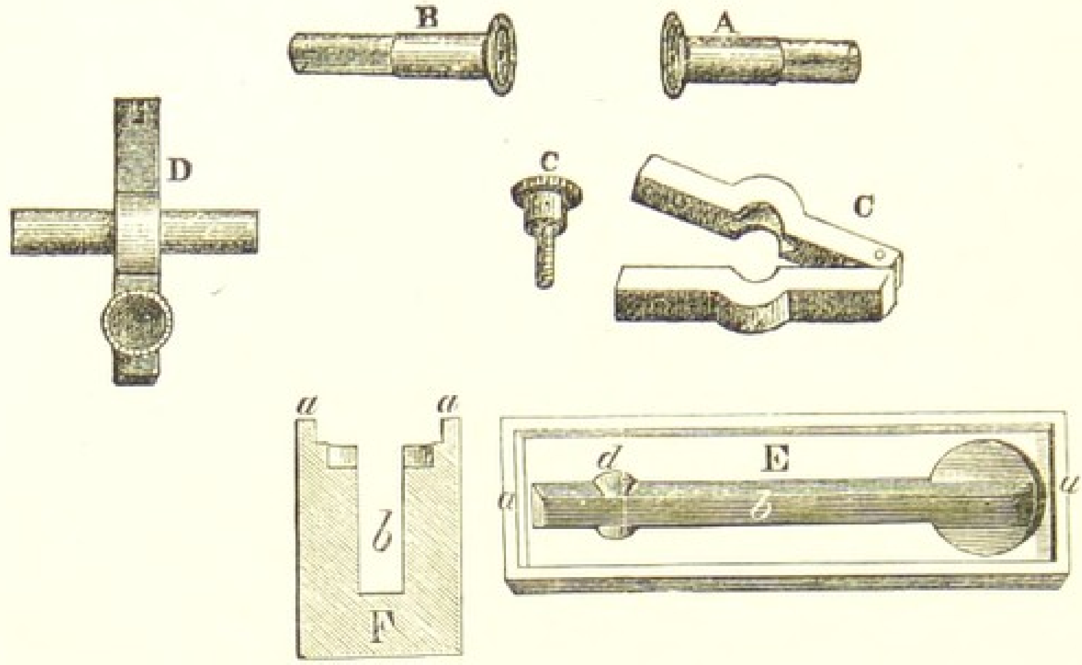


(A, fig. 3), the volume of the gas under examination is ascertained, and in the longer limb (B) the pressure to which the gas is subjected is measured. By turning a glass stopcock (*a*) the closed limb (A) can be put in connection with a chamber (C) called the "laboratory tube," in which the gas undergoes chemical treatment. By raising or lowering the vessel (D) of mercury connected by a flexible tube (*c*) with the foot of the longer limb, mercury is thrown into or withdrawn from the measuring apparatus; and by this means the motive power is provided which draws gas from the "laboratory tube" into the measuring tube, expels it again, and regulates the pressure during measurement. The measuring chamber or shorter limb is a stout glass tube of 0·75 inch internal diameter, bent at its lower end and joined to the pressure tube (B), 4 feet long and of 0·25 inch internal diameter. Near the bottom of B is inserted a glass tube (*b*) 1 inch long and 0·2 inch in diameter for the admission and withdrawal of mercury. It is connected with the movable mercury reservoir (D) by the webbed caoutchouc tube (*c*).

In order to permit of both small and large quantities of gas being measured with equal precision, the tube A decreases in bore towards the top. For 14 inches from the foot it maintains its full bore, but at *d* it is constricted for a length of 2 inches to a bore of 0·25 inch, and above that to 0·1 inch for 7 inches. This measuring chamber terminates in a capillary tube provided with a glass stopcock (*a*).

To connect the measuring tube with the laboratory vessel, the capillary is usually bent at right angles, and a steel cap shaped as at A in fig. 4, cemented on. The tube from the laboratory vessel terminates in a similar cap (B), and the ground faces of the two, after lubrication, are pressed together and kept in position by the clamp shown at C and D in fig. 4. The face of A has a sunk annulus into which a projecting ring upon B fits loosely. The sunk annulus is filled with resin cerate before the clamp is applied, and thus serves to keep the joint gas-tight.

FIG. 4.



These joints are, however, expensive, besides being liable to rust and to break away from the cement. A form of junction which is less subject to get out of order, and which from its greater flexibility is less liable to cause fracture, is shown in fig 3. About an inch above the stopcock on A, the capillary tube is expanded into a small funnel or cup (*e*). The tube from the laboratory vessel is bent twice at right angles, and then drawn out at its end so as to fit into the neck of the cup. The joint is rendered gas-tight either by grinding the stopper into the socket and making contact perfect by lubrication; or, preferably, the conical stopper is evenly covered with a piece of thin unvulcanised sheet india-rubber. The india-rubber is rendered air-tight by moistening it with water, and the cup is filled with mercury. The stopper must be kept firmly down in the cup by the aid of an elastic band (*f*), fastened at one end to the foot of the stand and at the other to a hook, which is slipped over the capillary tube near the stopcock (*g*).

The laboratory vessel (C) is a jar 4 inches high and an inch and a half internal diameter. It stands firmly on the shelf of a strong mahogany mercury trough (E), the construction of which is shown at E and F in fig. 4. It is $10\frac{1}{2}$ inches long, $3\frac{1}{4}$ inches broad, and $3\frac{1}{2}$ inches deep, outside measure. The rim (*aa*) is $\frac{3}{8}$ths inch broad and $\frac{5}{8}$ths inch deep. The excavation (*b*) is 9 inches long, 1 inch broad, and $2\frac{5}{8}$ inches deep. The shelf or bottom of the circular cavity on which the jar (C, fig. 3) rests is $1\frac{8}{10}$ths inch across, and is sunk to a depth of $\frac{8}{10}$ths inch below the top of the trough (*aa*). At *d* in fig. 4 (E), are two slight lateral indentations for the convenient manipulation of tubes containing specimens of gas for analysis. This trough rests on a small table at the top of a pillar sliding vertically in the hollow upright (F), fig. 3, and maintained at any required height by the screw (*h*).

The U-tube (AB) is supported by an iron retort-stand, with a clamp, not shown in the figure. Fixed to the table carrying the whole apparatus is an upright iron rod (G), which supports a pulley for raising or lowering the mercury reservoir (D). A double screw clamp, for regulating the supply of mercury through the caoutchouc tube (*c*), may be conveniently fixed to the upright rod, as shown at *i*.

The measuring tube is surrounded by a larger glass tube (HH), containing water to give a definite temperature to the gases during measurement, and a thermometer (*k*) hangs in this water-jacket. The uniform temperature of the water is secured by working the agitator (*l*) before each reading. This agitator consists of a piece of iron wire, about $\frac{1}{8}$th inch thick, with its lower end flattened and bent round to two-thirds of a circle. The two limbs of the U-shaped tube are so graduated that the zeros on both are at the same level. The pressure tube is graduated into single millimetres, the measuring tube at intervals of 10 mm., commencing at about 2 inches above the bend or foot.

Before this apparatus can be used, the measuring vessel must be calibrated and corrections must be made for difference of mercury level in the two tubes, due to capillarity.

To perform the calibration, it is convenient to procure a short piece of capillary tube like that used to connect the measuring tube and the laboratory tube, to fit it to the cup (*e*) at the top of A in a similar manner, and to bend it twice at right angles. The instrument is filled with mercury by raising the reservoir (D) till the mercury drips from the end of the temporary bent tube. The open extremity of this tube is then immersed in a beaker of distilled water, and the measuring tube filled with water by lowering the mercury reservoir (D). When the water in the shorter limb of AB is below the zero mark the beaker is removed, the reservoir raised, and mercury allowed to flow gently in at *b* until the top of the convex surface of the mercury in A just coincides with the zero of the graduated scale. This is best ascertained by the aid of a small telescope, sliding on a vertical rod. The temperature of the water in the jacket being now noted, the calibration may be commenced.

A small and light glass flask, the weight of which has been accurately ascertained, is placed in such a position as to receive drops of water when they are made to flow from the bent capillary tube. The cock (*a*) is then cautiously opened, and water allowed to drop into the flask until the mercury in A has risen to the first graduation above zero. The flask is then accurately weighed, and these operations are repeated for each division on the wide part of A; if, however, the tube be of tolerably uniform bore, it will be sufficient to weigh the water at each rise of mercury through 50 or even 100 mm.; but the last reading of mercury in A should be taken at the highest point at which the diameter has not been altered in attaching the narrower tube (*d*), and the next reading should in like manner be taken at the lowest and highest points of the first narrow tube (*d*), where the bore has not been deformed by the glass-blower. It is obvious that between the two points above and below the contractions no gaseous volume can be determined; but the gas can always when necessary be either compressed into the narrow tube or expanded into the wide one, by lengthening or shortening the column of mercury in the other limb of the apparatus. The operation of weighing the water expelled between the different divisions of the scale is continued until the last drop has issued from the capillary syphon tube. If, however, this tube is not of capillary bore, the mercury must only be allowed to rise to the cup and stopper joint (*e*), but in this case a trifling loss will occur in the measurements, owing to the volume of gas between the two stopcocks not being included in the calibration.

If the temperature of the water in the water-jacket is 4° C., the weight in grams of the water expelled from each of the different known lengths of the tube (A*d*) expresses in cubic centimetres the respective capacities of those lengths. If the temperature be not 4° C., the necessary correction must be made.

It now only remains to calculate the volume value of each division mark on the tube, and to prepare a table showing the volume of gas contained in the tube when the apex of the mercury stands at that division.

Since it is also advisable to make the calculations by the aid of logarithms, the logarithmic equivalents of these numbers ought to accompany them or take their places in the table.

The capillary depression of the mercury must be determined by taking several readings in the two limbs (and in all three widths of the measuring tube) when both are freely open to the air. The plus or minus correction for capillarity, which the readings of the pressures will require, should likewise be inserted in the table.

5. *The Eudiometrical Determinations.*—The following is the mode of conducting, with this apparatus, the analysis of the gaseous mixture obtained in the combustion of a water residue.

The apparatus is first examined as to efficiency. The reservoir (D) is replenished, if necessary, and the taps (*a*, *g*) and connections are lightly lubricated with resin cerate. The interior of the measuring tube should be clean and moist; if it is not clean, a little acidulated water may be drawn into the apparatus and again expelled, and the process repeated with distilled water. Any stoppage in the capillary tubes may be removed by a long bristle or fine platinum wire. The laboratory tube being disconnected from the measuring tube (A), the mercury reservoir is to be raised and the stopcock opened till the mercury begins to issue from the capillary opening.

The laboratory vessel (C) being put into position, one end of a piece of india-rubber tubing, reaching to its top, is temporarily placed inside it. By suction at the other end of this tube the greater part of the air is quickly removed; what remains is withdrawn by suction through the glass capillary tube.

The laboratory vessel and measuring tube are then joined together. If the connections are in good order, the mercury will be seen on lowering or raising the reservoir (D) to move along the capillary tube when the stopcocks are opened; but no air will be drawn in or mercury expelled when one of the stopcocks is closed.

The analysis is commenced by throwing up into the laboratory vessel a couple of drops of a solution of potassic bichromate from a bent pipette. The gas to be analysed will consist of carbonic acid, nitrogen, and nitric oxide. Occasionally, however, with a carelessly conducted combustion, sulphurous acid is also found, having escaped the absorbent action of the copper roll. The potassic bichromate will remove this gas if present.

The beaker or capsule containing the inverted tube of gas obtained by the combustion of the water residue (see p. 69) is then immersed in the mercury trough (E), the tube withdrawn from it, and the gas discharged into the laboratory vessel. If sulphurous acid be present, it will be absorbed in a minute or two, and the liquid will become olive coloured if the bichromate be in excess; but if it turn green more bichromate must be added. In this, and in subsequent operations where gas is to be brought into intimate contact with an absorbent, it is best to maintain a flow of mercury from the measuring tube into the laboratory vessel, as it promotes the contact of the gas with the absorbent. At the same time the trough should be made to vibrate gently, so as to cause the solution to wet the sides of the vessel. The junctions above described have sufficient elasticity to allow of this being done without fear of fracturing the capillary tubes.

The volume of the gas must now be measured. For this purpose the stopcocks (*a*, *g*) are opened, and the reservoir (D) lowered, till the gas has come over into the measuring tube, the stopcock (*g*) being closed just as the absorbent liquid approaches it, and the cock (*a*) immediately afterwards. Then, by the aid of the reservoir (D), the pressure is adjusted, so that the level of the mercury in the measuring tube coincides with one of the graduations.

The height of the mercury in the two tubes (A, B) is then noted, and also the readings of the barometer, and of the thermometer (*k*). These observations give the volume of total gas, and may be labelled A.

The carbonic acid is withdrawn from this total quantity by a saturated solution of caustic potash. Two or three drops of this absorbent are cast up from a small pipette into the laboratory vessel, and the gas transferred back from the measuring tube. At the end of about five minutes the gas is again measured, the temperature and pressure being noted as before. A second reading of the barometer is not, however, necessary. These observations may be called B.

A few drops of pyrogallic acid (Appendix I, G 7), are now passed up into the laboratory vessel, and the gas returned upon it from A. If the liquid, when thrown up against the sides of the glass, runs off without a stain, a bubble or two of pure oxygen (Appendix I, G 8) is admitted, and the mercury caused to flow slowly into the vessel (C) for about ten minutes. The object of this operation is precautionary. The gas remaining after the absorption of carbonic acid consists mainly of nitrogen with, generally, a little nitric oxide which has escaped the reducing action of the copper roll. When, however, the total quantity of gas furnished by the combustion of the water residue is very small, and the vacuum consequently but slightly impaired, it sometimes happens that traces of oxygen are given off from the incandescent oxide of copper, and pass so rapidly over the metallic copper as to escape absorption. If free oxygen should be present in the gas, it is absorbed by the potassic pyrogallate, and the remaining gas to be measured is nitrogen. There may be a trifling loss under such circumstances, for any nitric oxide which also escaped the copper roll will have been converted into the soluble peroxide.

If oxygen is absent, however, as is almost always the case, it is necessary to find, by difference, the amount of nitrogen present in the form of nitric oxide. For this purpose the bubble of oxygen is added, and it instantly transforms any nitric oxide that may be present into nitric peroxide, absorbable along with the excess of oxygen by the pyrogallate of potash. The absorption of oxygen is known to be complete when the dark coloured liquid, thrown by agitation upon the sides of the laboratory tube, runs off again without leaving a dark blood-red stain.

The measurement in A of the residual gas gives, by difference, the volume, if any, of nitric oxide, and completes the analysis.

These operations have furnished three uncorrected gaseous volumes, viz., A, volume of the three mixed gases; B, volume of nitric oxide and nitrogen: and C, volume of nitrogen. By the usual calculations, these volumes may be reduced to 0° C., and 760 mm. pressure, and then from the corrected volumes A′, B′, C′, so obtained, the quantities of carbonic anhydride and nitrogen may be deduced as follows:—

$$A' - B' = \text{volume of carbonic anhydride.}$$

$$\frac{B' - C'}{2} + C' = \frac{B' + C'}{2} = \text{volume of nitrogen.}$$

From these corrected volumes of carbonic anhydride and nitrogen, the weights of carbon and nitrogen can, of course, be readily calculated. This final and sole object of the analyst may, however, be obtained by a much shorter process; that is, by dispensing altogether with the intermediate determination of the corrected volumes, which is only necessary in the foregoing method of calculation to enable the operator to arrive at the corrected volumes of carbonic anhydride and nitrogen. In fact, if the original gaseous mixture be assumed, so far as volume-weight is concerned, to be nitrogen, the calculations become greatly simplified. They depend upon the following data:—

1. The weights of carbon and nitrogen contained in equal volumes of carbonic anhydride and nitrogen gases measured at the same temperature and pressure, are to each other as 6 : 14.

2. The weights of nitrogen contained in equal volumes of nitrogen and nitric oxide are as 2 : 1.

Now, if we assume, for the purpose of calculation, that the gaseous mixture submitted to analysis consists entirely of nitrogen, and that two successive portions of this nitrogen are removed from it by the action of reagents, then, if A be the weight of the total gas calculated as nitrogen, B the weight after absorption of the first portion (CO_2), and C the weight after the absorption of the second portion (N_2O_2); further, if x and y represent respectively the weights of carbon and nitrogen actually contained in the gaseous mixture, then the following simple equations express the values of x and y:—

$$x=\frac{3(A-B)}{7},$$

$$y=\frac{C+B}{2}.$$

By the use of the logarithmic table given in the Appendix (No. II, Table No. 6) for the reduction of cubic centimetres of nitrogen to grams for each tenth of a degree Centigrade, by the formula $\frac{\cdot 0012562}{(1+\cdot 00367\,t)760}$, the labour of calculation is reduced to a minimum. An example will, perhaps, render more intelligible the whole method of calculation here proposed. For this purpose, let us suppose the following values to have been obtained in an analysis of the gaseous products from a water residue :—

Vol. of original gas = A.

19·200 c.c. of dry gas at 16°·4 C. and 629·6 mm. pressure.

Vol. after first absorption (of CO_2) = B.

3·342 c.c. of dry gas at 16°·7 C. and 324·5 mm. pressure.

Vol. after second absorption (of N_2O_2) = C.

1·631 c.c. of dry gas at 16°·9 C. and 298·4 mm. pressure.

A =

$$\begin{array}{rl} \log\ 19\cdot 200 = & 1{,}28330 \\ \log 629\cdot 6\ \ = & 2{,}79906 \\ \log\frac{\cdot 0012562}{(1+\cdot 00367\,t)760}\text{ for }16^\circ\cdot 4\text{ C.} = & -6{,}19286 \\ \cline{2-2} & -2{,}27522 = \cdot 01885\text{ grm.} \end{array}$$

B =

$$\begin{array}{rl} \log\ \ 3\cdot 342 = & 0{,}52401 \\ \log 324\cdot 5\ \ = & 2{,}51121 \\ \log\frac{\cdot 0012562}{(1+\cdot 00367\,t)760}\text{ for }16^\circ\cdot 7\text{ C.} = & -6{,}19241 \\ \cline{2-2} & -3{,}22763 = \cdot 001689\text{ grm.} \end{array}$$

$$\mathrm{C}=$$

$$\begin{array}{rl}
\log\ 1{\cdot}631 = & 0{,}21245 \\
\log 298{\cdot}4\ = & 2{,}47480 \\
\log \dfrac{\cdot 0012562}{(1+\cdot 00367\, t)760} \text{ for } 16^{\circ}{\cdot}9\ \mathrm{C.} = & -6{,}19211 \\
\hline
& -4{,}87936 = \cdot 0007575 \text{ grm.}
\end{array}$$

Introducing these values for A, B, and C into the above equations, we get the following values for x (carbon) and y (nitrogen):—

$$x = \cdot 007355 \text{ grm.}$$
$$y = \cdot 00122325 \text{ grm.}$$

If these results had been obtained by the combustion of the solid residue from one litre of water, then, by moving the decimal point two places to the right, the values for x and y above quoted are transformed into parts by weight of carbon and nitrogen in 100,000 parts of the water thus:—

Carbon ·735 part in 100,000 of water.
Nitrogen ·122 ,, ,, ,,

From the quantity of nitrogen thus obtained there has to be deducted the amount of ammoniacal nitrogen present in the water, or rather this amount minus the loss incurred by the dissipation of ammonia during the evaporation of the water. Potable waters rarely contain so much as ·01 part of ammonia in 100,000 parts, and then the loss of ammoniacal nitrogen during evaporation is too insignificant to require correction. Very impure waters and certain deep well waters, however, sometimes contain much larger proportions of ammonia; and then the loss on evaporation with sulphurous acid becomes very considerable, as is seen from Table 3, in Appendix II, which embodies the results of numerous experiments made with artificial waters containing known quantities of ammonia.

It is of course undesirable to apply the larger corrections for loss of ammoniacal nitrogen; and I have therefore endeavoured to replace the sulphurous by some other acid, whose ammonia salt shall either suffer less loss of ammonia, or shall be broken up on evaporation with total loss of ammonia. As the result of many trials, all salts of ammonia suffer volatilisation or decomposition during the evaporation of their solutions; but of all salts tried, ammonic phosphate allows least ammonia to escape; and, therefore, in the analysis of sewage, or very impure waters, the slight acidification of the water ought to be effected with phosphoric instead of sulphurous acid. As this substitution is inadmissible where nitrates or nitrites are present in appreciable quantity, it is fortunate that sewage and other highly polluted liquids rarely contain these salts.

The ammonia in strongly ammoniacal waters may be entirely dissipated during evaporation, by substituting boracic acid or borax for sulphurous acid; but boracic acid does not completely decompose carbonates, and it is therefore necessary to treat the residue with solution of sulphurous acid, and again evaporate to dryness. The use of borax is recommended when great accuracy is required in the determination of organic nitrogen in strongly ammoniacal waters.

Table 4, in Appendix II, constructed from numerous experiments with artificial waters containing known weights of ammonia, gives the correction for loss of ammoniacal nitrogen when the water is acidified with phosphoric acid.

The appropriate deduction for ammoniacal nitrogen having been made from the total nitrogen obtained by combustion, the remaining weights of carbon and nitrogen still require correction for minute quantities of these elements adventitiously introduced during the analysis. It is desirable that each analyst should make several blank experiments to determine these coefficients of correction; evaporating a litre of *pure* water with the usual quantities of sulphurous acid and ferrous chloride, adding 0·1 gram of freshly ignited sodic chloride to form a tangible residue. The residue must be burnt and analysed in the usual way. As the result of numerous fairly concordant experiments made in my laboratory, the adventitious C and N introduced into the analytical results, obtained from one litre of water, are 0·00006 grm. of C and 0·00005 grm. of N.

Interpretation of the Results of Combustion.—The quality of a sample of potable water, that is to say, its suitability for dietetic purposes, is to be decided chiefly, though not exclusively, from the proportion of organic elements which it contains, and from that of organic carbon to organic nitrogen. The smaller the aggregate proportion of organic carbon and organic nitrogen, and the larger the proportion of organic carbon to organic nitrogen, the better, *cæteris paribus*, is the quality of the water. In the case of spring and deep well waters, however, little importance ought to be attached to the relative proportion of the organic elements, because in such waters the proportion of carbon to nitrogen is often low, even when the organic matter has been derived from vegetal sources. In these cases, however, the organic carbon ought not much to exceed 0·1 part in 100,000 parts of water.

In surface water, on the other hand, the proportion of organic carbon to organic nitrogen almost always affords trustworthy evidence as to whether the organic matter is of animal or vegetable origin. If the proportion be as low as 3 : 1, the organic matter is of animal origin; if it be as high as 8 : 1, it is chiefly, if not exclusively, of vegetable origin. Between these proportions, the analyst must be guided in his opinion by his knowledge of the surroundings of the source of the water, and by the presence or absence of evidence of previous sewage contamination (see p. 93); for if a water, to which animal matter has once gained access, has since been subjected only to the slight oxidation effected in rivers and streams, a portion, at least, of its organic matter must be of animal origin, for it has been proved (Rivers Pollution Commissioners' 6th Report, pp. 134-8) that there is no river in the United Kingdom long enough to secure the complete oxidation of the soluble animal matter present in polluted water.

Upland surface waters are least liable to animal contamination. Collected from bare uncultivated districts, the organic matter contained in them is almost entirely vegetable, and usually peat. The ratio of carbon to nitrogen is always high, the average being 10 : 1. The extremes are, however, very wide, from 4 : 1 to 21 : 1. This is owing to the more rapid loss of carbon than of nitrogen suffered by peaty matter during oxidation, and hence the proportion of carbon to nitrogen is lower in the water of lakes than in that of mountain streams which feed them, whilst in a change from low water to flood, the ratio of carbon to nitrogen in a mountain stream will often mount from the minimum to the maximum of the scale.

There are many lakes and streams which supply water containing not much more than 0·15 part of organic carbon in 100,000 parts. As a rule, however, the quantity is much more considerable, and sometimes the water is dark and unpalatable from excess of peaty matter.

Cultivated land does not, as a rule, yield so much organic matter to water as that which has not been broken up by cultivation; but from the fact of such land being manured with animal, sometimes even with human, excreta, the nature of the organic matter requires much more attention. The ratio of carbon to nitrogen varies from 4 : 1 to 10 : 1, averaging about 6 : 1. Whenever the ratio is below 6 : 1, and there is more than 0·3 part of organic carbon in 100,000 of water, accompanied by previous sewage contamination (say 2,000 parts in 100,000), the water ought to be condemned as unfit for dietetic purposes.

An opinion as to the quality of shallow well water must always be largely dependent upon the surroundings of the well. Shallow wells, however, are almost always polluted by animal matter, sometimes slightly, frequently to a very dangerous degree. The oxidising action of the porous earth, or rock, constituting the water-bearing stratum, is, in many cases, powerful enough to destroy much of the original polluting matter, leaving in solution small quantities only of organic matter, having sometimes a rather high C : N ratio. In other cases the soil is so overtasked in its oxidising function, that the ratio is a low one, and the water is then sometimes almost as filthy as common sewage.

The past pollution of such water must therefore receive careful attention, for there are circumstances (a heavy rainfall, for instance) which will quickly change the character of the soil from one extreme to the other, and thus the contamination, which has been before removed by oxidation, passes into the well in an active and virulent condition. The ratio of C : N in shallow wells varies from 1 : 1, or even less, to 9 : 1, with an average of 4 : 1.

Waters from deep wells and springs show the smallest quantities of organic elements, the thick strata through which the water has passed having destroyed by oxidation most of the organic matter. The amount of organic carbon ranges from about 0·02 to about 0·1 in 100,000 parts of water, with an average for deep wells of about 0·06 part carbon and 0·02 part of organic nitrogen. Spring water is even purer. The ratio of C : N varies from 2 : 1 to 6 : 1, with an average of 4 : 1. The ratio depends here probably more on the extent of the oxidation than on the nature of the organic matter. In sewage, the ratio varies from 1 : 1 to 3 : 1, with an average of about 2 : 1.

Subject to modifications from the other analytical determinations, the following classification will be useful in reporting upon the quality of samples of potable water. The reason for dividing waters into two sections, and adopting a different standard of organic purity for each, is given at page 57.

SECTION I.—UPLAND SURFACE WATER.

Class I. Water of great organic purity, containing a proportion of organic elements (organic carbon and organic nitrogen) not exceeding 0·2 part in 100,000 parts of water.

Class II. Water of medium purity, containing from 0·2 to 0·4 part of organic elements in 100,000.

Class III. Water of doubtful purity, containing from 0·4 to 0·6 part of organic elements in 100,000.

Class IV. Impure water, containing more than 0·6 part of organic elements in 100,000.

SECTION II.—WATER OTHER THAN UPLAND SURFACE.

Class I. Water of great organic purity, containing a proportion of organic elements not exceeding 0·1 part in 100,000.

Class II. Water of medium purity, containing from 0·1 to 0·2 part of organic elements in 100,000.

Class III. Water of doubtful purity, containing from 0·2 to 0·4 part of organic elements in 100,000.

Class IV. Impure water, containing upwards of 0·4 part of organic elements in 100,000.

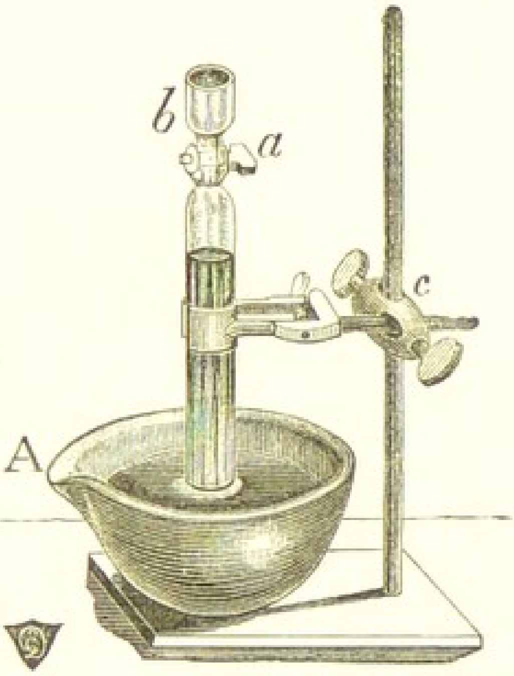
NITROGEN AS NITRATES AND NITRITES.

The Mercury Method.—This method of estimating nitrogen existing in water as nitrates and nitrites is founded on Walter Crum's process for the refraction of nitre.

It consists in agitating over mercury a concentrated solution of the nitrate or nitrite with a large excess of strong sulphuric acid, when the whole of the nitrogen is evolved as nitric oxide.

The process is conducted as follows:—The residue from the half litre of water used for the determination of the total solid matter is treated with a small quantity of hot distilled water, care being taken to ensure complete extraction of the soluble salts. It is advisable to rub the dish gently with the finger, or a short glass rod covered with india-rubber, so as to detach the solid matter and expose it thoroughly to the action of the water. This liquid, together with the subsequent washings of the dish, is filtered into a small beaker and evaporated over a steam-bath to a volume not exceeding 1 or 2 c.c., previous to its being introduced into the decomposition tube shown in fig. 5.

FIG. 5.



This tube is abont 8 inches long, and has a bore as large as can conveniently be closed by the thumb. It is constricted near one end, and furnished with a well fitting stopcock (*a*). It is filled with mercury to the stopcock, and inverted in the mercury basin (A), where it is held by a clamp (*c*). The concentrated filtrate and, afterwards, the washings of the beaker are transferred to the tube from the cup (*b*) at the top, by cautiously opening the stopcock. The beaker is rinsed out several times with pure and strong sulphuric acid, of which a volume about one and a half times as great as the total bulk of the concentrated filtrate must, in all, be introduced into the tube. By careful manipulation, it is easy to introduce successively the concentrated liquid and the rinsings into the tube by means of the cup and stopcock without the admission of a trace of air. If, however, air should inadvertently gain admission, it may, if of considerable volume, be withdrawn by suction applied to the cup (*b*), the stopcock being momentarily opened. A minute bubble of air may be expelled by pressing the thumb firmly against the opening at the bottom of the tube and momentarily opening the stopcock.

If a trace of gas is liberated immediately on the addition of sulphuric acid, it will consist of carbonic acid, and must be expelled. The evolution of nitric oxide does not take place until a minute or two after the violent agitation of the contents of the tube.

The tube is now unclamped, and so grasped that the moist thumb can firmly close the opening at the bottom, and being withdrawn from the trough, it is then violently agitated. The tube, during this operation, is inclined at a considerable angle, the cup pointing away from the operator. Holding the tube in this way, and briskly shaking it in a vertical direction, it is easy to impart a combined vertical and lateral movement to the liquids, which soon reduces the mercury near the acid to a state of fine division, without, however, breaking the continuity of that in the lower part of the tube. If nitrates or nitrites are present, a considerable pressure is soon felt against the thumb, and mercury spurts out in minute streams, as nitric oxide is evolved. The escape of the gas should be resisted, so as to maintain a considerable excess of pressure inside the tube, and thus prevent the possibility of air gaining access to the interior during the shaking. The shaking must be continued till no more gas is given off. The time required for this varies from three to five or six minutes.

When the quantity of nitrates is considerable, the nitric oxide is very tardy in coming off at first. The mercury also becomes dull and pasty, as if alloyed, and the shaking becomes difficult. In this case the mercury should be brought into contact with the acid as little as possible, so as to avoid loss of acid liquid when the mercury is afterwards expelled. At the end of the reaction the pasty appearance disappears. If no nitrates are present, the mercury, if it breaks up at all, forms only bright beads, and the turbidity of the liquid is very slight.

When the reaction is complete, the tube is carried to the mercury trough (E) of the gas apparatus (fig. 3) described at page 71, its contents are cast up into the laboratory vessel (*c*), and the gas is measured in the usual way. If half a litre of water is used for the determination, the volume of nitric oxide read off expresses the volume of nitrogen existing as nitrates and nitrites in one litre of the water, since nitric oxide occupies exactly double the volume of the nitrogen which it contains. From the number so obtained the weight of nitrogen in these forms, in 100,000 parts of water, is easily calculated by the use of Table 6, Appendix II.

When more than 0·08 part of nitrogen as ammonia is present in 100,000 parts of liquid, there is a risk of loss of nitrogen by decomposition of ammonic nitrite during the evaporation of the water. If, therefore, the operator applies the delicate test for nitrites described in Part I (page 40), and finds them to be present, a separate half litre of water must be taken for this determination, and the nitrites be converted into nitrates by cautiously adding dilute solution of permanganate of potash to the acidified water until the pink colour remains for about a minute. The liquid is then rendered slightly alkaline with carbonate of soda before evaporation.

For the separate determination of nitrites, see page 40.

Total Inorganic Nitrogen.

In a previous chapter, it has been shown that the *present* contamination of a water by organic substances can be satisfactorily inferred from the carbon and nitrogen contained in the organic matter. The present contamination is, however, rarely the total organic pollution to which such water has been subjected; oxidation is almost incessantly at work, sometimes slowly, as in streams, lakes, and rivers, at other times very rapidly, as in porous soils, transforming organic into mineral compounds.

It is important to know whether the organic matter thus destroyed was of animal origin, and if so whether the quantity was considerable. The only item in water analysis which furnishes direct evidence on these heads is the "total inorganic nitrogen."

When organic substances containing no nitrogen are oxidised, they are converted into carbonic acid and water—substances which in aërated water can, of course, no longer be identified. Nitrogenous organic bodies, however, such as sewage and animal matter, generally yield, in addition, nitrous and nitric acids and ammonia; these, reacting on mineral substances in the water, form nitrates, nitrites, and ammonium salts, which remain dissolved in the water and can be accurately determined.

The "total inorganic nitrogen" is the sum of the amounts of nitrogen found in these three forms, and is to be regarded, after certain deductions have been made, as the nitrogen of animal matter which existed in the water at a previous time. But as the inorganic nitrogen is liable to be reduced in quantity if it comes within the reach of the absorbent roots of plants, the inferences to be drawn from this previous pollution are less exact than those based upon the evidence of present contamination. As a rule, however, a water which contains anything more than the merest trace of inorganic nitrogen must have been polluted by animal matter at some previous period, and this "inorganic nitrogen" is a measure of the *minimum* amount of such contamination. For the method of obtaining a concrete expression for this amount of animal matter previously existing in the water, see the chapter on "Previous Sewage Contamination," page 93.

The importance of this inquiry into the past history of potable water will be evident from the following considerations.

1. The rapidity with which different kinds of organic matter oxidise is not uniform: and of all the varieties, that which is organised and living offers by far the greatest resistance to oxidation. Now, the researches of Chauveau, Pasteur, Koch, Burdon-Sanderson, Klein, and others leave no room for doubt that the specific poisons of the so-called zymotic diseases consist of organised and living organic matter; and it is now certain that water is the medium through which some at least of these diseases are propagated. It is evident, therefore, that an amount of exposure to oxidising influences which may resolve the dead organic matter present in water into innocuous mineral compounds may, and probably will, fail to affect those constituents which are endowed with life. Hence, much inorganic nitrogen means great risk of the presence of these zymotic poisons. The investigations into the cause of the outbreak of typhoid fever at Lausen, in Switzerland,* and at Caterham and Redhill, afford a remarkable confirmation of the virulence of these poisons.

2. The oxidising influences to which organic matter in water is subjected vary in activity at different times, and it by no means follows that because at the time of the analysis the offensive matter has already been converted into innocuous mineral compounds, the change would therefore be equally complete under future altered conditions as regards temperature, exposure to air or vegetation, and comparative volume of pure water. So long as there is a chance of the purifying effect on the water decreasing, there is always a risk of the harmless "inorganic nitrogen" becoming the

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* "Deutsche Vierteljahrsschrift für öffentliche Gesundheitspflege," Bd. VI, s. 154, and "Chem. Soc. Jour.," vol. xxix, p. 827.

"organic nitrogen" of some putrescent and perhaps contagious matter.

3. It is desirable that the analyst should know whether or not the water under investigation is liable to actual animal contamination; and this information is furnished by the determination of inorganic nitrogen.

4. The past history of the water is often of great service in judging of the present quality. In certain stages of oxidation, vegetable and animal matters are scarcely distinguishable by ultimate analysis. In such cases it is safest to assume that if the past contamination was animal the present will be so likewise. Indeed, in lake and river waters the oxidation of organic matter is so extremely slow as to render it almost impossible that animal matter once introduced can be completely resolved into inorganic compounds before the water reaches the sea.

5. The "inorganic nitrogen" in upland surface water is usually exceedingly small; it is often *nil*, and rarely exceeds ·03 part per 100,000. Even this small quantity may not have been derived from organic pollution. Rain water of the purest kind contains as much as 0·03 part of inorganic nitrogen per 100,000, derived from ammonia and oxides of nitrogen present in the air.

Directly, however, a district becomes cultivated, evidences of animal contamination begin to show themselves in the water running over or through it, and the inorganic nitrogen may rise as high as 1 part in 100,000, the average proportion being ·22 part per 100,000.

6. Owing to the much more rapid oxidation which takes place when water polluted with organic matter percolates through porous earth, deep wells and springs fed from impure sources generally contain very much larger proportions of inorganic nitrogen. Deep well water contains on an average ·5 part, and spring water ·4 part per 100,000; but these proportions may rise as high as 2 or 3 parts per 100,000. The previous history of such waters, however,

is often of comparatively little consequence, because the previous contamination is generally very remote, and the risk of the survival of zymotic germs consequently very slight.

7. The quantity of "inorganic nitrogen" at the moment of analysis is often much less than that originally contained in the animal matters which have undergone oxidation. This is sometimes due to the reduction of nitrates and nitrites to elementary nitrogen, by subsequent access of fresh organic matter to the water, and sometimes to their removal by aquatic plants.

8. As already mentioned, shallow wells do not furnish any useful averages of inorganic nitrogen. The proportion may be as low as ·2 or as high as 20 parts per 100,000, according to the extent of previous pollution. The proportion, however, usually ranges from 1 to 10 parts per 100,000 parts of water.

"Inorganic nitrogen" becomes an item of the utmost importance in dealing with these waters, for at times, when they are most liable to suffer from contamination, the oxidising power of the soil may be inadequate to destroy dangerous matters, and what has hitherto appeared as evidence of *past* contamination only may suddenly assume the form of present or actual pollution.

Previous Sewage or Animal Contamination.

When the results of water analysis show either the presence of a large amount of inorganic nitrogen, or that of actual animal matter, with even a comparatively small amount of inorganic nitrogen, it becomes desirable to draw particular attention to the past history of the water. This is best done by the use of a concrete expression for the previous animal matter, which, by its decomposition, has yielded the inorganic nitrogen found by analysis. For this purpose, a standard founded upon the animal matter dissolved in London sewage is convenient and generally intelligible. For facility of calculation, 100,000 parts of average filtered London sewage are assumed to contain 10 parts of combined nitrogen (in reality they contain only about 7½ parts).

In estimating, in terms of this standard, however, the previous sewage or animal contamination of water, from the proportion of inorganic nitrogen, it is necessary to note that rain water itself contains combined mineral nitrogen, although in minute quantities. The average proportion of inorganic and combined nitrogen found in rain water is nearly ·032 part per 100 000 parts of water; and after this number has been subtracted from the amount of inorganic nitrogen found in 100,000 parts of a potable water, the remainder, if any, represents the nitrogen derived from oxidised animal matters with which the water has been in contact. Thus, a sample of water which contains, in the form of nitrates, nitrites, and ammonia, ·326 part of nitrogen in 100,000 parts, has obtained $\cdot326 - \cdot032 = \cdot294$ part of that nitrogen from animal matters. Now, this last amount of combined nitrogen is, by the foregoing assumption, contained in 2,940 parts of average London sewage, and hence such a sample of water is said to exhibit evidence of 2,940 parts of previous sewage or animal contamination in 100,000 parts; or, in other words, 100,000 lbs. of the water contain the mineral residue of an amount of animal organic matter equal to that found in 2,940 lbs. of average London sewage. Briefly, the previous sewage or animal contamination of a water is calculated by the use of the following formula—

$$P = 10{,}000\ (N - \cdot032),$$

in which P is previous sewage contamination and N the amount of inorganic nitrogen in 100,000 parts of water.

In this estimation, the correction (·032 part) is probably too high; for it is only when the rain is caught for analysis as it falls, that this quantity escapes considerable diminution by the absorbent action of vegetation. For a similar reason we may look in vain for the full evidence of previous animal pollution in the effluent waters from fields irrigated with sewage. Nitrates and nitrites are also rapidly destroyed when the organic matter in the water containing them enters into putrefaction—a condition which often occurs in streams or reservoirs containing much polluting organic matter. The organic matter in deep well water, too, is often oxidised at the expense of nitrates.

Thus, everything tends to reduce the proportion of inorganic nitrogen, and, consequently, to obliterate the evidence of previous animal contamination; and as the estimated contamination can therefore be but a minimum quantity, it is the more necessary to give it prominent notice, especially when the water also contains actual animal matter. On this account, and also to prevent misconception of the term "previous sewage or animal contamination," it is desirable to send a printed copy of the following explanation with every report in which the term is mentioned. When the water contains sewage or animal matter the words in italics in the fifth paragraph should be erased.

PREVIOUS SEWAGE OR ANIMAL CONTAMINATION.

The excrementitious matters which exist in sewage are sometimes possessed of intensely infectious properties; and sewage mixing with water, even in the minutest proportion, is likely, by such properties, to spread epidemic diseases among populations which drink the water.

Thus is explained the peculiar power which impure waters have been shown to exercise on many occasions, in promoting great epidemics of typhoid fever and cholera.

The existence of an infectious property in water cannot be proved by chemical analysis, and is only learnt, too late, from the effects which the water produces on man. But though chemistry cannot prove any existing infectious property, it can prove, if existing, certain degrees of sewage-contamination. And every sewage-contamination which chemistry can trace ought, *primâ facie*, to be held to include the possibility of infectious properties.

Nearly the whole of the animal matter which gains access to drinking water consists of sewage, that is, solid and liquid excrements.

The column headed "Previous Sewage or Animal Contamination," in the accompanying analytical table, expresses, in terms of average London sewage, the amount of animal matter with which 100,000 lbs. of each water was, at some time or other, contaminated. Thus 100,000 lbs. of the water of had been polluted with an amount of animal matter equal to that contained in lbs. of average London sewage. *So far as chemical analysis can show, the whole of this animal matter had been oxidised and converted into mineral and innocuous compounds at the time the analysis was made; there is, however, always a risk lest some portion (not detectable by chemical or microscopical analysis) of the noxious constituents of the original animal matters should have escaped that decomposition which has resolved the remainder into innocuous mineral compounds. But* this evidence of previous contamination implies much more risk when it occurs in water from rivers and shallow wells than when it is met with in the water of deep wells or of deep-seated springs. In the case of river water there is great probability that the morbific matter, sometimes present in animal excreta, will be carried rapidly down the stream, escape decomposition, and produce disease in those persons who drink the water; as the organic matter of sewage undergoes decomposition very slowly when it is present in running water. In the case of shallow well water also, the decomposition and oxidation of the organic matter are liable to be incomplete during the rapid passage of polluted surface water into shallow wells. In the case of deep well and spring water, however, if the proportion of previous contamination do not exceed 10,000 parts in 100,000 parts of water, this risk is very inconsiderable, and may be regarded as *nil* if the direct access of water from the upper strata be rigidly excluded; because the excessive filtration to which such water has been subjected in passing downwards through so great a thickness of soil or rock, and the rapid oxidation of the organic matters contained in water when the latter percolates through a porous and aërated soil, afford a considerable guarantee that all noxious constituents have been removed.

It follows, from what has been already stated, that chemical analysis cannot discover the noxious ingredient or ingredients in water polluted by infected sewage or animal excreta; and as it cannot thus distinguish between infected and non-infected sewage, the only perfectly safe course is to avoid altogether the use, for domestic purposes, of water which has been polluted with excrementitious matter.

This is the more to be desired because there is no practicable process known whereby water, once contaminated by infected sewage, can be so purified as to render its domestic use entirely free from risk.

Nevertheless, as it is very difficult in some localities to obtain water which has not been more or less polluted by excrementitious matters, it is desirable to divide such previously contaminated drinking waters into three classes, viz.:—

1. Reasonably safe water.
2. Suspicious or doubtful water.
3. Dangerous water.

Reasonably safe water.—Water, although it exhibits previous sewage or animal contamination, may be regarded as reasonably safe when it is derived either from deep wells (say 100 feet deep) or from deep-seated springs, provided that surface water be carefully excluded from the well or spring, and that the proportion of previous contamination do not exceed 10,000 parts in 100,000 parts of water.

Suspicious or doubtful water is, 1st, shallow well, river, or flowing water which exhibits any proportion, however small, of previous sewage or animal contamination; and, 2nd, deep well or spring water containing from 10,000 to 20,000 parts of previous contamination in 100,000 parts of water.

Dangerous water is, 1st, shallow well, river, or flowing water, which exhibits more than 20,000 parts of previous animal contamination in 100,000; 2nd, shallow well, river, or flowing water containing less than 20,000 parts of previous contamination in 100,000 parts, but which is known, from an actual inspection of the well, river, or stream, to receive sewage, either discharged into it directly or mingling with it as surface drainage; 3rd, as the risk attending the use of all previously contaminated water increases in direct proportion to the amount of such contamination, the water of deep wells or deep-seated springs exhibiting more than 20,000 parts of previous contamination in 100,000 must be regarded as dangerous. River or running water should only be placed in the second class provisionally, pending an inspection of the banks of the river and tributaries, which inspection will obviously transfer it either to the class of reasonably safe water, if the previous contamination be derived exclusively from spring water, or to the class of dangerous water, if any part of the previous contamination be traced to the direct admission of sewage or excrementitious matters.

Total Combined Nitrogen.

This item is found by adding together the nitrogen present in the organic matter, in the ammonia, and in the nitrates and nitrites. The first represents the present pollution, and the second and third that which is past. The total combined nitrogen therefore sums up, as it were, the evidence of the *past* and *present* pollution of each water by nitrogenous organic matter of both animal and vegetable origin.

APPENDIX.

I.

Reagents used in Water Analysis.

The following is a category of the reagents required for the different operations described in this book, the strengths of the solutions given being those found most convenient in practice.

A.—FOR ESTIMATION OF AMMONIA.

1. *Nessler's Test.*—Dissolve 62·5 grams of potassic iodide in about a quarter of a litre of distilled water, and having set aside about 10 c c., run into the remainder a cold saturated solution of mercuric chloride till a permanent precipitate forms. Redissolve this by the potassic iodide held in reserve, and then add, with great care, more solution of mercuric chloride till, after stirring, a slight precipitate remains.

Add to the liquid 150 grams of potassic hydrate dissolved in distilled water, and make the whole up to a litre; allow to settle, and decant off the clear yellow liquid into a small bottle for use as required.

2. *Standard Solution of Ammonic Chloride.*—In one litre of distilled water, dissolve 1·5735 gram of pure dry ammonic chloride, and dilute 100 c.c. of this strong solution to one litre. Then 1 c.c. = ·00005 gram NH_3.

3. *Sodic Carbonate.*—Heat the dry carbonate strongly for an hour without fusing it. Preserve in a small wide-mouthed stoppered bottle.

4. *Water Free from Ammonia.*—Distil ordinary distilled

water or good common water with sodic carbonate, rejecting the distillate till it ceases to react with Nessler's test. The distillation should be stopped when the liquid left in the retort is reduced to about one-sixth of the original volume.

B.—FOR ESTIMATION OF NITROGEN AS NITRATES AND NITRITES.

THE MERCURY METHOD.—Pure concentrated sulphuric acid, also occasionally 10 per cent. solutions of potassic permanganate and sodic carbonate.

THE ALUMINIUM METHOD.—*Metallic aluminium* as thin foil.

Sodic Hydrate.—10 per cent. solution of sodic hydrate, freed, if necessary, from nitrates by dissolving 100 sq. cm. of aluminium foil in a litre, and afterwards boiling the liquid briskly in a porcelain or silver basin till one third of its volume has evaporated. Make up to the original volume with distilled water, free from ammonia.

Pumice.—Pieces about the size of peas are heated for an hour, and afterwards kept in a closely stoppered bottle.

Hydrochloric Acid.—If two or three drops contain an appreciable amount of ammonia, it must be rectified from sulphuric acid.

THE ZINC-COPPER METHOD.—Various processes for the preparation of the zinc-copper couple have been recommended by its inventors,—Gladstone and Tribe; but the following is their latest and simplest method, and it furnishes a couple of the greatest energy:—A mixture of 2 grams of finely divided copper (obtained by reducing powdered oxide of copper at as low a temperature as possible, and sifting through fine muslin) with 18 grams of coarse zinc filings, is introduced into a 2-ounce flask, fitted with a cork, through which passes a tube drawn out to a capillary opening. The flask is heated over a Bunsen flame until the zinc begins to soften, agitating all the time to ensure thorough mixture of the two metals and to prevent any part from being unduly heated. If the operation has been successfully conducted, the mass should consist of greyish-black grains, destitute of metallic lustre. If the zinc filings retain their form, the heating has not been carried far enough. If, on the other hand, the mass presents the appearance of half fused shot, with a yellowish brassy tint, the heating has been carried too far—the metals have become alloyed, and will be electrolytically inert. As soon as the proper point has been reached, the flask is removed from the flame, the agitation, however, being continued for a few seconds, to prevent fusion. The point of the capillary tube is then sealed up, and the whole is allowed to cool.

C.—FOR ESTIMATION OF NITRITES (GRIESS'S METHOD).

Meta-phenylenediamine. (*Meta-diamido-benzol*, fusing point 63° C.)—Dissolve 5 grams of the base in a litre of water and slightly supersaturate with sulphuric acid.

Dilute Sulphuric Acid.—One of pure acid to two of water.

Standard Potassic or Sodic Nitrite Solution.—A solution of alkaline nitrite, of which 1 c.c. is equivalent to 0·01 mgrm. nitrous anhydride (N_2O_3), prepared thus:—Dissolve 0·406 gram of pure silver nitrite in boiling distilled water, and add pure potassic or sodic chloride till no more argentic chloride is thrown down. Make up to one litre, let the argentic chloride settle, and dilute 100 c.c. of the clear solution to one litre. This solution should be kept in closely-stoppered bottles quite full.

D.—FOR ESTIMATION OF CHLORINE.

Standard Silver Solution.—Dissolve 2·3944 grams of argentic nitrate in a litre of distilled water. In use, it is convenient to measure it from a 10 c.c. burette graduated into tenths.

Potassic Chromate Solution.—A strong solution of pure neutral chromate, free from chlorine. It is best to deliver it from a dropping tube, which may pass through the cork of the supply bottle.

E.—FOR ESTIMATION OF HARDNESS.

Standard Calcic Chloride Solution.—Weigh 0·2 gram of Iceland spar, or other pure form of calcic carbonate, into a platinum dish, and add dilute hydrochloric acid gradually till it is dissolved. To prevent loss, cover the dish with a clock glass. Drive off excess of HCl by successive evaporations to dryness with distilled water, redissolve in distilled water, and make up to one litre.

Standard Soap Solution.—Potash soap keeps better than any other. To make it, rub together in a mortar, till well mixed, 40 parts of dry potassic carbonate and 150 parts of lead plaster (*Emplastrum plumbi*, B.P.). Add methylated spirit and triturate to a cream. Allow to rest for a few hours, then transfer to a filter and wash repeatedly with methylated spirit. Ascertain the strength of this by adding it to 50 c.c. of the calcic chloride solution; proceeding as in determining hardness. Dilute with water and alcohol till exactly 14·25 c.c. are required to form a permanent lather with 50 c.c. of solution of calcic chloride. The water is to be added in quantities such as to make the proportion of water to the spirit as one to two. If the standard solution be not required immediately, the strong solution may be conveniently prepared by placing the dry and powdered potassic carbonate and *Emp. plumbi* in a large bottle with methylated spirit. If the mixture be occasionally shaken, the reaction will be complete in a few days. The plumbic carbonate subsides, leaving a perfectly clear soap solution, which may be syphoned off.

It is advisable to make the soap solution a little too strong at first, then allow it to stand for twenty-four hours, filter if needed, and adjust accurately. This solution may be used with either of the tables given in Appendix II.

F.—FOR OXYGEN OR FORCHAMMER PROCESS.

Sulphuric Acid.—Strength, one of strong acid to three of water.

Standard Solution of Potassic Permanganate.—Two grains in 1,000 septems of pure water, equivalent to ·01 grain of available oxygen in 20 septems (or ·395 gram in a litre, equivalent to ·001 gram of available oxygen in 10 c.c.).

Potassic Iodide Solution.—One part in 10 of water.

Sodic Hyposulphite.—5·4 grains in 1,000 septems (or 1 gram per litre).

Starch.—Rub up 1 part starch with 20 parts of boiling water, filter, boil, and after allowing to stand for twenty-four hours syphon off the clear liquid.

G. FOR DETERMINATION OF ORGANIC ELEMENTS.

1. *Water free from Organic Matter and Ammonia.*—About 15 to 20 litres of ordinary distilled water, to which about 1 gram of potassic hydrate and 0·2 gram of potassic permanganate have been added, are maintained at about 100° C. for twenty-four hours under an inverted condenser, after which the condenser is reversed and the water distilled off. Apply Nessler's test to the distillate from time to time till 100 c.c. show no coloration, and collect that which comes over subsequently, stopping short of dryness.

As an additional precaution the water thus obtained may be acidified with sulphuric acid and redistilled.

Solution of Sulphurous Acid.—Sulphurous anhydride prepared by the action of *pure* sulphuric acid on clean copper cuttings is washed with a small quantity of water and then passed into water free from organic matter and ammonia, till a saturated solution is obtained. The copper cuttings should first be digested for twenty-four hours with concentrated sulphuric acid, and then washed with water before use as above.

3. *Hydric Sodic Sulphite Solution.*—Dissolve ignited sodic carbonate (A 3) in the pure water (G 1), and pass through it washed sulphurous anhydride (G 2) till carbonic anhydride ceases to be evolved.

4. *Ferrous Chloride Solution.*—Precipitate a solution of pure ferrous sulphate with sodic hydrate, wash thoroughly (finally with pure water, G 1), and dissolve in the smallest possible quantity of pure hydrochloric acid. Two or three drops should not contain an appreciable amount of ammonia. It is convenient to keep the solution in a bottle with a ground glass cap instead of a stopper, a small dropping tube being kept in it ready for use.

5. *Potassic Bichromate.*—A saturated solution.

7. *Potassic Hydrate.*—A saturated solution.

7. *Pyrogallic Acid.*—A cold saturated solution of the sublimed acid.

Oxygen.—Blow a bulb of about 20 c.c. capacity at the end of a piece of combustion-tube, and draw out the tube above the bulb so as to form a neck about a foot long, and $\frac{3}{16}$ of an inch in diameter. After filling the bulb with dried and coarsely powdered potassic chlorate, bend the narrow tube a few inches above the bulb to an angle of 45°, and recurve its end so as to form a convenient gas delivery tube. Clamp this little retort so that the delivery tube is about $\frac{1}{4}$ of an inch under mercury, and heat the bulb gently. Reject the first 60 to 80 c.c. of gas, and collect the rest in clean test tubes. Transfer the tubes from the trough in very small beakers, and number in the order collected. If 10 c.c. of the gas in the first tube leaves but a minute bubble after treatment with potassic hydrate and pyrogallic acid, all the tubes are fit for use. If not, the others must be successively tested till a sufficiently pure sample is obtained.

9. *Meta-phosphoric Acid.*—Dissolve 100 grams of the glacial acid in a litre of water; 10 c.c. should not contain an appreciable amount of ammonia.

10. *Calcic Phosphate.*—Add solution of calcic chloride to

a solution of common hydric disodic phosphate, wash the precipitate with water by decantation, dry, and heat to redness for an hour.

11. *Cupric Oxide* can be prepared by oxidising sheet copper in a muffle. The roasted copper scraps from the makers of sulphate of copper also answer well. That which has been made by calcining the nitrate is liable to contain traces of nitrogen. Previous to use it must be recalcined, and this is conveniently effected in iron tubes longer than the combustion furnace in which they are laid, and 1¼ inch internal diameter. In a Hofmann's double combustion furnace, two tubes may be heated at the same time if the central row of long clay burners be replaced by short ones.

The furnace is tilted to an angle of 15° so as to cause a current of air through the tubes, and a red heat is maintained for two or three hours. When cold, the oxide should be extracted by a stout clean iron wire and thrown on a sieve of clean copper gauze, the coarse and the fine being put into separate stoppered bottles. The stoppers of the bottles should be protected from dust by caps, or inverted beakers should be placed over them. A blank combustion must be performed with every parcel of oxide calcined. It should yield only a minute bubble of gas, which should be almost wholly absorbed by potassic hydrate. (The quantity of carbonic acid found should not correspond to more than ·00005 gram of C.)

12. *Copper Gauze Cylinders* for the decomposition of oxides of nitrogen in the combustion-tube. These are about 1½ inch long, and of slightly different sizes to fit the tubes employed. They are made by wrapping fine copper gauze tightly round a copper wire.

Before use, they should be superficially oxidised by heating to redness in a stream of atmospheric air, and afterwards reduced in a stream of hydrogen. They are preserved in a wide-mouthed stoppered bottle, and may be used several times before being again reduced.

II.

TABLES.

For convenient reference all the tables required in water analysis are collected in this Appendix.

1. *Clark's Table of Hardness.* 1,000 *grains of water used.*

Degree of hardness.	Measures of soap solution.	Difference for the next degree of hardness.	Degree of hardness.	Measures of soap solution.	Difference for the next degree of hardness.
Distilled water = 0.	1·4	1·8	9	19·4	1·9
1	3·2	2·2	10	21·3	1·8
2	5·4	2·2	11	23·1	1·8
3	7·6	2·0	12	24·9	1·8
4	9·6	2·0	13	26·7	1·8
5	11·6	2·0	14	28·5	1·8
6	13·6	2·0	15	30·3	1·8
7	15·6	1·9	16	32·0	1·7
8	17·5	1·9			

In this table each measure of soap solution = 10 grains, and each degree of hardness = 1 grain of carbonate of lime per gallon.

2. *Table of Hardness in parts per* 100,000. 50 *c.c. of water used.*

c.c. of Soap solution.	$CaCO_3$ per 100,000.	c.c. of Soap solution.	$CaCO_3$ per 100,000.	c.c. of Soap solution.	$CaCO_3$ per 100,000.	c.c. of Soap solution.	$CaCO_3$ per 100,000.	c.c. of Soap solution.	$CaCO_3$ per 100,000.
·7	·00	3·8	4·29	6·9	8·71	10·0	13·31	13·1	18·17
·8	·16	·9	·43	7·0	·86	·1	·46	·2	·33
·9	·32	4·0	·57	·1	9·00	·2	·61	·3	·49
1·0	·48	·1	·71	·2	·14	·3	·76	·4	·65
·1	·63	·2	·86	·3	·29	·4	·91	·5	·81
·2	·79	·3	5·00	·4	·43	·5	14·06	·6	·97
·3	·95	·4	·14	·5	·57	·6	·21	·7	19·13
·4	1·11	·5	·29	·6	·71	·7	·37	·8	·29
·5	·27	·6	·43	·7	·86	·8	·52	·9	·44
·6	·43	·7	·57	·8	10·00	·9	·68	14·0	·60
·7	·56	·8	·71	·9	·15	11·0	·84	·1	·76
·8	·69	·9	·86	8·0	·30	·1	15·00	·2	·92
·9	·82	5·0	6·00	·1	·45	·2	·16	·3	20·08
2·0	·95	·1	·14	·2	·60	·3	·32	·4	·24
·1	2·08	·2	·29	·3	·75	·4	·48	·5	·40
·2	·21	·3	·43	·4	·90	·5	·63	·6	·56
·3	·34	·4	·57	·5	11·05	·6	·79	·7	·71
·4	·47	·5	·71	·6	·20	·7	·95	·8	·87
·5	·60	·6	·86	·7	·35	·8	16·11	·9	21·03
·6	·73	·7	7·00	·8	·50	·9	·27	15·0	·19
·7	·86	·8	·14	·9	·65	12·0	·43	·1	·35
·8	·99	·9	·29	9·0	·80	·1	·59	·2	·51
·9	3·12	6·0	·43	·1	·95	·2	·75	·3	·68
3·0	·25	·1	·57	·2	12·11	·3	·90	·4	·85
·1	·38	·2	·71	·3	·26	·4	17·06	·5	22·02
·2	·51	·3	·86	·4	·41	·5	·22	·6	·18
·3	·64	·4	8·00	·5	·56	·6	·38	·7	·35
·4	·77	·5	·14	·6	·71	·7	·54	·8	·52
·5	·90	·6	·29	·7	·86	·8	·70	·9	·69
·6	4·03	·7	·43	·8	13·01	·9	·86	16·0	·86
·7	·16	·8	·57	·9	·16	13·0	18·02		

3. *Loss of Nitrogen by Evaporation of* NH_3 [$SOHo_2$]. *Parts in* 100,000.

NH_3.	Loss of N.	NH_3.	Loss of N.	NH_3.	Loss of N.	NH_3.	Loss of N.	NH_3.	Loss of N.	NH_3.	Loss of N.
6·0	1·727	4·8	1·451	3·6	·977	2·4	·503	1·2	·250	·09	·014
5·9	1·707	4·7	1·411	3·5	·937	2·3	·463	1·1	·238	·08	·013
5·8	1·688	4·6	1·372	3·4	·898	2·2	·424	1·0	·226	·07	·012
5·7	1·668	4·5	1·332	3·3	·858	2·1	·384	·9	·196	·06	·010
5·6	1·648	4·4	1·293	3·2	·819	2·0	·345	·8	·166	·05	·009
5·5	1·628	4·3	1·253	3·1	·779	1·9	·333	·7	·136	·04	·007
5·4	1·609	4·2	1·214	3·0	·740	1·8	·321	·6	·106	·03	·006
5·3	1·589	4·1	1·174	2·9	·700	1·7	·309	·5	·077	·02	·004
5·2	1·569	4·0	1·135	2·8	·661	1·6	·297	·4	·062	·01	·003
5·1	1·549	3·9	1·095	2·7	·621	1·5	·285	·3	·047	·009	·001
5·0	1·530	3·8	1·056	2·6	·582	1·4	·274	·2	·032	...	...
4·9	1·490	3·7	1·016	2·5	·542	1·3	·262	·1	·017	...	...

4. *Loss of Nitrogen by Evaporation of* NH_3 [PO_2Ho].

Volume evaporated.	NH_3 per 100,000.	Loss of N per 100,000.	Volume evaporated.	NH_3 per 100,000.	Loss of N per 100,000.	Volume evaporated.	NH_3 per 100,000.	Loss of N per 100,000.	Volume evaporated.	NH_3 per 100,000.	Loss of N per 100,000.
100 c.c.	10·0	·483	100 c.c.	7·2	·386	100 c.c.	4·4	·283	100 c.c.	1·6	·143
...	9·9	·480	...	7·1	·382	...	4·3	·279	...	1·5	·137
...	9 8	·476	...	7·0	·379	...	4·2	·275	...	1·4	·132
...	9·7	·473	...	6·9	·375	...	4·1	·271	...	1·3	·127
...	9·6	·469	...	6·8	·372	...	4·0	·267	...	1·2	·122
...	9·5	·466	...	6·7	·368	...	3 9	·262	...	1·1	·117
...	9·4	·462	...	6·6	·365	...	3·8	·257	...	1·0	·112
...	9·3	·459	...	6·5	·361	...	3·7	·252	250 c.c.	0·9	·096
...	9·2	·455	...	6·4	·358	...	3·6	·247	...	0·8	·080
...	9·1	·452	...	6·3	·354	...	3·5	·242	...	0·7	·070
...	9·0	·448	...	6·2	·351	...	3·4	·236	...	0·6	·060
...	8·9	·445	...	6·1	·348	...	3·3	·231	500 c.c.	0·5	·050
...	8·8	·441	...	6·0	·345	...	3·2	·226	...	0·4	·040
...	8·7	·438	...	5·9	·341	...	3·1	·221	...	0·3	·030
...	8 6	·434	...	5·8	·337	...	3·0	·216	1000 c.c.	0·2	·020
...	8·5	·431	...	5·7	·333	...	2 9	·211	...	0·1	·010
...	8·4	·428	...	5·6	·330	...	2·8	·205	...	0·09	·009
...	8·3	·424	...	5·5	·326	...	2·7	·200	...	0·08	·008
...	8·2	·421	...	5·4	·322	...	2·6	·195	...	0·07	·007
...	8·1	·417	...	5·3	·318	...	2·5	·190	...	0·06	·006
...	8·0	·414	...	5·2	·314	...	2·4	·184	...	0·05	·005
...	7·9	·410	...	5·1	·310	...	2·3	·179	...	0·04	·004
...	7·8	·407	...	5·0	·306	...	2·2	·174	...	0·03	·003
...	7·7	·403	...	4·9	·302	...	2·1	·169	...	0·02	·002
...	7·6	·400	...	4·8	·298	...	2·0	·164	...	0·01	·001
...	7·5	·396	...	4·7	·294	...	1·9	·158	...	...	...
...	7·4	·393	...	4·6	·291	...	1·8	·153	...	...	...
...	7·3	·389	...	4·5	287	...	1·7	·148	...	...	...

5. *Tension of Aqueous Vapour for each $\frac{1}{10}$th degree Centigrade from 0° to 30° C. (Regnault).*

Temp. C.	Tension in mm. of Mercury.	Temp. C.	Tension in mm. of Mercury.	Temp. C.	Tension in mm. of Mercury.	Temp. C.	Tension in mm. of Mercury.	Temp. C.	Tension in mm. of Mercury.
0	4·6	6·0	7·0	12·0	10·5	18·0	15·4	24·0	22·2
·1	4·6	·1	7·0	·1	10·5	·1	15·5	·1	22·3
·2	4·7	·2	7·1	·2	10·6	·2	15·6	·2	22·5
·3	4·7	·3	7·1	·3	10·7	·3	15·7	·3	22·6
·4	4·7	·4	7·2	·4	10·7	·4	15·7	·4	22·7
·5	4·8	·5	7·2	·5	10·8	·5	15·8	·5	22·9
·6	4·8	·6	7·3	·6	10·9	·6	15·9	·6	23·0
·7	4·8	·7	7·3	·7	10·9	·7	16·0	·7	23·1
·8	4·9	·8	7·4	·8	11·0	·8	16·1	·8	23·3
·9	4·9	·9	7·4	·9	11·1	·9	16·2	·9	23·4
1·0	4·9	7·0	7·5	13·0	11·2	19·0	16·3	25·0	23·5
·1	5·0	·1	7·5	·1	11·2	·1	16·4	·1	23·7
·2	5·0	·2	7·6	·2	11·3	·2	16·6	·2	23·8
·3	5·0	·3	7·6	·3	11·4	·3	16·7	·3	24·0
·4	5·1	·4	7·7	·4	11·5	·4	16·8	·4	24·1
·5	5·1	·5	7·8	·5	11·5	·5	16·9	·5	24·3
·6	5·2	·6	7·8	·6	11·6	·6	17·0	·6	24·4
·7	5·2	·7	7·9	·7	11·7	·7	17·1	·7	24·6
·8	5·2	·8	7·9	·8	11·8	·8	17·2	·8	24·7
·9	5·3	·9	8·0	·9	11·8	·9	17·3	·9	24·8
2·0	5·3	8·0	8·0	14·0	11·9	20·0	17·4	26·0	25·0
·1	5·3	·1	8·1	·1	12·0	·1	17·5	·1	25·1
·2	5·4	·2	8·1	·2	12·1	·2	17·6	·2	25·3
·3	5·4	·3	8·2	·3	12·1	·3	17·7	·3	25·4
·4	5·5	·4	8·2	·4	12·2	·4	17·8	·4	25·6
·5	5·5	·5	8·3	·5	12·3	·5	17·9	·5	25·7
·6	5·5	·6	8·3	·6	12·4	·6	18·0	·6	25·9
·7	5·6	·7	8·4	·7	12·5	·7	18·2	·7	26·0
·8	5·6	·8	8·5	·8	12·5	·8	18·3	·8	26·2
·9	5·6	·9	8·5	·9	12·6	·9	18·4	·9	26·4
3·0	5·7	9·0	8·6	15·0	12·7	21·0	18·5	27·0	26·5
·1	5·7	·1	8·6	·1	12·8	·1	18·6	·1	26·7
·2	5·8	·2	8·7	·2	12·9	·2	18·7	·2	26·8
·3	5·8	·3	8·7	·3	12·9	·3	18·8	·3	27·0
·4	5·8	·4	8·8	·4	13·0	·4	19·0	·4	27·1
·5	5·9	·5	8·9	·5	13·1	·5	19·1	·5	27·3
·6	5·9	·6	8·9	·6	13·2	·6	19·2	·6	27·5
·7	6·0	·7	9·0	·7	13·3	·7	19·3	·7	27·6
·8	6·0	·8	9·0	·8	13·4	·8	19·4	·8	27·8
·9	6·1	·9	9·1	·9	13·5	·9	19·5	·9	27·9
4·0	6·1	10·0	9·2	16·0	13·5	22·0	19·7	28·0	28·1
·1	6·1	·1	9·2	·1	13·6	·1	19·8	·1	28·3
·2	6·2	·2	9·3	·2	13·7	·2	19·9	·2	28·4
·3	6·2	·3	9·3	·3	13·8	·3	20·0	·3	28·6
·4	6·3	·4	9·4	·4	13·9	·4	20·1	·4	28·8
·5	6·3	·5	9·5	·5	14·0	·5	20·3	·5	28·9
·6	6·4	·6	9·5	·6	14·1	·6	20·4	·6	29·1
·7	6·4	·7	9·6	·7	14·2	·7	20·5	·7	29·3
·8	6·4	·8	9·7	·8	14·2	·8	20·6	·8	29·4
·9	6·5	·9	9·7	·9	14·3	·9	20·8	·9	29·6
5·0	6·5	11·0	9·8	17·0	14·4	23·0	20·9	29·0	29·8
·1	6·6	·1	9·9	·1	14·5	·1	21·0	·1	30·0
·2	6·6	·2	9·9	·2	14·6	·2	21·1	·2	30·1
·3	6·7	·3	10·0	·3	14·7	·3	21·3	·3	30·3
·4	6·7	·4	10·1	·4	14·8	·4	21·4	·4	30·5
·5	6·8	·5	10·1	·5	14·9	·5	21·5	·5	30·7
·6	6·8	·6	10·2	·6	15·0	·6	21·7	·6	30·8
·7	6·9	·7	10·3	·7	15·1	·7	21·8	·7	31·0
·8	6·9	·8	10·3	·8	15·2	·8	21·9	·8	31·2
·9	7·0	·9	10·4	·9	15·3	·9	22·1	·9	31·4

6. *Reduction of Cubic Centimetres of Nitrogen to Grams.*

$\log. \dfrac{0·0012562}{(1+0·00367\,t)760}$ for each tenth of a degree from 0° to 30° C.

t. C.	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
0°	$\bar{6}$·21824	808	793	777	761	745	729	713	697	681
1	665	649	633	617	601	586	570	554	538	522
2	507	491	475	459	443	427	412	396	380	364
3	349	333	318	302	286	270	255	239	223	208
4	192	177	161	145	130	114	098	083	067	051
5	035	020	004	*989	*973	*957	*942	*926	*911	*895
6	$\bar{6}$·20879	864	848	833	817	801	786	770	755	739
7	723	708	692	676	661	645	629	614	598	583
8	567	552	536	521	505	490	474	459	443	428
9	413	397	382	366	351	335	320	304	289	274
10	259	244	228	213	198	182	167	151	136	121
11	106	090	075	060	045	029	014	*999	*984	*969
12	$\bar{6}$·19953	938	923	907	892	877	862	846	831	816
13	800	785	770	755	740	724	709	694	679	664
14	648	633	618	603	588	573	558	543	528	513
15	497	482	467	452	437	422	407	392	377	362
16	346	331	316	301	286	271	256	241	226	211
17	196	181	166	151	136	121	106	091	076	061
18	046	031	016	001	*986	*971	*956	*941	*926	*911
19	$\bar{6}$·18897	882	867	852	837	822	807	792	777	762
20	748	733	718	703	688	673	659	644	629	614
21	600	585	570	555	540	526	511	496	481	466
22	452	437	522	408	393	378	363	349	334	319
23	305	290	275	261	246	231	216	202	187	172
24	158	143	128	114	099	084	070	055	041	026
25	012	*997	*982	*968	*953	*938	*924	*909	*895	*880
26	$\bar{6}$·17866	851	837	822	808	793	779	764	750	735
27	721	706	692	677	663	648	634	619	605	590
28	576	561	547	532	518	503	489	475	460	446
29	432	417	403	388	374	360	345	331	316	302

The following transcript (with a few explanatory additions) from a laboratory note-book serves to illustrate both the use of the foregoing tables and the arithmetical operations incident to water analysis :—

Carbon and Nitrogen Determinations in 1 *litre of Water.*

A. Total volume of gas after contact with bichromate of potash.		Division on measuring tube (see page 74).	Temperature.	Barometer.
Height of mercury in measuring tube...... (see page 70)	208·9 mm.	30=3·334 c.c.	20°·4 C.	753·0 mm.
" " pressure tube	130·0 "			95·8 "
Difference ..	78·9 "	Pressure on dry gas at temp. 20°·4 C..		657·2 "
Plus tension of aqueous vapour (see Table V.)	17·8 "			
Minus correction for capillarity at division 30 (see page 75), which is on *wide* part of measuring chamber	−·9 "			
	95·8 "	To be deducted from height of barometer.		

B. Volume after absorption of CO_2 by potash solution.		Division on measuring tube.	Temperature.	Barometer.
Measuring tube	426·1 mm.	50=·361 c.c.	20°·4 C.	753·0 mm.
Pressure tube	229·9 "			216·2 "
Difference	196·2 "	Pressure on dry gas at 20°·4 C.		536·8 "
Plus tension of aqueous vapour	17·8 "			
Plus correction for capillarity at division 50, which is on *narrowest* part of measuring chamber	2·2 "			
	216·2 "	To be deducted from height of barometer.		

C. Volume after absorption of N_2O_2 by oxygen and potassic pyrogallate.		Division on measuring tube.	Temperature.	Barometer.
Measuring tube.......	426·1 mm.	50=·361 c.c.	20°·3 C.	753·0 mm.
Pressure tube	190·4 "			255·6 "
Difference	235·7 "	Pressure on dry gas at 20°·3 C.		497·4 "
Plus tension of aqueous vapour	17·7 "			
Plus correction for capillarity at division 50 ..	2·2 "			
	255·6 "	To be deducted from height of barometer.		

	A.	B.	C.
Log. of volume corresponding to division on measuring tube	0·52290	$\bar{1}$·55766	$\bar{1}$·55766
Log. of $\frac{0\cdot0012562}{(1+0\cdot00367\,t)760}$ (see Table 6)	$\bar{6}$·18688	$\bar{6}$·18688	$\bar{6}$·18703
Log. of pressure on dry gas	2·81769	2·72981	2·69670
Log. of weight of gas calculated as N	$\bar{3}$·52747	$\bar{4}$·47435	$\bar{4}$·44139
Natural Number =	·0033688	·0002980	·0002763

To calculate out these numbers into carbon and nitrogen, see formulæ given at page 80.

·0033688 = A
·0002980 = B
·0030708
3
7) ·0092124
·0013160 = weight of carbon

= ·132 part per 100,000
− ·006 correction for blank combustion (see page 83)
Carbon = ·126 part per 100,000.

·0002980 = B
·0002763 = C
2) ·0005743
·0002871 = weight of nitrogen
= ·029 part per 100,000
− ·005 correction for blank combustion
Nitrogen = ·024 part per 100,000
− ·003 deduction for N as NH_3
Organic nitrogen = ·021 part per 100,000.

Ammonia in ½ litre = 0·4 c.c. of standard ammonic chloride solution = ·004 part per 100,000.

Chlorine. 50 c.c. of water taken required 8·75 c.c. standard argentic nitrate = 8·75 parts per 100,000.

Hardness (see Table 2).			Soap solution.	Parts per 100,000.
	Total	10 c.c. of the water made up to 50 c.c. with distilled water required	5·0 c.c.	= 30·00
	Permanent	25 c.c. made up as before	4·8 c.c.	= 11·42
	Temporary			= 18·58

Solid Residue, $\frac{1}{2}$ litre of water taken.

Dish + Residue = 51·5180		1st weighing	51·5280
Platinum dish = 51·2210		2nd ,,	51·5180
		3rd ,,	51·5180

·2970 = 59·40 parts per 100,000.

Nitrogen as Nitrates and Nitrites in $\frac{1}{2}$ litre.

		Division on measuring tube.	Tempe-rature.	Baro-meter.
Measuring tube…..	222·5 mm.	20 = 19·022 c.c.	19°·0 C.	753·0 mm.
Pressure tube ……	183·8 ,,			54·1 ,,
Difference …..	38·7 ,,	Pressure on dry gas at 19°·0 ………….		698·9 ,,
Plus tension of aqueous vapour……..	16·3 ,,			
Correction for capillarity …………	−·9 ,,			
	54·1 ,,	To be deducted from height of barometer.		

Log. of volume (19·022 c.c.)……………..	1·27925
Log. of $\frac{0·0012562}{(1+0·00367\ t)760}$ for 19° C. ……..	$\bar{6}$·18897
Log. of pressure ………………………	2·84441
Log. of weight of gas calculated as N……..	$\bar{2}$·31263

Natural number ………………. = ·02054 N per litre
Nitrogen as nitrates and nitrites …. = 2·054 parts per 100,00.

Previous sewage contamination = 2·054 + 003 (N as NH_3) − ·032 (see page 94) × 10,000 = 20,250 parts per 100,000.

III.

CONVERSION OF PARTS PER 100,000 INTO GRAINS PER GALLON, OR THE REVERSE.

To convert parts per 100,000 into grains per gallon, multiply by 7 and move the decimal point one place to the left.

To convert grains per gallon into parts per 100,000, multiply by 10 and divide by 7.

To convert grams per litre into grains per gallon, multiply by 70.

IV.

TYPICAL ANALYSES. *Parts per* 100,000.

Description.	Total Solids.	Organic Carbon.	Organic Nitrogen.	Ammonia.	Nitrogen as Nitrates and Nitrites.	Total Combined Nitrogen.	Previous Sewage or Animal Contamination	Chlorine.	Hardness.			Remarks.
									Temporary.	Permanent.	Total.	
Rain.												
Rothamsted, August 13, 1869 ...	2·16	·062	·007	0·27	0	·029	0	·10	...	...	·8	Clear.
London, Lancaster Gate, November 8, 1873	2·76	·383	·040	·210	·008	·221	1490	·5	...	1·1	1·1	Arsenic ·020.
Upland Surface Water.												
Vyrnwy, September 3, 1878	3·40	·148	·016	0	0	·016	0	·71	...	...	1·27	Clear.
Haweswater Beck, Sept., 1878 ...	2·80	·183	·019	·002	0	·020	0	·8	...	...	1·82	Clear.
Bala Brook, December, 1874	5·10	·149	·023	·003	0	·025	0	1·15	1·0	1·9	2·9	Turbid.
Thirlmere Lake (Cumberland), January, 1877	2·36	·172	·017	·008	0	·024	0	·75	0	·9	·9	Turbid.
Water supplied to Greenock, July 26, 1870	5·42	·501	·037	·002	0	·039	0	1·00	0	1·9	1·9	Yellowish, slightly turbid.
Surface Water from Cultivated Districts.												
Thames at Sunbury, Jan., 31, 1873	31·24	·314	·049	·002	·305	·356	2750	1·80	17·2	7·0	24·2	Turbid.
Severn above Mythe Bridge, February, 1878	23·64	·234	·037	0	·130	·167	980	3·0	3·7	9·1	12·8	Slightly turbid.
Deeping Fen drainage, November 24, 1873	110·40	1·327	·159	0·80	0	·225	340	12·75	25·2	42·1	67·3	Turbid.

Deep Wells and Springs.												
Nottingham, well in town, in New Red Sandstone, 1869 ……	62·84	·050	·020	0	3·508	3·528	34760	5·6	9·6	10·21	19·81	Clear.
Ryde, chalk spring, April, 1877…	26·40	·050	·004	0	·228	·232	1960	2·57	16·7	3·9	20·6	Clear.
Ilminster, spring from the Lias, March 12, 1872 ………………	58·12	·049	·014	·009	1·332	1·353	13070	4·8	26·1	17·4	43·5	Clear.
Broughton-in-Furness, Gillet Style Spring, November, 1877	6·54	·057	·042	0	·035	·077	30	1·15	·4	3·4	3·8	Clear.
Shallow Wells.												
Twickenham, August, 1887 ……	82·08	·739	·093	·740	2·708	3·411	32850	7·8	22·5	21·8	44·3	Clear.
Tottenham, December 30, 1878…	130·44	·108	·053	·002	3·974	4·029	39440	8·4	35·2	39·8	75·0	Clear.
Biana, well 10 feet deep, May 23, 1879 ………………………	114·32	1·809	·268	185	7·569	7·989	76890	6·8	…	…	92·0	Clear.
Bognor near Sea ………………	75·24	·286	·027	0	0	·027	0	16·25	19·3	17·4	36·7	Turbid.
Teignmouth, 30 feet in New Red Sandstone, December, 1874……	40·00	·056	·008	·001	·530	·539	4990	3·20	11·4	11·1	22·5	Slightly turbid.
Oakfield, Wimbledon, Feb., 1874	23·28	·109	·038	·026	·062	·121	510	4·00	1·0	9·4	10·4	Dissolved lead; contained no nitrites or phosphates, and but little carbonic acid.
Ice.												
Norwegian Block Ice ……………	0·47	·029	·005	·005	0	·009	0	·05	0	0	0	Clear.
Sea Water.												
Hastings, two miles from shore…	3955·0	·291	·135	·005	·013	·152	0	2050	52·0	646·0	698·0	Clear.
									Suspended matter.			
Sewage.									Mineral.	Organic.	Total.	
Tunstall Sewage, Feb., 1871 ……	114·40	4·858	1·692	4·300	0	5·233	…	14·15	18·12	34·36	52·48	
Crewe Sewage, Nov. 6, 1878 ……	98·08	5·014	1·780	1·650	0	3·080	…	16·0	83·72	262·08	346·00	
Birmingham, effluent from Saltley Sewage Farm …………	77·70	·980	·154	·380	·441	·908	…	7·05	·76	·28	1·04	

V.

AVERAGE COMPOSITION OF UNPOLLUTED WATER. *Parts per* 100,000.

Description.	Total Solid Matter.	Organic Carbon.	Organic Nitrogen.	Ammonia.	Nitrogen as Nitrates and Nitrites.	Total combined Nitrogen.	Previous Sewage or Animal Contamination.	Chlorine.	Hardness.			Number of samples analysed.
									Temporary.	Permanent.	Total.	
RAIN WATER.	2·95	·070	·015	·029	·003	·042	42	·22	...	...	·3	39
UPLAND SURFACE WATER.												
From Non-calcareous Strata.												
From Igneous Rocks	5·15	·278	·033	·001	·002	·035	0	1·13	·1	2·0	2·1	18
From Metamorphic, Cambrian, Silurian, and Devonian Rocks	5·12	·293	·024	·002	·006	·031	3	·92	·3	2·5	2·5	81
From Yoredale and Millstone Grits and the Coal Measures	8·75	·373	·037	·003	·010	·050	6	1·05	·4	4·3	4·7	47
From Lower London Tertiaries and Bagshot Beds	8·40	·379	·048	·004	·007	·058	0	2·06	·3	3·5	3·8	3
From Calcareous Strata.												
From calcareous portions of Silurian and Devonian Rocks	13·71	·302	·026	0	·021	·047	77	1·20	1·2	7·4	8·6	3
From Mountain Limestone	17·07	·370	·047	·001	·011	·059	26	1·24	5·7	7·0	12·7	7
From calcareous portion of Coal Measures	22·79	·346	·037	·003	·016	·056	33	1·52	4·0	8·3	12·3	26
From the Lias, New Red Sandstone, Conglomerate Sandstone, and Magnesian Limestone	18·80	·286	·042	·002	·010	·054	4	1·49	7·6	6·5	14·1	9
From the Oolites	17·46	·326	·025	·004	·042	·070	130	1·55	6·6	5·8	12·4	1

DEEP WELL WATER.											
In Devonian Rocks and Millstone Grit	32·68	·068	·012	·005	·294	·310	2,671	2·70	8·8	8·6	17·4	7
In the Coal Measures	83·10	·119	·034	·044	·207	·278	2,243	18·05	15·1	20·6	35·7	9
In Magnesian Limestone	61·14	·076	·030	0	1·426	1·456	13,937	4·31	16·9	26·9	43·8	3
In New Red Sandstone	30·63	·036	·014	·003	·717	·734	6,895	2·94	7·4	10·5	17·9	28
In the Lias	70·98	·146	·027	·001	·389	·417	3,730	4·42	21·9	8·2	30·1	2
In the Oolites	33·60	·037	·010	·022	·625	·654	6,118	2·69	13·8	6·8	20·6	5
In the Hastings Sand, Greensands, and Weald Clay	45·20	·068	·014	·016	·196	·223	1,864	5·38	16·8	10·5	27·3	20
In the Chalk	36·88	·050	·017	·001	·610	·628	5,801	2·76	21·2	6·5	27·7	66
In the Chalk below London Clay	78·09	·093	·028	·048	·068	·135	797	15·02	9·7	8·7	18·4	13
In Thanet Sand and Drift	53·84	·113	·020	·072	·116	·202	1,517	6·32	14·4	7·6	22·0	4
SPRING WATER.												
From Granite and Gneiss Rocks	5·94	·042	·008	·001	·106	·115	846	1·69	·4	2·6	3·0	8
From Silurian Rocks	12·33	·051	·014	·001	·178	·192	1,587	1·84	1·5	5·3	6·8	15
From Devonian Rocks and Old Red Sandstone	25·06	·054	·012	·001	·764	·777	7,339	3·85	4·8	7·2	12·0	22
From Mountain Limestone	32·06	·087	·010	·001	·224	·235	2,008	4·63	10·9	8·9	19·8	15
From Yoredale and Millstone Grits and the Coal Measures	21·91	·050	·014	·001	·393	·408	3,707	1·85	5·2	7·9	13·1	22
From Magnesian Limestone	66·52	·058	·038	·002	1·686	1·726	16,560	3·40	24·9	34·8	59·7	1
From New Red Sandstone	28·69	·065	·017	·001	·330	·349	3,047	2·19	8·1	10·7	18·8	15
From the Lias	36·41	·073	·019	·001	·467	·487	4,406	2·48	21·3	8·8	30·1	7
From the Oolites	30·33	·043	·011	·001	·402	·414	3,730	1·55	18·2	6·2	24·4	35
From the Hastings Sand and Greensands	30·05	·053	·012	0	·326	·338	2,941	2·98	13·6	6·6	20·2	19
From the Chalk	29·84	·044	·010	·001	·382	·392	3,511	2·45	18·1	5·5	23·6	30
From Fluvio-marine Drift and Gravel	61·32	·086	·019	·001	·354	·374	3,264	2·76	18·0	19·6	37·6	10

VI.

AVERAGE COMPOSITION OF VARIOUS WATERS. *Parts per* 100,000.

Description.	Total Solid Matter.	Organic Carbon.	Organic Nitrogen.	Ammonia.	Nitrogen as Nitrates and Nitrites.	Total combined Nitrogen.	Previous Sewage or Animal Contamination.	Chlorine.	Hardness.			Number of Samples analysed.
									Temporary.	Permanent.	Total.	
LONDON WATER SUPPLY.												
Average of monthly analyses during the year 1888 :—												
From the Thames	28·31	·146	·028	0	·234	·262	2,020	1·8	...	...	20·0	60
From the Lea	31·18	·099	·023	0	·270	·293	2,380	1·9	...	...	22·1	24
From deep wells in Chalk	40·89	·028	·009	0	·470	·479	4,380	2·4	...	...	30·2	12
BIRMINGHAM WATER SUPPLY.												
Average of monthly analyses, 1888	26·92	·147	·021	·001	·238	·260	2,070	1·6	...	...	16·2	12
GLASGOW SUPPLY FROM LOCH KATRINE.												
Average of monthly analyses, 1888	2·62	·154	·033	0	·004	037	0	0·7	...	...	1·0	12
									Suspended matter.			
SEWAGE.									Mineral.	Organic.	Total.	
Fresh sewage; average from 16 water-closet towns	72·2	4·696	2·205	6·703	·003	7·728	...	10·66	24·18	20·51	44·69	50
Ditto from 15 midden towns	82·4	4·181	1·975	5·435	0	6·451	...	11·54	17·81	21·30	39·11	37

In the above and following tables the most important determinations are printed in black type. Where the amount of "previous sewage or animal contamination" is not printed in black type, it is considered to be of no importance (see page 97). For the conversion of these figures into grains per gallon, see Appendix III, page 113.

VII.

CONCLUSIONS AND RECOMMENDATIONS OF THE RIVERS COMMISSIONERS.

The following conclusions and recommendations, in reference to potable water are extracted from the report of the Rivers Pollution Commissioners on the Domestic Water Supply of Great Britain. See also the author's "Experimental Researches in Pure, Applied, and Physical Chemistry," pages 644—683, for a detailed description of the data upon which these conclusions and recommendations rest.

1. *As to the Chemical Quality of Water from different Sources.*—Of the various kinds of water used for dietetic and domestic purposes, *rain water*, when collected at a distance from towns upon specially cleansed surfaces, and kept in clean receptacles, contains the smallest proportion of total solid impurity; but the organic contamination, even of such specially collected water, somewhat exceeds that of water from springs and deep wells.

2. Rain water collected from the roofs of houses and stored in underground tanks is much more impure; it is often polluted to a dangerous extent by excrementitious matters, and is rarely of sufficiently good quality to be employed for dietetic purposes with safety.

3. Water collected from the surface of uncultivated land, and either allowed to subside in lakes or reservoirs or filtered through sand, constitutes *upland surface water*, of good quality for domestic, and of still better quality for manufacturing, purposes. Numerous large towns, both in England and Scotland, are supplied with water of this description. If the

gathering ground be non-calcareous, the water is soft and well adapted for washing and for almost all manufacturing operations. It is nearly always wholesome, but sometimes suffers in palatability by containing an excessive quantity of peaty matter in solution.

4. Water collected from the surface or the drains of cultivated land is always more or less polluted with the organic matter of manure, even after subsidence in lakes or reservoirs. Such *polluted surface or drainage water* is not of good quality for domestic purposes, but it may be used with less risk to health than polluted shallow well water, if human excrementitious matters do not form part of the manure applied to the land.

5. Surface water, which drains wholly or partially from cultivated land, should always be efficiently filtered before it is supplied for domestic use.

6. *River water*, usually in England, but less generally in Scotland, consists chiefly of the drainage from land which is more or less cultivated. When it is further polluted by the drainage of towns and inhabited places, or by the foul discharges from manufactories, its use for drinking and cooking becomes fraught with great risk to health. A very large proportion of the running waters of Great Britain are either at present thus dangerous or are rapidly becoming so.

7. Still more dangerous to health is *shallow well water*, when the wells are situated, as is usually the case, near privies, drains, or cesspools. Such water often consists largely of the leakage and soakage from receptacles for human excrements; but, notwithstanding the presence of these disgusting and dangerous matters, it is generally bright, sparkling, and palatable.

8. Of the different varieties of potable water, the best for dietetic purposes are *spring* and *deep well waters*. They contain the smallest proportion of organic matter, and are almost always bright, sparkling, palatable, and wholesome, whilst their uniformity of temperature throughout the year renders

them cool and refreshing in summer, and prevents them from freezing readily in winter. Such waters are of inestimable value to communities, and their conservation and utilisation are worthy of the greatest efforts of those who have the public health under their charge.

9. The average composition of the four great classes of unpolluted water is given in the following table, which is condensed from the results yielded by the analyses of 589 samples.

AVERAGE COMPOSITION OF UNPOLLUTED WATER.

Results of Analysis expressed in parts per 100,000.

Description.	Dissolved Matters.											Number of Samples Analysed.
									Hardness.			
	Total Solid Impurity.	Organic Carbon.	Organic Nitrogen.	Ammonia.	Nitrogen as Nitrates and Nitrites.	Total Combined Nitrogen.	Previous Sewage or Animal Contamination.	Chlorine.	Temporary.	Permanent.	Total.	
Class I.—Rain water	2·95	·070	·015	·029	·003	·042	42	·822	·4	·5	·3	39
Class II. — Upland surface water ...	9·67	·322	·032	·002	·009	·042	10	1·13	1·5	4·3	5·4	195
Class III. — Deep well water	43·78	·061	·018	·012	·495	·522	4,743	5·11	15·8	9·2	25·0	157
Class IV. — Spring water	28·20	·056	·013	·001	·383	·396	3,559	2·49	11·0	7·5	18·5	198

Note.—For the conversion of these numbers into grains per gallon, see Appendix No. III, page 113.

This concrete result of our analyses proves:—Firstly, that in respect of freedom from that most objectionable of impurities, organic matter (organic carbon and organic nitrogen), these waters range themselves in the following order:—

1. Spring water,
2. Deep well water,
3. Rain water,
4. Upland surface water;

the last being very much inferior to the first three. Secondly, that the evidence of previous sewage or animal contamination is strongest in the case of spring and deep well water; but this evidence may, in the case of these waters, be safely disregarded. And, thirdly, that, as to hardness, rain water and upland surface water are, on the average, very much softer than spring and deep well water.

10. In respect of wholesomeness, palatability, and general fitness for drinking and cooking, our researches lead us to the following classification of waters in the order of their excellence, and founded upon their respective sources:—

Wholesome..	1. Spring water.	Very palatable.
	2. Deep well water.	
	3. Upland surface water.	Moderately palatable.
Suspicious ..	4. Stored rain water.	
	5. Surface water from cultivated land.	Palatable.
Dangerous ..	6. River water to which sewage gains access.	
	7. Shallow well water.	

11. A large proportion of the water supplied for domestic purposes is used for washing, and in many towns considerable volumes are used in manufactories. For these purposes, it is of the utmost importance that the waters should be soft—a quality which is not always associated with wholesomeness and palatability. Classified according to softness, waters from the various sources fall into the following order:—

1. Rain water.
2. Upland surface water.
3. Surface water from cultivated land.
4. Polluted river water.
5. Spring water.

6. Deep well water.
7. Shallow well water.

The interests of the manufacturer and the laundress are thus opposed to those of the householder, inasmuch as they lead to a preference for moderately palatable water, or even unwholesome water, over that which is very palatable and wholesome. Most of the waters from springs and deep wells can be easily and cheaply softened on the large scale by Clark's process (see page 26), and thus the sanitary authorities of towns have at their disposal a method of rendering hard water from springs and deep wells available for washing and manufacturing purposes, without diminishing either its palatability or its wholesomeness.

12. The chemical qualities of water are profoundly influenced by the character of the geological formations from which the water is derived. Rocks and soils which impart to water salts other than those of potash and soda render it more or less hard; and as such hardening salts are almost invariably compounds of lime and magnesia, with carbonic and sulphuric acids, it follows that chalk, limestone, dolomite, and rocks containing the carbonates of lime and magnesia, or sulphate of lime, are those which are almost exclusively instrumental in communicating hardness to water. The following formations yield, as a rule, soft water:—

Igneous.
Metamorphic.
Cambrian.
Silurian (non-calcareous).
Devonian (non-calcareous).
Millstone grit.
Coal measures (non-calcareous).
Lower greensand.
London and Oxford clay.
Bagshot beds.
Non-calcareous gravel.

On the other hand, the following geological formations almost invariably yield hard water:—

Silurian (calcareous).
Devonian (calcareous).
Mountain limestone.
Coal measures (calcareous).
New red sandstone.
Conglomerate sandstone.
Lias.
Oolites.
Upper greensand.
Chalk.

13. The influence of geological formation upon the palatability and wholesomeness of *surface water* is often inconsiderable, owing to the deposit of peaty matters upon the surfaces of the rocks or soils. Unpolluted surface waters from the most widely different geological formations differ but little in the proportions of organic matter which they contain; but, where the water percolates or soaks through great thicknesses of rock, its quality, when it subsequently appears as *spring or deep well water*, depends greatly upon the chemical character of the material through which it has passed. When the formation contains much soluble saline matter, the water becomes loaded with mineral impurities, as is frequently the case when it percolates through certain of the Carboniferous rocks, the Lias, and the Saliferous marls. When the rock is much fissured or permeated by caverns or passages, like the mountain limestone, for instance, the effluent water differs but little from surface drainage, and retains most of the organic impurities with which it was originally charged. But when it is uniformly porous, like the chalk, oolite, greensand, or new red sandstone, the organic matter, at first present in the water, is gradually oxidised and transformed into innocuous mineral compounds. In effecting this most desirable transformation, and thus rendering the waters sparkling, colourless, palatable, and wholesome, the following are the most efficient water-bearing strata:—Chalk, oolite, greensand, new red and conglomerate sandstone.

14. Surface water or river water which contains in 100,000 parts more than 0·2 part of organic carbon, or ·03 part of organic nitrogen, is not desirable for domestic

supply, and ought, whenever practicable, to be rejected.

15. Spring and deep well water ought not to contain, in 100,000 parts, more than 0·1 part of organic carbon or ·03 part of organic nitrogen. If the organic carbon reaches 0·15 part in 100,000 parts, the water ought to be used only when a better supply is not obtainable.

In all cases in which spring and deep well water of good quality are available, we recommend that they should be employed in preference to surface or river water for domestic supply.

II. *As to the possibility of rendering Polluted Water again Wholesome.*—1. When the sewage of towns or other polluting organic matter is discharged into running water, the suspended matters may be more or less perfectly removed by subsidence and filtration, but the foul organic matters in solution are very persistent. They oxidise very slowly, and they are removed only to a slight extent by sand filtration. There is no river in the United Kingdom long enough to secure the oxidation and destruction of any sewage which may be discharged into it, even at its source.

2. Of all the processes which have been proposed for the purification of sewage, or of water polluted by excrementitious matters, there is not one which is sufficiently effective to warrant the use, for dietetic purposes, of water which has been so contaminated.

3. In our opinion, therefore, rivers which have received sewage, even if that sewage has been purified before its discharge, are not safe sources of potable water.

III. *As to the Propagation of Epidemic Diseases by Potable Water.*—1. The existence of specific poisons, capable of producing cholera and typhoid fever, is attested by evidence so abundant and strong as to be practically irresistible. These poisons are contained in the discharges from the bowels of persons suffering from these diseases.

2. The admixture of even a small quantity of these in-

fected discharges with a large volume of drinking water is sufficient for the propagation of those diseases amongst persons using such water.

3. The most efficient artificial filtration leaves, in water, much invisible matter *in suspension*, and constitutes no effective safeguard against the propagation of these epidemics by polluted water.

Boiling the infected water for half an hour is a probable means of destroying its power of communicating these diseases.

4. Other epidemics, such as dysentery and diarrhœa, are also probably propagated by drinking water, but the evidence is here neither so abundant nor conclusive as it is in the case of cholera and typhoid fever.

IV. *As to the alleged Influence of the Hardness of Potable Water upon Health.*—1. Whilst waters of excessive hardness may be productive of calculus, and perhaps other diseases, soft and not excessively hard waters, if equally free from deleterious organic substances, are equally wholesome.

2. In towns where the chief sanitary conditions prevail with tolerable uniformity, the rate of mortality is uninfluenced by the softness or hardness of the water supplied to the inhabitants.

V. *As to the Superiority of Soft over Hard Water for Washing, Cooking, and Manufacturing Operations.*—1. The washing of linen can only be performed with soft water. If the available water be hard, it must be artificially softened—an operation which, on the domestic scale, must be performed at great expense by the aid of either fuel, soda, or soap. In personal ablution, also, the use of soft water is much more pleasant and efficient. It is also more economical; but, by the general use of a very small quantity of water, the waste of softening material is here much less than in a laundry.

2. In cooking, the extraction of the soluble parts of such

materials as are submitted to boiling, or to digestion at a high temperature, is more completely and economically effected by soft than by hard water.

3. In manufacturing operations, involving the use of water, soft water is, almost without exception, preferable to hard.

Dangerous encrustations in steam boilers are prevented by the use of soft water.

VI. *As to the Softening of Hard Water.*—1. All hard water can be softened either by distillation or by the addition of a sufficient quantity of soap or carbonate of soda. Water, the hardness of which is due to the carbonates of lime and magnesia (temporary hardness), may be softened either by boiling for half an hour, or by the addition of a proper quantity of slaked lime. Except the last, all these processes are expensive, and inapplicable on the large scale.

2. Water, the hardness of which is wholly or chiefly of the temporary kind, may be easily, cheaply, and efficiently softened, on the large scale, by the proper use of lime, and the wholesomeness and palatability of such water are sometimes increased, and never diminished, by the process.

3. The lime method of softening may be applied with ease and great economy to the whole supply of even the largest towns, provided the hardness of the water be wholly or chiefly of a temporary kind.

VII. *As to the Improvement of Water by Filtration.*—1. Sand filtration, as carried out in waterworks, not only clarifies the water by removing suspended impurities, but also diminishes the proportion of organic matter in solution, to an extent dependent upon the thickness of the filtering medium, and the rate at which the water passes through that medium.

2. Domestic filtration, as usually practised, is of little or no use, but, properly performed, it is much more efficient than sand filtration on the large scale, in improving the quality of

water polluted by organic matters. The best materials for domestic filters are spongy iron and animal charcoal.*

3. Although the improvement of excrementally-polluted water by filtration may reasonably be considered, on theoretical grounds, to afford some feeble protection against the propagation of epidemic diseases by water, no trustworthy evidence can be adduced in support of such a view.†

VIII. *As to the Deterioration of Water during its Transmission through Mains and Service Pipes.*—1. Potable water can be transmitted through mains of even great length, if they be properly laid, without any appreciable deterioration of quality; but if the joints are caulked with hemp, or other similar organic material, the water is often seriously polluted for months, or even years, after the laying of the mains.

2. The experience of Glasgow, Manchester, and other towns proves conclusively that leaden service pipes can be safely used for the delivery even of water which acts violently upon lead, if the pipes be kept constantly charged with water.‡

IX. *As to the Constant and Intermittent Systems of Supply.* —1. All storage of drinking water in houses is attended with the risk of pollution. Good water is spoiled, and bad water rendered worse by the intermittent system of supply. All drinking water ought to be drawn direct from the main.

2. Under proper supervision, the waste of water is less on the constant than it is on the intermittent system of supply.

3. These and other advantages have led to the adoption of the constant system in a great majority of British towns.

X. *As to the Water Supplies of British Cities, Towns, and*

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* Long experience has shown that animal charcoal is not efficient.

† Recent researches have, however, shown that even sand filtration is very efficient in the removal of the germs of micro-organisms.

‡ More recent experience, however, at Huddersfield and elsewhere, has demonstrated that some waters act upon lead continuously, even when the mains are kept constantly charged.

Inhabited Places.—1. A large majority of the cities and large towns are abundantly supplied with palatable and wholesome water. In manufacturing towns the supply is generally also soft.

2. In other towns, and in villages and other inhabited places, the water available for domestic purposes is frequently neither abundant nor wholesome. In these cases it is a widely spread custom to drink either the water of rivers into which the excrements of man are discharged, or the water from shallow wells, which are largely fed by soakage from middens, sewers, and cesspools.

3. Immense numbers of the population are thus daily exposed to the risk of infection from typhoidal discharges, and, periodically, to that from cholera dejections.

4. The supply of villages and hamlets with wholesome water is often a problem of great difficulty, since the number of inhabitants is too small to permit of the execution of expensive works for such an object. We, therefore, recommend that in any scheme for the utilisation for town supply of the pure water of a river basin, the wants of all neighbouring villages and hamlets should be provided for as far as practicable; and we further recommend that the owners of land should be permitted to include the cost of village water supply among those expenditures on land improvement which they are now enabled, with the sanction of your Majesty's Inclosure Commissioners, to charge upon their estates.

5. Whenever the necessities of the case compel the supply of water to a town from a river or stream into which the excrements of man, whether purified or not, are discharged, we recommend that storage reservoirs should be provided, of sufficient capacity to render unnecessary the abstraction of water from such rivers or streams during floods. These storage reservoirs ought to be so constructed and worked as to allow of the discharge of their contents into the river or stream whenever the quality of the latter becomes superior to that of the previously impounded water.

VIII.

Standards of Purity recommended by the Rivers Pollution Commissioners.

We recommend that, with certain exceptions in reference to standards *d* and *e*, the following liquids be deemed polluting and inadmissible into any stream:—

(*a.*) Any muddy liquid which has not been subjected to perfect rest in subsidence ponds of sufficient size for a period of at least six hours, *or* which, having been so subjected to subsidence, contains *in suspension* more than one part by weight of dry organic matter in 100,000 parts by weight of the liquid, *or* which, not having been so subjected to subsidence, contains *in suspension* more than three parts by weight of dry mineral matter, or one part by weight of dry organic matter in 100,000 parts by weight of the liquid.

(*b.*) Any liquid containing, *in solution*, more than two parts by weight of organic carbon, or 0·3 part by weight of organic nitrogen in 100,000 parts by weight.

(*c.*) Any liquid which shall exhibit by daylight a distinct colour when a stratum of it one inch deep is placed in a white porcelain or earthenware vessel.

(*d.*) Any liquid which contains, in solution, in 100,000 parts by weight, more than two parts by weight of any metal, except calcium, magnesium, potassium, and sodium.

(*e.*) Any liquid which, in 100,000 parts by weight, contains, *whether in suspension or solution*, in chemical combination or otherwise, more than 0·05 part by weight of metallic arsenic.

(*f.*) Any liquid which, after acidification with sulphuric acid, contains, in 100,000 parts by weight, more than one part by weight of free chlorine.

(*g.*) Any liquid which contains, in 100,000 parts by weight, more than one part by weight of sulphur, in the condition either of sulphuretted hydrogen or of a soluble sulphuret.

(*h.*) Any liquid possessing an acidity greater than that which is produced by adding two parts by weight of real muriatic acid to 1,000 parts by weight of distilled water.

(*i.*) Any liquid possessing an alkalinity greater than that produced by adding one part by weight of dry caustic soda to 1,000 parts by weight of distilled water.

(*k.*) Any liquid exhibiting a film of petroleum or hydrocarbon oil upon its surface, or containing, in suspension, in 100,000 parts, more than 0·05 part of such oil.

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THE END.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.